The crystal structure of hongosile, a recently discovered natural zeolite, is composed of sodium, calcium, aluminum, silicon, hydrogen, and oxygen. Its unique atomic structure of ten and twelve rings was determined by J. J. Flush and J. V. Smith. Geophysics at the University of Chicago. Modeling tools used to construct the cover photograph are being developed in the Catalysis and Surfaces Project at BIOSYM Technologies, Inc., San Diego, California. Structure of hongosile courtesy of Flush, J. J.; Smith, J. V. Am. Mineral. 1996, 81, 501-507, and computer graphic by John M. Newsam, BIOSYM Technologies, Inc.

Sponsoring Editor: Jane Fox
Project Coordinator: Elm Street Publishing Services, Inc.
Cover Design: Kay Fulton
Cover Photo: Professor John M. Newsam, BIOSYM Technologies, Inc.
Compositor: Better Graphics, Inc.
Printer and Binder: R. R. Donnelley & Sons Company
Cover Printer: Lehigh Press Lithographers


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Library of Congress Cataloging-in-Publication Data
Huheey, James E.
p. cm.
Includes bibliographical references and index.
I. Keiter, Ellen A. II. Keiter, Richard L.
546.21 1993
QD451.2.H84 1993
97 98 99 12 11 10 9
97-36083

To Catherine, Cathy, Terry, Mercedes, Thorfin, Irene, Alvin, Eric, and Lime.
# Contents

Preface xi  
To the Student xiv  
Excerpts from the Preface to the Third Edition xvi  

<table>
<thead>
<tr>
<th>Chapter 1</th>
<th>What Is Inorganic Chemistry? 1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Inorganic Chemistry, the Beginnings 1</td>
</tr>
<tr>
<td></td>
<td>Inorganic Chemistry, an Example 2</td>
</tr>
<tr>
<td></td>
<td>Chemical Structure of Zeolites and Other Chemical Systems 3</td>
</tr>
<tr>
<td></td>
<td>Chemical Reactivity 5</td>
</tr>
<tr>
<td></td>
<td>Conclusion 7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter 2</th>
<th>The Structure of the Atom 10</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>The Hydrogen Atom 10</td>
</tr>
<tr>
<td></td>
<td>The Polyelectronic Atom 20</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter 3</th>
<th>Symmetry and Group Theory 46</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Symmetry Elements and Symmetry Operations 46</td>
</tr>
<tr>
<td></td>
<td>Point Groups and Molecular Symmetry 53</td>
</tr>
<tr>
<td></td>
<td>Irreducible Representations and Character Tables 59</td>
</tr>
<tr>
<td></td>
<td>Uses of Point Group Symmetry 63</td>
</tr>
<tr>
<td></td>
<td>Crystallography 74</td>
</tr>
</tbody>
</table>
Chapter 4  
Bonding Models in Inorganic Chemistry: 1. Ionic Compounds  
The Ionic Bond  
Lattice Energy  
Size Effects  
The Predictive Power of Thermochemical Calculations on Ionic Compounds  
Covariant Character in Predominantly Ionic Bonds  
Conclusion  

Chapter 5  
Bonding Models in Inorganic Chemistry: 2. The Covalent Bond  
Valence Bond Theory  
Molecular Orbital Theory  
Electronegativity  

Chapter 6  
The Structure and Reactivity of Molecules  
The Structure of Molecules  
Structure and Hybridization  
Bond Lengths  
Experimental Determination of Molecular Structure  
Some Simple Reactions of Covalently Bonded Molecules  

Chapter 7  
The Solid State  
The Structures of Complex Solids  
Imperfections in Crystals  
Conductivity in Ionic Solids  
Solids Held Together by Covalent Bonding  
Solid-State Materials with Polar Bonds  

Chapter 8  
Chemical Forces  
Internuclear Distances and Atomic Radii  
Types of Chemical Forces  
Hydrogen Bonding  
Effects of Chemical Forces  

Chapter 9  
Acid-Base Chemistry  
Acid-Base Concepts  
Measures of Acid-Base Strength  
Hard and Soft Acids and Bases  

Chapter 10  
Chemistry in Aqueous and Nonaqueous Solvents  
Water  
Nonaqueous Solvents  
Molten Salts  
Electrode Potentials and Electrotransitive Forces  

Chapter 11  
Coordination Chemistry: Bonding, Spectro, and Magnetism  
Bonding in Coordination Compounds  
Valence Bond Theory  
Crystal Field Theory  
Molecular Orbital Theory  
Electronic Spectra of Complexes  
Magnetic Properties of Complexes  

Chapter 12  
Coordination Chemistry: Structure  
Coordination Number 1  
Coordination Number 2  
Coordination Number 3  
Coordination Number 4  
Coordination Number 5  
Coordination Number 6  
Coordination Number 7  
Coordination Number 8  
Higher Coordination Numbers  
Generalizations about Coordination Numbers  
Linkage Isomerism  
Other Types of Isomerism  
The Chelate Effect
Chapter 13  Coordination Chemistry: Reactions, Kinetics, and Mechanisms 537
Substitution Reactions in Square Planar Complexes 538
Thermodynamic and Kinetic Stability 547
Kinetics of Octahedral Substitution 548
Mechanisms of Redox Reactions 557

Chapter 14  Some Descriptive Chemistry of the Metals 577
General Periodic Trends 578
Chemistry of the Various Oxidation States of Transition Metals 580
The Chemistry of Elements Potassium-Zinc: Comparison by Electron Configuration 582
The Chemistry of the Heavier Transition Metals 587
Oxidation States and EMFs of Groups 1-12 588
The Lanthanide and Actinide Elements 599
Coordination Chemistry 608
The Transactinide Elements 613

Chapter 15  Organometallic Chemistry 623
The 18-Electron Rule 624
Metal Carbonyl Complexes 630
Nitrosyl Complexes 650
Dinitrogen Complexes 653
Metal Alkyls, Carbenes, Carbynes, and Carbides 655
Nonaromatic Alkene and Alkyne Complexes 662
Metalloccenes 669
Reactions of Organometallic Complexes 686
Catalysis by Organometallic Compounds 705
Stereochemically Nonrigid Molecules 723
Conclusion 730

Chapter 16  Inorganic Chains, Rings, Cages, and Clusters 738
Chains 738
Rings 765
Preface

It has been twenty years since the senior author and Harper & Row, Publishers produced the first edition of Inorganic Chemistry: Principles of Structure and Reactivity. In that time: (a) The senior author has become 20 years more senior; (b) two new authors have joined the project; (c) Harper & Row, Publishers has become HarperCollins Publishers; and, most important, (d) inorganic chemistry has continued to grow from its already lusty existence of two decades ago. It is becoming increasingly impossible for someone to monitor all areas of inorganic chemistry. The new authors bring to the book their interests in coordination chemistry, organometallics, and physical methods, as well as fresh viewpoints on a number of other topics. Nevertheless, the philosophy of the book remains unchanged: To bring to the reader the essentials of inorganic chemistry in an easily readable format with emphasis on the fact that inorganic chemistry is an exciting field of research rather than a closed body of knowledge.

We three authors brought very different undergraduate experiences to the teaching of inorganic chemistry and the revision of this edition. One of us received a B.S. degree from a Ph.D. granting institution, one from a private non-Ph.D. liberal arts college, and one from a public non-Ph.D. liberal arts college. We have taught undergraduate and graduate inorganic courses in a variety of settings. When we sat down to discuss the revision, there were a number of things that we agreed upon: (1) The book would be substantially updated. (2) The material presented would continue to be thoroughly referenced, and the references would continue to appear on the pages of interest. A relevant reference would not be omitted just because it had appeared in previous editions. (3) New illustrations, many from the original literature, would be added. (4) A greater selection of problems, many of them new, would be provided. Many problems would require library assistance, while others would cover the fundamental aspects of each topic. (5) A chapter on symmetry would be added. (6) Solid state chemistry would be given more emphasis. (7) The kinetics chapter would be more fully developed. (8) The descriptive and organometallic chemistry of the lanthanides and actinides would be included in the corresponding chapters for the transition metals.

General consensus (among both authors and users) comes more easily than agreement on specifics. Our discussions of the symmetry chapter are a good example. All of us agreed that the teaching of symmetry considerations at most institutions had
for the most part been delegated to the inorganic chemists. But how much should be taught, and how much should the remainder of the book depend upon this chapter? At a minimum we believed that a good introduction to point groups was essential. We also wanted to include some character table applications but not so much that the inorganic chemistry in the book couldn’t be taught without it. Applications appear here and there in the text but can be avoided if desired. The chapter, as completed, has concentrated on familiarizing the student with many applications of symmetry as used by the inorganic chemist, including spectroscopy and crystallography, without purporting to be a rigorous exposition of the subject.

We may anticipate an eventual consensus on the amount and place of symmetry in the chemistry curriculum, but for now we have assumed no prior background in the subject. We have thus tried to illustrate a wide variety of uses of symmetry without delving deeply into the background theory. We hope that those new to the topic can find a useful introduction to the application of symmetry to problems in inorganic chemistry. On the other hand, those having previous experience with the subject may wish to use this chapter as a brief review. And, recognizing that things are in a state of flux, we have attempted to make it possible to study various topics such as orbital overlap, crystal field theory, and related material, as in the past, with minimal reference to symmetry if desired.

Students using this book come from exceedingly diverse backgrounds. Some will have had extensive experience in physical and organic chemistry, perhaps even a previous course in descriptive inorganic chemistry. For many, however, this will be the first contact with inorganic chemistry, and some may have had only limited experience with bonding theory in other courses. For this reason, the early chapters present the fundamentals of atomic and molecular structure from the inorganic chemist’s perspective. The well-prepared reader may use these chapters as a brief review as well as mortar to chink between previous blocks of knowledge. The middle chapters of the book present the “heart of inorganic chemistry,” solid-state chemistry beyond simple salts, acid-base chemistry in a variety of solvents and the gas phase, and coordination chemistry discussed in terms of bonding, spectra, magnetism, structure, and reactivity.

In line with the philosophy of a topical approach and flexible course content, the last six chapters of the book are essentially independent of each other, and one or more may readily be omitted depending on the inclination of the instructor and the time available.

The fourth edition, in its entirety, works nicely for that unfortunately rare beast, the two-semester course. But that means that it is balanced and should work equally well for a one-semester course—the instructor must pick and choose. We firmly believe that it is more useful to provide a large number of topics, wherein one can select the topics to be covered, than to dictate a “minimum core.” We hope the book includes the topics that all instructors find essential, but we hope that it also includes their favorite topics; it obviously includes ours. A solutions manual that contains answers to all end-of-chapter problems accompanies the fourth edition.

We would like to thank our colleagues in departments that we have visited on sabbatical leaves: Fred Hawthorne, Herb Kaesz, Charles Stoupe, Joan Selverstone Valentine, and Jeff Zink (University of California at Los Angeles), and Owen Anderson, Gary Maciel, Jack Norton, Tony Rappé, and Steve Stranks (Colorado State University). We would also like to thank the Chemistry Departments at UCLA and CSU, the Zoology Department at Southern Illinois University, as well as our own departments for making possible sabbatical visits to take advantage of these resources.

We are grateful to Michael W. Anderson, University of Cambridge; Anthony Ardura, E. I. du Pont de Nemours; B. Dubois, Pechiney Institute; Jacob Klinowski, University of Cambridge; John Newsam, BIOSYM Technologies; Joseph J. Fluh, University of Chicago; Arnold L. Rheingold, University of Delaware; P. Sainfort, Pechiney Institute; Charlotte L. Stern, University of Illinois, Urbana-Champaign; Sir John Wormald Thomas, The Royal Institution of Great Britain; and Scott Wilson, University of Illinois, Urbana-Champaign, for special help with illustrations from their work.

The writing of this text has benefited from the helpful advice of many reviewers. They include Ivan Bernal, Donald H. Berry, Patricio A. Binianni, Andrew B. Bocerstiy, P. Michael Boorman, Jeremy Burdett, Ben DeGrutt, Russell S. Dugie, Daniel C. Harris, Roald Hoffmann, Joel F. Liebman, John Milne, Terrance Murphy, Jack Plakazewicz, Philip Power, Arnold L. Rheingold, Richard Thompson, Glenn Vogel, Marc Walters, James H. Weber, and Jeff Zink.

We began this preface indicating “changes” that have occurred in the last two decades. We have dealt with new authorship and new inorganic chemistry above. Concerning the merger of Harper & Row, Publishers, New York, and Collins, Publishers, London, the entropy generated was quite unexpected. When the dust had settled, there emerged two stellar performers: Jane Pipro, Chemistry Editor, and Cate Rzasa, Project Editor, who helped us in many ways. We are happy to acknowledge our debt to them.

Finally, there are many, many faculty and students who have helped in the original writing and further development of this book, often anonymously in the brief citation of colleagues and reviewers. They know who they are, and we hope they will accept our sincere thanks for all that they did.

James E. Huheey
Ellen A. Keiler
Richard L. Keeler
To the Student

Once after a departmental seminar, an older professor was heard to remark that he felt intimidated by all of the new theory and experimental spectroscopic methods known by the new chemistry graduates. A young graduate student was stunned; she was sure it would take her years just to learn enough of the chemistry that he already knew to get her degree. Meanwhile, two other professors were arguing heatedly over the relative importance of facts versus theory. One said descriptive chemistry was the most important because "facts don't change!"

"Well, some 'facts' seem to change—I read yesterday that iridium is the densest element; ten years ago when I was a student, I was told that osmium was the densest."

"They don't change as fast as theories; theories just come and go; besides, what's wrong with someone repeating an experiment and doing it better—getting a more accurate value?""

"That's the point; new theories are necessary to explain new experimental data, and theories give us something to test, a framework around which we can dream..."

"Dream: We need a little less 'inspiration' and a lot more perspiration..."

And so it goes. . . . These chemists and these arguments present a microcosm of perpetual debates in chemistry and the essence of the great difficulty in writing an upper level textbook of inorganic chemistry. The field is vast; large numbers of inorganic articles are published every week. New synthetic techniques allow the isolation and identification of great numbers of highly reactive compounds. Theoretical descriptions have become increasingly sophisticated, as have spectroscopic methods. Inorganic chemistry interacts with organic, physical, and even biological chemistry. Borderlines between molecular and solid-state chemistry are rapidly disappearing. The older chemist may know many facts and theories but realizes it is only a small portion of the whole. The new graduate, with well-developed skills in a few areas, also has a sense of inadequacy. Perhaps the student faced with his or her first advanced inorganic course feels this most acutely. The textbook for the course reflects the instructor's choice of what portion of inorganic chemistry should be taught, what mix of facts and theory, and what relative weight of traditional and new science. Authors also make their choices and those are seen in the variety of available textbooks on the market. Some are heavily factual, usually bulky, and especially useful for finding out something about all of the principal compounds of a particular element. Others present a blend of fact and theory but minimize the book bulk by limiting each topic to a few paragraphs. This has the advantage of including most topics but the disadvantage of having to look elsewhere for a fuller development. Any single book, of course, has this problem to a certain degree, thus the need for many references. Our book, Inorganic Chemistry: Principles of Structure and Reactivity, fourth edition, is also a blend of fact and theory, but we think it is large enough for a full meal. There is no reason to expect a book that deals with the chemistry of 109 elements to be smaller than a standard organic chemistry textbook!

We've enjoyed writing this book; we hope that you will enjoy reading it. If you do, we'd like to hear from you.

James E. Huheey
Ellen A. Keiter
Richard L. Keiter
Chapter 1

What Is Inorganic Chemistry?

It is customary for chemistry books to begin with questions of this type—questions that are usually difficult or impossible to answer in simple “twenty-five-words-or-less” definitions. Simple pictures, whether of words or of art, cannot portray all aspects of a subject. We most recently had this impressed upon us when our editor asked us to suggest some aspect of inorganic chemistry for the cover of this book. The very nature of a cover implies a relatively simple, single item, such as a molecule, a structure, a reaction, or a property (or perhaps a simple combination of two or three of these). Should we choose the structure of the new high-temperature superconductors which recently gained a Nobel Prize for their discoverers? You probably have read about them in the popular press and wondered why “high temperature” was colder than a Siberian winter! Should we choose a metal “cluster compound” that acts, at the molecular level, like a microscopic fragment of the metal? How about an inorganic molecule that is optically active (that’s not a subject limited to organic chemistry), or carboxypeptidase A (that’s an enzyme, but interest in it is certainly not limited to biochemists)? Maybe a symmetrical crystal of a compound like sodium thiosulfate, photographer’s “hypo,” or a multicolor, polarized micrograph of an inorganic compound. But no single design can possibly portray the many, varied aspects of inorganic chemistry. In the same way, any short and simple definition of a complex subject is apt to be disappointing and even misleading. So let’s just try to see where inorganic chemistry came from, what an inorganic chemist does, and, perhaps, where the subject is going.

Inorganic Chemistry, the Beginnings

The term inorganic chemistry originally meant nonliving chemistry, and it was that part of chemistry that had arisen from the arts and recipes dealing with minerals and ores. It began by finding naturally occurring substances that had useful properties, such as flint or chert that could be worked into tools (middle Pleistocene, ca. 5 x 10⁵ years ago or less). This search continues (see below), but now it is included in the sciences of mineralogy and geology. Chemistry deals more with the changes that can be effected in materials. One of the most important early reactions was the
Table 3.8  

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Disorder

In order to keep the section on crystallography relatively short, this discussion has not included the theoretical basis for X-ray diffraction. However, from other courses you are probably aware of Bragg's Law and the diffraction of X-rays by regularly spaced atoms comparable to the diffraction of visible light on phonograph records or compact disks. Thus one necessity for obtaining X-ray diffraction data is the presence of crystalline material (= regularly spaced atoms). Amorphous materials do not have the regular spacing necessary for diffraction. However, even seemingly pure crystals may be subtle mixtures of two related compounds leading to erroneous results. And since crystalization is a kinetic process, even an otherwise pure compound may not crystallize in the single thermodynamically most favorable perfect crystal. There may be a statistical disorder: with most of the unit cells having molecules lined up in the preferred conformation but a fraction of the unit cells with molecules in a different conformation of slightly higher energy. Since the X-ray diffraction results are summed over all of the unit cells, the resultant structure will exhibit this disorder.

If a molecule has a high rotational symmetry except for a small symmetry breaking atom or group (R), the molecule may pack in any of n-fold ways with R having no effect on the packing, but showing up as 1/n R at each of the n possible positions.

For example, a model compound for studying the interaction of the dioxygen molecule with the heme group (Fe₄N₄C₄O) in hemoglobin has four-fold rotational disorder of the distal oxygen atom, and so that atom, labeled O₂ (Note: In crystallographic structures the subscript refers to "oxygen number two"; O₂ does not refer to the dioxygen molecule as a whole), shows up as four "one-quarter atoms".

In the same way the N-methylimidazole ligand (the group below the iron atom) shows a two-fold disorder with respect to where the methyl group is located. The model compound has pseudo-four-fold symmetry and the rotational disorder can have no effect on the molecular packing. This is especially evident looking at the O₂ buried in the molecule; see Fig. 19.4 for the complete structure.

In some cases, such as the above, the confusion is minimal, although the presence of fractional atoms may be startling the first time one encounters them. In other cases, the problem may be considerably more serious. Perhaps the "classic" case in inorganic chemistry was the difficulty in the resolution of the structure of Fe₃(CO)₁₂. Because of disorder in the solid, a "Star of David" of six half atoms was found, as shown below.

The structure of Fe₃(CO)₁₂ is an example in which the disordering occurs about a center of inversion, a symmetry-related disorder. We have seen that the positions

---

38 Whether a molecule is actually dynamically moving in the crystal or merely statistically disordered among several possible positions is a moot point as far as X-ray crystallography is concerned since the interaction time of the X ray with the crystal is of the order of 10⁻¹⁴, faster than atomic movements. In the case of titin adhesion domain we have other evidence (see Chapter 15) for believing that the iron atoms are moving. But they need not—the disorder arises from the location of a molecule without a center of symmetry [Fe₃(CO)₁₂] on a symmetry element of the unit cell (the center of inversion).

---

Obviously, if R is large enough to affect the packing of the molecule in the crystal then the possibility of rotational disorder does not exist.
associated with the vibration. Consider the very simplest molecules possible. In X₂ molecules there will be only one stretching vibration, there will be no change in dipole moment (because there is no dipole moment either before or during vibration as long as the two X atoms are identical), and so that vibration will not be infrared active. The molecules H₂, F₂, Cl₂, and N₂ show no IR absorptions. However, carbon monoxide, isoelectronic with nitrogen, has a small dipole moment, and the molecular vibration is infrared active because the dipole moment changes as the bond length changes. The absorption frequency is 2143 cm⁻¹, an important value for coordination chemistry.²² The point is that the electromagnetic infrared wave can interact with the electric dipole moment; in essence, the infrared wave's electric field can "grab" the vibrating electric dipole moment resulting in a molecular vibration of the same frequency but increased amplitude. Consider next the water molecule. As we have seen, it has a dipole moment, so we expect at least one IR-active mode. We have also seen that it has C₃ᵥ symmetry, and we may use this fact to help sort out the vibrational modes. Each normal mode of vibration will form a basis for an irreducible representation of the group of the molecule.²³ A vibration will be infrared active if its normal mode belongs to one of the irreducible representations corresponding to the x, y and z vectors. The C₃ᵥ character table lists four irreducible representations: A1, A₂, B₁, and B₂. If we examine the three normal vibrational modes for H₂O, we see that both the symmetrical stretch and the bending mode are symmetrical not only with respect to the C₃ axis, but also with respect to the mirror planes (Fig. 3.21). They therefore have A₁ symmetry and are IR active. The third mode is not symmetrical with respect to the C₃ axis, nor is it symmetrical with respect to the mirror planes, so it has B₂ symmetry. Because y transforms as B₂, this mode is also IR active. The three vibrations absorb at 3652 cm⁻¹, 1545 cm⁻¹, and 3756 cm⁻¹, respectively.

²² See Chapters 11 and 15.
²³ For a more thorough discussion of group theory and vibrational spectroscopy, see Harris, D. C.; Bernstein, M. D. Symmetry and Spectroscopy; Dover: New York, 1989, Chapter 3.
of symmetry, i, and none of the IR and Raman bands can be coincidental; if it were tetrahedral, there should be IR and Raman bands at the same frequencies. The presence of six fundamental bands, three in the infrared and three in the Raman, none coincidental, is very strong evidence of the square planar structure of XeF₄.

Covalent bonds can be described with a variety of models, virtually all of which involve symmetry considerations. As a means of illustrating the role of symmetry in bonding theory and laying some foundation for discussions to follow, this section will show the application of symmetry principles in the construction of hybrid orbitals. Since you will have encountered hybridization before now, but perhaps not in a symmetry context, this provides a facile introduction to the application of symmetry.

You should remember that the basic procedure outlined here (combining appropriate atomic orbitals to make new orbitals) is applicable also to the derivation of molecular orbitals and ligand group orbitals, both of which will be encountered in subsequent chapters.

The atomic orbitals suitable for combination into hybrid orbitals in a given molecule or ion will be those that meet certain symmetry criteria. The relevant symmetry properties of orbitals can be extracted from character tables by simple inspection. We have already pointed out (page 60) that the pₓ orbital transforms in a particular point group in the same manner as an x vector. In other words, a pₓ orbital can serve as a basis function for any irreducible representation that has x listed among its basis functions in a character table. Likewise, the pᵧ and pₗ orbitals transform as y and z vectors. The dₓᵧ orbits (dₓᵧ, dₓᵧ, dₓᵧ, dₓᵧ, and dₓᵧ) transform as the binary products x-y, x-z, y-x, and z-x, respectively. Recall that degenerate groups of vectors, orbitals, etc., are denoted in character tables by inclusion within parentheses.

An s orbital, because it is spherical, will always be symmetric (i.e., it will remain unchanged) with respect to all operations of a point group. Thus it will always belong to a representation for which all characters are equal to 1 (a "totally symmetric" representation), although this is not explicitly indicated in character tables. The totally symmetric representation for a point group always appears first in its character table and has an A designation (A, A, A, etc.). When these or any other Mulliken symbols are used to label orbitals or other one-electron functions, the convention is to use the lower case a, α, etc.

To see how the s, p, and d atomic orbitals on a central atom are affected by the symmetry of the molecule to which they belong, consider the octahedral (O₆) square pyramidal (C₄ᵥ), and seesaw (C₂ᵥ) species shown in Fig. 3.25. For the AB₆ case, we find from the character table for the O₆ point group (Appendix D) that the pₓ, pᵧ, and pₗ orbitals belong to the t₁ᵥ representation. Since they transform together, they represent a triply degenerate set. The five d orbitals, on the other hand, form two sets of degenerate orbitals. The dₓᵧ, dₓᵧ, and dₓᵧ orbitals belong to the t₂ᵥ representation and the dₓᵧ, dₓᵧ, and dₓᵧ orbitals transform together as a triply degenerate t₁ᵥ set. The s orbital, always, belongs to the totally symmetric representation, A₁. If we imagine removing one of the B atoms from AB₆, we are left with square pyramidal AB₅ (Fig. 3.25b). By referring to the character table for the C₄ᵥ point group, we can see that the pₓ orbital now belongs to the a₁ representation and the pᵧ and pₗ orbitals to the e representation. Thus in going from O₆ to C₄ᵥ symmetry, the triply degenerate p orbitals have been split into two sets, one nondegenerate and one doubly degenerate. Similarly, the d orbitals are distributed among a larger number of sets than was the case in the octahedral molecule. The e level is split into two, a
Excerpts from the Preface to the Third Edition

It has been my very good fortune to have had contact with exceptional teachers and researchers when I was an undergraduate (Thomas B. Cameron and Hans H. Jaffe, University of Cincinnati) and a graduate student (John C. Bailar, Jr., Theodore L. Brown, and Russell S. Drago, University of Illinois); and to have had stimulating and helpful colleagues where I have taught (William D. Hobey and Robert C. Plumb, Worcester Polytechnic Institute; Jon M. Bellama, Alfred C. Boyd, Samuel O. Grim, James V. McArdle, Gerald Ray Miller, Carl L. Rollinson, Nancy S. Rowan, and John A. Tossell, University of Maryland). I have benefited by having had a variety of students, undergraduate, graduate, and thesis advisees, who never let me relax with a false feeling that I "knew it all." Finally, it has been my distinct privilege to have had the meaning of research and education exemplified to me by my graduate thesis advisor, Therald Moeller, and to have had a most patient and understanding friend, Hobart M. Smith, who gave me the joys of a second profession while infecting me with the "mihi itch." Professors Moeller and Smith, through their teaching, research, and writing, planted the seeds that grew into this volume.

Four librarians, George W. Black, Jr., of Southern Illinois University at Carbondale, and Sylvia D. Evans, Elizabeth W. McElroy, and Elizabeth K. Tomlinson, of the University of Maryland, helped greatly with retrieval and use of the literature. I should like to give special thanks to Gerald Ray Miller who read the entire manuscript and proofs at the very beginning, and who has been a ready source of consultation through all editions. Caroline L. Evans made substantial contributions to the contents of this book and will always receive my appreciation. Finally, the phrase "best friend and severest critic" is so hackneyed through casual and unthinking use, paralleled only by its rarity in the reality, that I hesitate to proffer it. The concept of two men wrangling over manuscripts, impassioned to the point of literally (check Webster's) calling each other's ideas "poppycock" may seem incompatible with a friendship soon to enter its second quarter-century. If you think so, you must choose to ignore my many trips to Southern Illinois University to work with Ron Brandon, to visit with him and his family, to return home with both my emotional and intellectual "batteries" recharged.

My family has contributed much to this book, both tangible and intangible, visible and (except to me) invisible. My parents have tolerated and provided much over the

James E. Huheey
are aligned along the Pt-Cl bonds, as shown. The $C_4$ and $C_4'$ axes are secondary axes perpendicular to $C_a$. The $C_2$ axes are chosen so as to include as many atoms as possible, and thus they lie along the $x$ and $y$ coordinates. The $C_4$ axes lie midway between the $x$ and $y$ axes. The $a_x$ and $a_y$ planes include the $C_2$ and $C_4'$ axes, respectively.

Translation of the $\text{PtCl}_4^{2-}$ ion in the $x$ and $y$ directions can be represented by the two vectors shown on the platinum atom (Fig. 3.19). In contrast to all of the cases we have so far considered, certain operations of the $D_{4h}$ group lead to new combinations for both vectors that do not bear a simple $+1$ or $-1$ relationship to the original positions. For example, under a clockwise $C_4$ operation, the $x$ vector is rotated to the $+y$ direction, and the $y$ vector is rotated to a $-x$ position. The character for this operation is zero. (This arises because the diagonal elements of the matrix for this operation are all zero; other elements in the matrix are nonzero but do not contribute to the character.) The $S_x$ and $S_y$ operations lead to a similar mixing of the $x$ and $y$ functions and also have characters of zero. Because of this mixing, the $x$ and $y$ functions are inseparable within the $D_{4h}$ symmetry group and are said to transform as a doubly degenerate or two-dimensional representation.

The remaining characters of the $E$ representation can be generated by considering the combined effect of each operation on the $x$ and $y$ vectors. When the identity operation is applied, both vectors remain unchanged; hence the character for the operation is two times $+1$ or $+2$. Similarly, the $S_z$ operation (reflection in the plane of the molecule) leaves the vectors unmoved and yields a character of $+1$. Under the $C_2$ operation (around the $z$ axis), the $x$ vector is brought to a $+x$ position and the $y$ vector to a $-y$ position, giving a character of $2(-1) = -2$. Inversion through the center of symmetry leads to the same result. For a $C_4$ operation around the $y$ axis, the $y$ vector is unmoved ($+1$), while the $x$ vector is rotated to the opposite direction ($-1$), yielding a total character of zero. The outcome is identical for reflection through the mirror plane that includes the $y$ axis (a $C_2$ operation).

### Reducible Representations

In applying the methods of group theory to problems related to molecular structure or dynamics, the procedure that is followed usually involves deriving a reducible representation for the phenomenon of interest, such as molecular vibration, and then decomposing it into its irreducible components. A reducible representation can sometimes be accomplished by inspection, for the more general case, the following reduction formula can be used:

$$N = \frac{1}{h} \sum_{x} x \cdot n_x$$

(3.1)

In this expression, $N$ is the number of times a particular irreducible representation appears in the representation being reduced, $h$ is the total number of operations in the group, $x$ is the character for a particular class of operations, and $n_x$ is the number of operations in the class, and the summation is taken over all classes. The degeneracy of reducible representations will be covered in the next section. For now, we can illustrate use of the reduction formula by applying it to the following reducible representation, $\Gamma_2$, for the motional degrees of freedom (translation, rotation, and vibration) in the water molecule:

$$\Gamma_2 = 9 -1 1 3$$

To decompose this representation, Eq. 3.1 must be applied for each of the four irreducible representations in the $C_{2h}$ point group:

$$A_1: N = \frac{1}{2} [(9)(1) + (-1)(1) + (1)(1)] = 3$$

$$A_2: N = \frac{1}{2} [(9)(1) + (-1)(1) + (1)(1)] = 3$$

$$B_1: N = \frac{1}{2} [(9)(1) + (-1)(1) + (1)(1)] = 3$$

$$B_2: N = \frac{1}{2} [(9)(1) + (-1)(1) + (1)(1)] = 3$$

Thus the reducible representation is resolved into three $A_1$, one $A_2$, two $B_1$, and three $B_2$ species. It can easily be confirmed that the characters for this combination sum to give the characters of $\Gamma_2$.

### Uses of Point Group Symmetry

#### Optical Activity

The reader will already have encountered chirality extensively in organic chemistry based upon asymmetric carbon atoms. Although the usual definition of chirality in organic texts is based upon a nonsuperimposable mirror image, and thus allows chirality in species such as klinec and spiro compounds, few introductory organic texts discuss chirality other than that based on asymmetric carbon atoms. Inorganic molecules may be optically active based on asymmetric nitrogen, phosphorus, or sulfur atoms, but by far the largest number of chiral inorganic compounds do not have a single asymmetric atom at all, but are chiral because of the overall molecular symmetry, specifically the absence of an improper axis of rotation. Most of these are

---

18 As we have seen, the formal definition of optical activity is based upon the absence of an improper axis of rotation. The two definitions are equivalent.


20 These are discussed in Chapter 6.
Fig. 3.18 Effects of symmetry operations in \( C_2 \), symmetry: rotation about the \( z \) axis:
(a) identity, \( E \); (b) rotation about the \( C_2 \) axis, (c, d) reflection in \( a \), planes.

Translations (and \( p \) orbitals) along the \( x \) and \( z \) axes in the water molecule conform to different symmetry patterns than the one just developed for the \( y \) axis. When the \( E, C_{2y}, \sigma_{xy}, \) and \( \sigma_{yz} \) operations are applied, in that order, to a unit vector pointing in the + \( x \) direction, the labels +1, −1, +1, and −1 are generated. A vector pointing in the + \( z \) direction will be unchanged by any of the symmetry operations and thus will be described by the set +1, +1, +1, +1.

The principles of group theory dictate that the total number of irreducible representations belonging to a point group will be the same as the number of types or classes of symmetry operations characterizing the group. Hence we expect four irreducible representations for the \( C_{2v} \) point group. We can generate the fourth one by considering rotations of the water molecule about the \( z \) axis. To see this, imagine an arrow curved clockwise about the \( z \) axis (when viewed down this axis, see Fig. 3.18).

Like the linear translations, this motion will be symmetric with respect to any operation that causes no change in direction and will be antisymmetric for any operation that leads to reversal. Both \( E \) and \( C_{2y} \) leave the direction unchanged (+1), but reflection in either mirror plane causes a reversal (−1). The result is +1, +1, +1, and −1 as the fourth symmetry pattern for the \( C_{2v} \) group.

Many of the symmetry properties of a point group, including its characteristic operations and irreducible representations, are conveniently displayed in an array known as a character table.

The character table for \( C_{2v} \):)

<table>
<thead>
<tr>
<th>( C_{2v} )</th>
<th>( E )</th>
<th>( C_{2y} )</th>
<th>( \sigma_{xy} )</th>
<th>( \sigma_{yz} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_1 )</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
</tr>
<tr>
<td>( E )</td>
<td>+1</td>
<td>+1</td>
<td>−1</td>
<td>−1</td>
</tr>
<tr>
<td>( B_1 )</td>
<td>+1</td>
<td>−1</td>
<td>+1</td>
<td>−1</td>
</tr>
<tr>
<td>( B_2 )</td>
<td>+1</td>
<td>+1</td>
<td>−1</td>
<td>+1</td>
</tr>
<tr>
<td>( B_{2g} )</td>
<td>+1</td>
<td>−1</td>
<td>+1</td>
<td>−1</td>
</tr>
<tr>
<td>( B_{2u} )</td>
<td>+1</td>
<td>+1</td>
<td>−1</td>
<td>+1</td>
</tr>
<tr>
<td>( E_{g} )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( E_{u} )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

The column headings are the classes of symmetry operations for the group, and each row depicts one irreducible representation. The +1 and −1 numbers, which correspond to symmetric and antisymmetric behavior, as we have seen, are called characters.

In the columns on the right are some of the basis functions which have the symmetry properties of a given irreducible representation. \( R_y, R_x, \) and \( R_z \) stand for rotations around the specified axes. The binary products on the far right indicate, for example, how the \( d \) atomic orbitals will behave ("transform") under the operations of the group.

The symbols in the column on the far left of the character table (Mulliken labels) are part of the language of symmetry. Each one specifies, in shorthand form, several features of the representation to which it is attached. One such feature is the dimension, which is related to the mathematical origin of the characters. Strictly speaking, each character is derived from a matrix representing a symmetry operation, and is in fact equal to the sum of the diagonal elements of the matrix. For the \( C_{2v} \) group, all of these matrices are of the simplest possible form: They consist of a single element (the character) and are thus one-dimensional. However, for groups with rotational axes of order three or higher, two- and three-dimensional matrices occur, leading to characters with values as high as 2 and 3, respectively. (This will be illustrated shortly for the \( D_{2h} \) point group.) One-dimensional representations, such as those in the \( C_{2v} \) group, are labeled \( A \) if symmetric or \( B \) if antisymmetric with respect to the highest order rotational axis. If two or more representations in a group fit the \( A \) or \( B \) classification, a subscript is added to indicate symmetric (1) or antisymmetric (2) behavior with respect to a second symmetry element. This second element will be a \( C_2 \) axis perpendicular to the principal axis or, in the absence of such an axis, a vertical mirror plane. Two-dimensional representations are denoted by \( E \) (not to be confused with the identity operation \( E \)), and three-dimensional cases by \( T \). As we have seen before, the labels \( g \) and \( u \) may be used if there is a center of inversion. The supercripts \( ^{+} \) and \( ^{-} \) may be used to signify symmetric and antisymmetric behavior with respect to a horizontal plane.

The tetrachloroplatinum(II) anion, \( \text{PtCl}_4^{2-} \), was given earlier (Fig. 3.14c) as an example of a molecule belonging to the \( D_{2h} \) point group. The character table for this group is

<table>
<thead>
<tr>
<th>( D_{2h} )</th>
<th>( E )</th>
<th>( 2C_2 )</th>
<th>( 2C_2' )</th>
<th>( i )</th>
<th>( 2S_4 )</th>
<th>( e )</th>
<th>( 2e )</th>
<th>( 2a_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_1 )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( A_2 )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( E )</td>
<td>+1</td>
<td>+1</td>
<td>−1</td>
<td>−1</td>
<td>+1</td>
<td>+1</td>
<td>−1</td>
<td>−1</td>
</tr>
<tr>
<td>( B_{1g} )</td>
<td>+1</td>
<td>−1</td>
<td>+1</td>
<td>−1</td>
<td>+1</td>
<td>+1</td>
<td>−1</td>
<td>−1</td>
</tr>
<tr>
<td>( B_{2g} )</td>
<td>+1</td>
<td>−1</td>
<td>+1</td>
<td>−1</td>
<td>+1</td>
<td>+1</td>
<td>−1</td>
<td>−1</td>
</tr>
<tr>
<td>( B_{1u} )</td>
<td>+1</td>
<td>−1</td>
<td>+1</td>
<td>−1</td>
<td>+1</td>
<td>+1</td>
<td>−1</td>
<td>−1</td>
</tr>
<tr>
<td>( B_{2u} )</td>
<td>+1</td>
<td>−1</td>
<td>+1</td>
<td>−1</td>
<td>+1</td>
<td>+1</td>
<td>−1</td>
<td>−1</td>
</tr>
<tr>
<td>( E_{g} )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( E_{u} )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Note that two of the irreducible representations in this group are two-dimensional, labeled \( E_g \) and \( E_u \). Each has a pair of basis functions listed for it. To see how \( x \) and \( y \) translation serve as a basis for the \( E_u \) representation, refer to Fig. 3.19 which shows the \( \text{PtCl}_4^{2-} \) ion labeled with a coordinate system assigned according to the usual conventions. The \( z \) axis coincides with the \( C_4 \) rotational axis, and the \( x \) and \( y \) axes...
Table 3.5
Derivation of \( r' \) for BCl₃

<table>
<thead>
<tr>
<th>Unshifted atoms</th>
<th>Contributions per atom</th>
<th>( r'_{\text{Red}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

of the number of unshifted atoms by the contribution for each operation gives the reducible representation \( \Gamma_{\text{Red}} \) for water shown in Table 3.3.

We determined earlier (page 63) that the irreducible components of this representation are three \( A_1 \), one \( A_2 \), two \( B_1 \), and three \( B_2 \) species. To obtain from this total set the representations for vibration only, it is necessary to subtract the representations for the other two forms of motion, rotation and translation. We can identify them by referring to the \( C_2 \) character table. The three translational modes will belong to the same representations as the \( x \), \( y \), and \( z \) basis functions, and the rotational modes will transform as \( R_x \), \( R_y \), and \( R_z \). Subtraction gives

\[
\Gamma_{\text{Red}} = 3A_1 + A_2 + 2B_1 + 3B_2
\]

This is, of course, the same result as obtained above by analyzing the symmetries of the vibrational modes.

As a second example of the use of character tables in the analysis of IR and Raman spectra, we turn to BCl₃, with \( D_3h \) symmetry. Because it has four atoms, we expect six vibrational modes, three of which will be stretching modes (because there are three bonds) and three of which will be bending modes. Table 3.5 shows the derivation of \( r' \) for the molecule's twelve degrees of freedom. Application of the reduction equation and subtraction of the translational and rotational representations gives

\[
\Gamma_{\text{Red}} = A_1 + A_2 + 3E' + 2A_1^+ + E''
\]

We see that the six fundamental vibrations of BCl₃ transform as \( A_1 \), \( A_2 \), and \( 2E' \). Each \( E' \) representation describes two vibrational modes of equal energy. Thus the \( 2E' \) notation refers to four different vibrations, two of one energy and two of another. The \( A_1 \) mode is Raman active, the \( A_2 \) is IR active, and the \( E' \) modes are both Raman and IR active.

In thinking about the actual vibrations associated with these modes, we expect the \( A_1 \) mode to be the symmetrical stretch because it remains unchanged under all of the symmetry operations (Fig. 3.23a). Another motion is a symmetrical out-of-plane bending deformation with the boron atom moving in one direction while the three chlorine atoms move in unison in the opposite direction (Fig. 3.23b). The four remaining vibrations (two stretching and two bending) are not as easily categorized because they are distributed among two doubly degenerate modes, both of which

![Fig. 3.23 Normal modes of vibration of the BCl₃ molecule: (a) symmetrical stretching mode, \( A_1 \); (b) out-of-plane bending mode, \( A_2 \); (c) symmetrical stretching mode, \( E' \); and (d) in-plane bending mode, \( E'' \). (Modified from Harris, D. C.; Bertolucci, M. D. Symmetry and Spectroscopy. Dover: New York, 1989. Reproduced with permission.)](image)
Table 3.1

<table>
<thead>
<tr>
<th>Point groups of chiral and achiral molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chiral</td>
</tr>
<tr>
<td>$C_1$ (asymmetric)</td>
</tr>
<tr>
<td>$C_2$ (dissymmetric)</td>
</tr>
<tr>
<td>$D_{2h}$ (dissymmetric)</td>
</tr>
<tr>
<td>$D_{2d}$ (plane of symmetry)</td>
</tr>
<tr>
<td>$T_h$ (improper axis)</td>
</tr>
<tr>
<td>$C_{3v}$ (center and plane of symmetry)</td>
</tr>
<tr>
<td>$C_{2v}$ (plane of symmetry)</td>
</tr>
<tr>
<td>$C_{3}$ (dissymmetric)</td>
</tr>
<tr>
<td>$C_{3v}$ (dissymmetric)</td>
</tr>
<tr>
<td>$C_{3v}$ (dissymmetric)</td>
</tr>
<tr>
<td>$C_{3v}$ (dissymmetric)</td>
</tr>
</tbody>
</table>

A molecule will have a dipole moment if the summation of all of the individual bond moment vectors is nonzero. The presence of a center of symmetry, $i$, requires that the dipole moment be zero, since any charge on one side of the molecule is canceled by an equal charge on the other side of the molecule. Thus, $\text{CoF}_2^+$ (Fig. 3.4a), trans-$\text{NCl}_2$ (Fig. 3.3a), and the staggered conformer of ferrocene (Fig. 3.8b) do not have dipole moments. If two or more $C_i$ axes are present ($n > 1$), a dipole cannot exist since the dipole vector cannot lie along more than one axis at a time. Thus $\text{SiF}_4$ (Fig. 3.4a), $\text{PF}_5$ (Fig. 3.4b), eclipsed ferrocene (Fig. 3.8a), and all $D_n$ molecules (cf. Fig. 3.14) do not have dipole moments. The presence of a horizontal mirror plane prevents the possibility of there being a dipole moment, but one or more vertical mirror planes do not. The dipole moment vector must obviously lie in such planes, and there may be a $C_i$ axis in the plane along which the dipole lies. Examples of such molecules are cis-$\text{N}_2\text{F}_2$ (Fig. 3.6) and $\text{O} = \text{N} = \text{Cl}$ (Fig. 3.11b). Common point groups are listed as “symmetry allowed” or “symmetry forbidden” with respect to possible dipole moments in Table 3.2. In addition, it is always possible that certain heteronuclear bond moments might be zero or two different bonds might have identical moments that cancel. Indeed, some molecules have very small but finite dipole moments: $\text{Si} = \text{Te}$ (0.57 x $10^{-30}$ C m; 0.17 D), cis-$\text{FeN} = \text{NF}$ (0.53 x $10^{-30}$ C m; 0.16 D), NO (0.50 x $10^{-30}$ C m; 0.15 D), $\text{SbF}_3$ (0.40 x $10^{-29}$ C m; 0.12 D), CO (0.37 x $10^{-29}$ C m; 0.11 D), $\text{FClO}_3$ (0.077 x $10^{-30}$ C m; 0.023 D).

In infrared spectroscopy photons having energies corresponding to the excitation of certain molecular vibrations are absorbed and the transmission of the infrared light at those frequencies is reduced (Fig. 3.20). In Raman spectroscopy, allowed molecular excitations result in differences in the frequency of scattered light. That is, incident light, which may be of any wavelength (usually visible), undergoes scattering. Most of the scattered light has the same frequency as that impinging upon the sample, but a small fraction is shifted by amounts corresponding to the energy differences of the vibrational states (Fig. 3.20).

The number of vibrational modes of a molecule composed of $N$ atoms is $3N - 6$ (or $3N - 5$ if linear). We may find which of these are infrared and Raman active by the application of a few simple symmetry arguments. First, infrared energy is absorbed for certain changes in the vibrational energy levels of a molecule. For a vibration to be infrared active, there must be a change in the dipole moment vector...
Figure 3.29 A four-fold improper axis (4) operation. The 4 axis is perpendicular to the plane of the paper, \(A_3\) and \(A_4\) (+) are above the plane, \(A_2\) and \(A_1\) (-) are below. When a point \(A\), \((x, y, z)\) coordinates: +a, +b, +c) is rotated clockwise by 90°, followed by inversion, it becomes point \(A_4\) (-b, +a, -c). In the same way, \(A_2\) becomes \(A_3\), \(A_3\) becomes \(A_2\), and \(A_4\) becomes \(A_1\).

The Schroedinger system allows for three-dimensional lattices to have the same symmetry elements as we have seen in molecular point groups: the center of symmetry (center of inversion), mirror planes (labeled with the symbol \(m\)), and simple \(n\)-fold rotational axes (designated by the \(n\) value, \(n = 1, 2, 3, 4,\) and 6). A mirror plane perpendicular to a principal axis is labeled \(n/m\). In addition, there are three other symmetry elements: axes of rotatory inversion, glide planes, and screw axes.

In the International system, the axis of rotatory inversion (labeled \(\tau\)) is one of \(n\)-fold rotation followed by inversion (see Fig. 3.29). A glide plane operation is a translation followed by a reflection in a plane parallel to the translation axis. In the simplest case, consider a lattice with unit cell of length \(a\) along the \(x\) axis (Fig. 3.30). Movement of a distance \(a/2\) along the \(x\) axis, followed by reflection, accomplishes the symmetry operation. A glide plane is labeled \(a\), \(b\), or \(c\) depending on the axis along which translation occurs.

Another symmetry element that may be present in a crystal is a screw axis (designated by \(n\alpha\)) which combines the rotational symmetry of an axis with translation along that axis. A simple two-fold (2\(\alpha\)) screw axis is shown in Fig. 3.31. In contrast to the glide plane, only translation and rotation are involved in this operation, and therefore a chiral molecule retains its particular handedness.

It can be shown mathematically that five-fold axes cannot appear in a truly periodic crystal of single unit cells repeating in space. Nevertheless, some interesting "quasicrystals" have recently been discovered that have unusual symmetry properties. See Problem 3.39.
Reduction of $\Gamma_1$ (Eq. 3.1) shows that it is composed of $e_u$, $a_2u$, and $b_3u$. The $D_{2h}$ character table reveals that no orbitals transform as $b_3u$, but that $b_3$ belongs to $a_2u$, while $a_2$ and $b_2$ belong to $e_u$. That these three orbitals on platinum are allowed by symmetry to participate in out-of-plane $\pi$ bonding is reasonable since they are all oriented perpendicular to the plane of the ion (the xy plane). Selection of orbitals on platinum suitable for in-plane $\pi$ bonds is left as an exercise. (Hint: In choosing vectors to represent the suitable atomic orbitals, remember that the in-plane and out-of-plane $\pi$ bonds will be perpendicular to each other and that the regions of overlap for the former will be on each side of a bonding axis. Thus the in-plane vectors should be positioned perpendicular to the bonding axes.)

Crystallography

The symmetry of crystals not only involves the individual point group symmetry of the molecules composing the crystals, but also the translational symmetry of these molecules in the crystal. The latter is exemplified by a packet fence or a stationary row of ducks in a shooting gallery. If we turn on the mechanism so the ducks start to move and then blink our eyes just right, the ducks appear motionless—the ducks move the distance between them while we blink, and all ducks are identical. Under these conditions we could not tell if the ducks were moving or not, because they would appear identical after the change to the way they appeared before the change. If we think of the ducks as lattice points, a row of them like this is a one-dimensional crystal. In a three-dimensional crystal, a stacked array of unit cells, the repeating units of the system are like the rows of ducks and display translational symmetry.

Determining the crystal structure of a compound by X-ray diffraction has become so important (and so routine) to the inorganic chemist that nearly fifty percent of the papers currently published in the journal *Inorganic Chemistry* contain at least one structure. What information is conveyed when we read that the solid state structure of a substance is monoclinic $P2_1/c$? We can answer this question by starting with a few basics.

Diffraction patterns can be described in terms of three-dimensional arrays called lattice points. The simplest array of points from which a crystal can be created is called a unit cell. In two dimensions, unit cells may be compared to tiles on a floor. A unit cell will have one of seven basic shapes (the seven crystal systems), all constructed from parallelepipeds with six sides in parallel pairs. They are defined as follows:

1. **Triclinic**: $a \neq b \neq c$, $\alpha \neq \beta \neq \gamma$.
2. **Monoclinic**: $a \neq b \neq c$, $\alpha = 90^\circ$, $\beta \neq \gamma$.
3. **Orthorhombic**: $a \neq b \neq c$, $\alpha = \beta = \gamma = 90^\circ$.
4. **Tetragonal**: $a = b = c$, $\alpha = \beta = \gamma = 90^\circ$.
5. **Trigonal**: $a = b = c$, $\alpha = \beta = \gamma = 120^\circ$.
6. **Hexagonal**: $a = b = c$, $\alpha = \beta = \gamma = 90^\circ$, $c/a = \sqrt{3}$.
7. **Cubic**: $a = b = c$, $\alpha = \beta = \gamma = 90^\circ$.

Table 3.6

<table>
<thead>
<tr>
<th>System</th>
<th>Relations between edges and angles of unit cell</th>
<th>Lengths and angles to be specified</th>
<th>Characteristic symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>$a \neq b \neq c$, $\alpha \neq \beta \neq \gamma$</td>
<td>$a$, $b$, $c$</td>
<td>1-fold (identity or inversion) symmetry only</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>$a \neq b \neq c$, $\alpha = 90^\circ$, $\beta \neq \gamma$</td>
<td>$a$, $b$, $c$</td>
<td>2-fold axis (2 or $\overline{2}$) in one direction only (y axis)</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>$a \neq b \neq c$, $\alpha = \beta = \gamma = 90^\circ$</td>
<td>$a$, $b$, $c$</td>
<td>2-fold axes in three mutually perpendicular directions</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>$a = b = c$, $\alpha = \beta = \gamma = 90^\circ$</td>
<td>$a$, $c$</td>
<td>4-fold axis along z axis only</td>
</tr>
<tr>
<td>Trigonal and Hexagonal</td>
<td>$a = b = c$, $\alpha = \beta = \gamma = 120^\circ$</td>
<td>$a$, $c$</td>
<td>3-fold or 6-fold axis along z axis only</td>
</tr>
<tr>
<td>Cubic</td>
<td>$a = b = c$, $\alpha = \beta = \gamma = 90^\circ$</td>
<td>$a$, $d$</td>
<td>Four 3-fold axes each inclined at $54^\circ$ to cell axes (i.e. parallel to body-diagonals of unit cell)</td>
</tr>
</tbody>
</table>


According to the symmetry of the crystal, which leads to certain relations between the unit cell edges and angles for each system (Table 3.6). Although these relations between cell dimensions can be said to characterize a particular crystal system, they are not the criteria by which a crystallographer assigns a crystal to one of the systems during a structure determination. Rather, the assignment is made on the basis of the crystal's symmetry features. For example, a structure may appear, within experimental error, to have all unit cell edges (a, b, and c) of different length and all angles ($\alpha$, $\beta$, and $\gamma$) equal to 90°, suggesting that it is orthorhombic. However, if it is found to possess only a single two-fold axis, it must be classified as monoclinic.

Only fourteen space lattices, called Bravais lattices, are possible for the seven crystal systems (Fig. 3.28). Designations are $P$ (primitive), $I$ (body-centered), $F$ (face-centered), $C$ (face-centered in one set of faces), and $R$ (rhombohedral). Thus our monoclinic structure $P2_1/c$ belongs to the monoclinic crystal system and has a primitive Bravais lattice.

The internal molecular structure of a unit cell may be complicated because a lattice point may be occupied by a group of atoms or molecules, rather than a single...
Irreducible Representations and Character Tables

The symmetry operations that belong to a particular point group constitute a mathematical group, which means that as a collection they exhibit certain interrelationships consistent with a set of formal criteria. An important consequence of these mathematical relationships is that each point group can be decomposed into symmetry patterns known as irreducible representations which aid in analyzing many molecular and electronic properties. An appreciation for the origin and significance of these symmetry patterns can be obtained from a qualitative development.\(^\text{16}\)

Until now we have considered symmetry operations only insofar as they affect atoms occupying points in molecules, but it is possible to use other references as well. For example, we might consider how a dynamic property of a molecule, such as translation along an axis, is transformed by the symmetry operations of the point group to which the molecule belongs. Recall the symmetry elements and coordinate system given previously for the water molecule, which belongs to the \(C_2v\) point group (Fig. 3.9). The coordinates are assigned according to the convention that the highest fold axis of rotation—\(C_2\) in this case—is aligned with the \(z\) axis, and the \(x\) axis is perpendicular to the plane of the molecule.

Now let translation of the molecule in the \(+y\) direction be represented by unit vectors on the atoms, and imagine how they will change when undergoing the \(C_2\) symmetry operations (Fig. 3.17). At the end of each symmetry operation, the vectors will point in either the \(+y\) or the \(-y\) direction, that is, they will show either symmetric or antisymmetric behavior with respect to the operation. If we represent the former with +1 and the latter with −1, we can characterize each operation with one of these labels. Identity (\(I\)) does not alter the position of the arrows (\(+1\)). Rotation about the \(C_2\) axis causes the \(+y\) vectors to change to \(-y\) (−1). Reflection in the \(v_{xy}\) plane causes \(+y\) to change to \(-y\) (−1), but reflection in the plane of the molecule, \(v_z\), results in the vectors remaining unchanged (+1). The set of four labels (+1, −1, −1, +1) generated in this simple analysis constitutes one irreducible representation within the \(C_2v\) point group. It is irreducible in the sense that it cannot be decomposed into a simpler or more fundamental form. Not only does it describe the effects of \(C_2\) operations on \(y\) translation but on other \("y-vector functions"\) as well, such as the \(p_y\) orbital. Thus \(y\) is said to serve as a basis function for this irreducible representation within the \(C_2v\) point group.

\(^{16}\) For more thorough and mathematical developments in terms of group theory, see the books listed in Footnote 1.
of atoms in unit cells are related by symmetry elements. If a molecule lies on a fixed symmetry element (center of inversion, rotational axis, mirror plane) and does not itself possess that symmetry element, there will be a superposition of images. Usually in such a situation, the overall shape of the molecule and distribution of polar bonds will be similar for the two (or more) disordered fragments. This is the case in triiron dodecacarbonyl (the complete structure is illustrated in Fig. 15.7). The two possible orientations of the "iron triangle" are superimposed to give the hexagonal arrangement observed.

Due to the superposition of two inversionally related half molecules in Fe$_3$(CO)$_{12}$, the determination of the arrangement of the carbonyl groups proved a difficult task. In fact, nearly 17 years elapsed before it was successfully solved by a process of computer simulation and modeling.

A current example of a solid that is disordered at room temperature is buckminsterfullerene. Until recently, only two allotropes of carbon were known: diamond and graphite. However, on the basis of ions detected in a mass spectrometer with m/e = 720, a C$_{60}$ molecule was hypothesized. Now this third allotrope, C$_{60}$, has been isolated from the vaporization products of graphite. One heats carbon rods in an inert atmosphere of helium or argon, and extracts the soot that forms with benzene. The proposed structure is analogous to a soccerball with bonds along the seams and carbon atoms at the junctures of the seams (Fig. 3.33). The name "buckminsterfullerene" was suggested because of a fancied likeness to a geodesic dome. This was quickly reduced by the waggish to "buckyball".

The synthesis of macroscopic amounts of buckyball led to the study of many interesting properties of this molecule which continue unabated as this book goes to press. The C$_{60}$ molecule is nearly spherical, and while the molecules themselves pack nicely in a cubic closest packed structure, each molecule has essentially the free rotation of a ball bearing, and because of this disorder the structure could not be determined at room temperature.

---

Fig. 3.33 Comparison of (a) a soccer ball and (b) structure of the C$_{60}$ molecule.

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43 Or a football in the European and South American sense.
44 Note added in proof: The entire March 1992 issue of Accounts of Chemical Research is devoted to buckyballs.
directed toward the vertices of a tetrahedron. The general procedure for determining \( \psi \), requires four hybrid orbitals on the central atom, or \( \text{CrO}_4^{4-} \), consistent with the geometry of the molecule. Thus a tetrahedral molecule or ion, what atomic orbitals can be combined to form these hybrid orbitals starts with the modulating its own outer shell nonbonding electrons will have a spatial orientation y2 or d. The outcome is a complete loss of orbital degeneracy. As an example consider the square planar bonding. The same basic approach that was applied to the construction of hybrid orbitals was directed from the central atom toward the atoms to which it is bound and the hybrid orbitals would overlap along the bond axes with appropriate orbitals of the pendant atoms. In other words, these hybrid orbitals will be involved in sigma bonds. The general procedure for determining what atomic orbitals can be combined to form these hybrid orbitals starts with the recognition that the hybrid orbitals will constitute a set of basis functions for a representation within the point group of the molecule. This representation, which will be reducible, can be obtained by considering the effect of each symmetry operation of the point group on the hybrid orbitals. Once generated, the representation can be factored into its irreducible components (page 62). At that point, we can obtain the information we are seeking from the character table for the molecule, because atomic orbitals which transform as these irreducible components will be the ones suitable for combination into hybrid orbitals.

In carrying out the procedure for a tetrahedral species, it is convenient to let four vectors on the central atom represent the hybrid orbitals we wish to construct (Fig. 3.26). Derivation of the reducible representation for these vectors involves performing on them, in turn, symmetry operations from each class in the \( T_d \) point 'group. As in the analysis of vibrational modes presented earlier, only those vectors that do not move will contribute to the representation. Thus we can determine the character for each symmetry operation we apply by simply counting the number of vectors that remain stationary. The result for \( \text{AB}_4 \) is the reducible representation, \( \Gamma^4 \).

Application of the reduction formula (Eq. 3.1) yields \( a_1 \) and \( t_2 \) as the irreducible components. Referring to the \( T_d \) character table, we see that no orbitals are listed for the totally symmetric \( a_1 \) representation; however, recall that \( s \) orbitals are always in this class. For the \( t_2 \) case, there are two possible sets of degenerate orbitals: \( p_x, p_y, \) and \( d_{xy}, d_{yz}, d_{zx} \). Thus the four hybrid orbitals of interest can be constructed from either one \( s \) and three \( p \) orbitals, to give the familiar \( sp^3 \) hybrid orbitals, or from one \( s \) and three \( d \) orbitals to yield \( sd^2 \) hybrids. Viewed strictly as a symmetry question, both are equally possible. To decide which mode of hybridization is most likely in a given molecule or ion, orbital energies must be taken into account. For methane and other cases involving carbon, the \( d \) orbitals lie too high in energy compared to the \( 2s \) orbitals for significant mixing of the two to occur. However, for tetrahedral species involving transition metals, such as \( \text{MnO}_4^- \) or \( \text{CrO}_4^{2-} \), there are \( d \) and \( s \) orbitals similar enough in energy that the hybrid orbitals involved in bonding may be a mixture of \( sp^3 \) and \( sd^2 \). It is important to understand that a character table tells us only what orbitals have the right symmetry to interact; only energy considerations can tell us whether in fact they do.

In deriving hybrid orbitals in the foregoing example, we assumed that these orbitals were directed from the central atom toward the atoms to which it is bound and that the hybrid orbitals would overlap along the bond axes with appropriate orbitals of the pendant atoms. In other words, these hybrid orbitals will be involved in sigma bonds. The same basic approach that was applied to the construction of hybrid orbitals for the \( s \) orbitals involving a central atom can also be used to select atomic orbitals that are available for \( \pi \) bonding. As an example consider the square planar ion, \( \text{PtCl}_4^- \). Two types of bonds between the platinum atom and each chlorine atom are possible here: "out-of-plane," with the two regions of overlap above and below the plane of the ion, and "in-plane" having both overlap areas in the molecular plane. Atomic orbitals on platinum that will be capable of participating in out-of-plane \( \pi \) bonding will be perpendicular to the plane of the ion and can be represented by the vectors shown in Fig. 3.27. As before, a reducible representation may be obtained by carrying out the operations of the appropriate point group (\( D_{2h} \)) and, for each operation, recording the number of vectors that remain unmoved:

\[
\begin{align*}
E & : 2C_4 \quad C_2 \quad C_2' \quad C_2'' \quad i \quad 2S_4 \quad s_2 \quad 2s' \quad 3s' \\
\Gamma_1 & : 4 \quad 0 \quad 0 \quad -2 \quad 0 \quad 0 \quad 0 \quad -4 \quad 2 \quad 0
\end{align*}
\]
2 - What Is Inorganic Chemistry?

Chemical Structure of Zeolites and Other Chemical Systems

This discovery was made in the 1850s, and it was the first ion exchange water-softening process utilized commercially. The ion exchangers used today in home softening units are closely related in structure and exchange properties, but are more stable for long-term use.

More recently, synthetic zeolites have made their appearance in a closely related, yet quite distinct, application. Not everyone, even in areas of quite hard water, has a water softener. In an effort to counter the negative effects of hard water, manufacturers early adopted the practice of adding "builders" to soaps and synthetic detergents. At first these were carbonates ("washing soda") and borates ("borax"). More recently, these have been polyphosphates, \( \text{PO}_4^{3-} \) \( n + 1 \), which compete with the hard water cations, that is, tied them up so that they did not interfere with the cleaning process. The synthetics of polyphosphates and the study of their chelating properties with \( \text{Mg}^{2+}, \text{Ca}^{2+} \), and other cations, are other aspects of inorganic chemistry. However, phosphate is one of the three main ingredients of fertilizer, and too much phosphorus leads to the eutrophication of lakes and streams. In an effort to reduce the amount of phosphates used, manufacturers started using a synthetic zeolite detergent in the form of microcrystal powder to absorb those unwanted cations.

Today, this is the largest usage of zeolites on a tonnage basis.

Lest you be muttering, "So out with phosphate pollution, in with zeolite pollution", zeolites seem to be one of the few things we can add to the ecosystem without negative consequences. The very structures of zeolites make them thermodynamically unstable, and they degrade readily to more stable aluminosilicates that are naturally occurring clays. But that raises other interesting questions: If they are metastable, why do they form, rather than their more stable decomposition products? How can we synthesize them?

Another use of zeolites has been as "molecular sponges." This very descriptive, if slightly misleading, name comes from a remarkable property of these zeolites: their ability to selectively adsorb molecules on the basis of their size. A mixture of gases may be separated according to their molecular weights (sizes) just as a coarse mixture may be separated into "hulls" that selectively adsorb larger, noxious molecules, but are inert to smaller, ubiquitous molecules such as water, dimedon (\( \text{N}_2\text{O}_4 \)), and dioxygen (\( \text{O}_2 \)). These are zeolites that have a special affinity for small molecules (like \( \text{H}_2\text{O} \)) but exclude larger molecules. They are thus excellent drying agents for various laboratory solvents.

Before we can understand how these molecular interactions can take place, we must understand the structures of zeolites. Important for us, at least a century, the use of structural information to understand chemistry is more important now than ever before. The determination of chemical structures is a combination of chemical experiments, theoretical calculations, and nuclear magnetic resonance. Because we have seen glimpses of "structure" molecules all our lives in TV commercials and company logos, it is almost impossible for us to realize that it has not been long in terms of human history since arguments were made that such structures could not be studied (or even could not exist) because it was impossible to see atoms (if they existed). The crystallographer's ability to take a crystal in hand and to determine the arrangement of invisible atoms is a crystallographer (Fig. 1.1) is a

1 The first chemical reactions, such as the discovery of tin, were not consciously applied as "laws and rules" that led to chemistry. Perhaps the idea conscious application of chemistry by humans was that of the action of poisons on sugar in making and brewing, or be somewhat less well defined process of cooking.


3 The symbol Z represents all of the zeolite structure except the exchangeable Na+ ion.

4 When you buy an ordinary "5-10-5" fertilizer, you are buying nitrogen (5%), expressed as \( \text{N}_2 \), phosphate (10%, expressed as \( \text{P}_2\text{O}_5 \)), and potassium (5%, expressed as \( \text{K}_2\text{O} \)).
molecules such as H$_2$O (Fig. 3.13b), NH$_3$ (Fig. 3.13c), and pentaamminechlorocobalt(III) cation (Fig. 3.13d) possess $C_{nv}$ symmetry.

**Question:** If the planes of the phenyl rings in triphenylphosphine (Fig. 3.13c) were parallel to the three-fold axis (i.e., if the intersection of their planes coincided with that axis), what would the point group of triphenylphosphine be?

**Dihedral groups.** Molecules possessing $nC_2$ axes perpendicular to the principal axis ($C_{n}$) belong to the dihedral groups. If there are no mirror planes, as in tris(ethylenediamine)cobalt(III) cation (Fig. 3.14a), the molecule belongs to the $D_{n}$ group. Addition of a mirror plane perpendicular to the principal axis results in the $D_{nh}$ group which includes molecules such as phosphorus pentachloride (Fig. 3.14b), the tetrachloroplatinate(II) anion (Fig. 3.14c), the trans-tetraamminedichlorocobalt(III) cation (Fig. 3.14d), and eclipsed ferrocene (Fig. 3.8a).

Linear molecules with a center of symmetry, such as BeF$_2$ and all of the $X_2$ molecules (Fig. 3.14e-g), possess a horizontal mirror plane and an infinite number of $C_2$ axes perpendicular to the principal axis and thus have $D_{nah}$ symmetry.

**Question:** If the mirror planes contain the principal $C_2$ axis and bisect the angle formed between adjacent $C_2$ axes, they are termed *dihedral planes*. Molecules such as the staggered conformer of ferrocene (Fig. 3.8b), the staggered conformer of ethene (Fig. 3.8b), the staggered conformer of ethane (Fig. 3.15a), the square-antiprismatic octafluorozirconate(IV) anion (Fig. 3.15b), bis(dimethyltin)[μ-tetracarbonyliron]tin (Fig. 3.15c), octasulfur (Fig. 3.15d), and the staggered conformer of dibenzenechromium (Fig. 3.15e) that contain such dihedral planes belong to the $D_{nh}$ groups.

**Question:** If the triphenylphosphine molecule were planar, what would be its point group?

5. A *flowchart for assigning point symmetry*. The symmetry elements, and the rules and procedures for their use in determining the symmetry of molecules, can be formalized in a flow chart such as that shown in Fig. 3.16. It contains all of the point groups discussed above (enclosed in square boxes) as well as a few others not commonly encountered. In addition, the symmetries assigned above "by inspection" may be derived in a more systematic way by the use of this diagram.

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13 $C_{nv}$.

14 $D_{nh}$.
What Is Inorganic Chemistry?

Chemical Reactivity

Although it is not possible for the chemist to absolutely control the movement of individual atoms or molecules in zeolite structures, the nature of the structure itself results in channels that direct the molecular motions (Fig. 1.3). Furthermore, the sizes and shapes of the channels determine which molecules can form most readily, and which can leave readily. A molecule that cannot leave (Fig. 1.4) is apt to react further. This may have important consequences: A catalyst (ZSM-5) that is structurally related to boggsite is used in the alkylation of toluene by methanol to form para-xylene. The methanol can provide methyl groups to make all three (ortho, meta, and para)
3-Symmetry and Group Theory

Point Group: Molecular Symmetry

Fig. 3.10 Point groups and molecules of high symmetry: (a) icosahedron, (b) the \(\text{Si}_2\text{H}_6^+\) ion, (c) octahedron, (d) sulfur hexafluoride, (e) hexacyanocobaltate(III) anion, (f) tetrahedron, (g) ammonium cation, and (h) tetrafluoroborate anion.

planes, a center of symmetry, as well as six \(S_6\) and ten \(S_5\) axes collinear with the \(C_3\) and \(C_2\) axes.

b. Octahedral, \(O_h\).—The octahedron (Fig. 3.10c) is commonly encountered in both coordination compounds and higher valence nonmetal compounds (Fig. 3.10d, e). It has four \(C_3\) axes, three \(C_4\) axes, six \(S_2\) axes, three \(S_6\) planes, six \(S_5\) planes, and a center of symmetry. In addition, there are three \(C_3\) and three \(S_2\) axes that coincide with the \(C_3\) axes.

c. Tetrahedral, \(T_d\).—Tetrahedral carbon is fundamental to organic chemistry, and many simple inorganic molecules and ions have tetrahedral symmetry as well (Fig. 3.10f, h). A tetrahedron (Fig. 3.10h) has four \(C_3\) axes, three \(C_2\) axes, six mirror planes, and three \(S_5\) improper rotational axes.

2. Groups with low symmetry. There are three groups of low symmetry that possess only one or two symmetry elements.

a. \(C_1\).—Molecules of this symmetry have only the symmetry element \(E\), equivalent to a one-fold rotational axis. Common, simple chiral molecules with an asymmetric center have only this symmetry (Fig. 3.11a).

b. \(C_2\).—In addition to the symmetry element \(E\), which all molecules possess, these molecules contain a plane of symmetry. Thus although they have very low symmetry, they are not chiral (Fig. 3.11b).

c. \(C_3\).—These molecules have only a center of inversion in addition to the identity element. The anti conformations of \(R,S\)-1,2-dichloro-1,2-difluoroethane (Fig. 3.11c) and \(R,S\)-1,2-dimethyl-1,2-difluoroethane disulfide (Fig. 3.3) have \(C_3\) symmetry.

3. Groups with an \(n\)-fold rotational axis, \(C_n\).—After the obvious groups with high or low symmetries have been eliminated by inspection, the remaining point groups should be assigned by looking for characteristic symmetry elements, such as an \(n\)-fold axis of rotation, \(C_n\). Molecules containing only one such axis, like \(\text{gauche-H}_2\text{O}_2\) (Fig. 3.12a), triis(2-aminoethyloxo)covalent (Fig. 3.12b), or triphenylphosphine in its most stable conformation (Fig. 3.12c), have \(C_n\) symmetry.

If, in addition to the \(C_n\) axis, there is a horizontal plane perpendicular to that axis, the molecule is said to have \(C_{nh}\) symmetry. An example of this relatively unimportant group is trans-dichloroethylene (Fig. 3.13a). If there are \(n\) mirror planes containing the rotation axis, \(C_n\), the planes are designated vertical planes, and the molecule has \(C_{nv}\) symmetry. Many simple inorganic...
Fig. 3.31 A screw-axis \((Z,)\) operation. The molecule moves a distance \(a/2\) along the \(x\) axis while undergoing a \(C_2\) rotation. Note that the chirality of the molecule does not change.

An equivalence table of the 32 crystallographic point groups in the two systems is given in Table 3.7. The complete set of symmetry operations for a crystal is known as its space group. There are 230 possible space groups for three-dimensional crystals. Note that whereas there is an infinity of possible point groups, the number of space groups, despite the addition of translational symmetry, is rigorously limited to 230. For each structure worked out by the crystallographer, an assignment to one of these possible space groups is essential. Fortunately, this task is made easier by the conspicuous evidence left by elements of translational symmetry; all forms of translational symmetry, including lattice centering, create empty spaces in the diffraction pattern called "systematic" absences.

We can now complete our answer to the question, "What information is conveyed when we read that the crystal structure of a substance is monoclinic \(P2_1/c\)?" The structure belongs to the monoclinic crystal system and has a primitive Bravais lattice. It also possesses a two-fold screw axis and a glide plane perpendicular to it. The existence of these two elements of symmetry requires that there also be a center of inversion. The latter is not specifically included in the space group notation as it would be redundant.

Figure 3.32 illustrates the unit cell of \(\text{Os}_8(\text{CO})_{17}\), a compound that crystallizes in the monoclinic space group \(P2_1/c\). In addition to the identity element, it exhibits two two-fold screw axes, two glide planes, and an inversion center. As an aid in the identification of these elements, the four molecules of the unit cell are...
xylene isomers. The "linear" para isomer leaves readily (Fig. 1.5), but the angular ortho and meta isomers do not. They may react further, that is, rearrange, and if para-xylene forms, it may then leave.1

In a related process, ZSM-5 may be used to convert methanol into a high-octane gasoline. Petroleum-poor countries like New Zealand and South Africa are currently using this process to produce gasoline. If the production of para-xylene and gasoline sounds too much like "organic chemistry" for the introduction to an inorganic textbook, it must be pointed out that there is a large branch of chemistry, called "organometallic chemistry," that deals with an area intermediate between inorganic and organic chemistry and broadly overlapping both; both organic and inorganic chemists work in organometallic chemistry, with the broad generalization often being that the products are "organic" and mostly of interest to the organic chemist, and the intermediates and catalysts are of more interest to the inorganic chemist.

Zeolites may be used in purely inorganic catalysis, however. One reaction that may be used to reduce air pollution from mixed nitrogen oxides, NO*, in the industrial production of nitric acid is catalytic reduction by ammonia over zeolitic cata-

\[ 6\text{NO} + 4\text{NH}_3 \rightarrow (3 + 2x)\text{N}_2 + 6\text{H}_2\text{O} \]

(1.4)

The seriously polluting nitrogen oxides are thus reduced to two harmless molecules. The strong bond energies of the diatomic molecule and the water molecules are the driving forces; the zeolitic catalyst, in the ideal case, provides the pathway without being changed in the process.

A related catalytic removal of NO from automobile exhaust may come about from the reaction:

\[ 2\text{NO} + \text{Cu}^{+} \rightarrow \text{N}_2 + \text{O}_2 \]

(1.5)

using a Cu(I)/Cu(II) exchanged zeolite as a redox catalyst.8

To return to the problem of the general invisibility of atoms, how does the chemist follow the course of a reaction if the molecules cannot be imaged? One way is to use spectroscopy. Thus the conversion of methanol, first to dimethyl ether, then to the higher aliphatic and aromatic compounds found in gasoline, can be followed by nuclear magnetic resonance (NMR) spectroscopy (Fig. 1.6). As the reaction proceeds, the concentration of the methanol (as measured by the intensity of the NMR peak at 550 ppm) steadily decreases. The first product, dimethyl ether (500 ppm), increases at first and then decreases as the aliphatic and aromatic products eventually predominate.

So why did we pick boggsite for the cover? Is it "the most important" inorganic compound known? Certainly not! It is currently known from only one locality and in the form of extremely small crystal fragments. It is unlikely that it occurs anywhere on earth in sufficient quantities to be commercially important. Yet its discovery adds to our knowledge of the structural possibilities of zeolites and the conditions under which they form. And if we know enough about the structure of a material, we can usually synthesize it if we try hard enough. The synthesis of zeolites has progressed, though it must be admitted that there is much yet to be understood in the process. Boggsite is enough like ZSM-5, yet different, that it has attracted considerable attention. There is currently a massive effort in the chemical industry to try to synthesize this very interesting material. It may become an important industrial catalyst. Then again, it may not—only time will answer that question.

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1 So, in line of 'chemical tweezers' (STM and related apparatus) we claim to affect particular stereochromatic syntheses by using specially shaped zeolites. But it is stated that these specially shaped zeolites are also synthesized—without "chemical tweezers". How? The answer is not as difficult as it may seem.


9 Part of the difficulty in determining the crystal structure was in picking out a suitable crystal fragment from the matrix in which it was embedded. Only one was found, 0.07 x 0.08 x 0.16 mm in size. See Footnote 10.

Improper Rotation, $S_n$  A $C_n$ axis is often called a "proper" rotational axis and the rotation about it a "proper" rotation. An improper rotation may be visualized as occurring in two steps: rotation by $360^\circ / n$ followed by reflection across a plane perpendicular to the rotational axis. Neither the axis of rotation nor the mirror plane need be true symmetry elements that can stand alone. For example, we have seen that SiF$_4$ has $C_3$ axes but no $C_4$ axis. Nevertheless, it has three $S_4$ axes, one through each pair of opposite faces of the cube below:

![Diagram of improper rotation](image)

Thus $S_4$ is equivalent to $i$. Confirm this to your satisfaction with trans-N$_2$F$_4$, which contains a center of symmetry and thus must have a two-fold improper axis of rotation. Note that the SiF$_4$ molecule, although it possesses true $C_3$ axes, does not have a center of symmetry, and thus cannot have an $S_3$ axis. Furthermore, $S_4$ is equivalent to $a$ because, as we have seen, $C_1 = E$ and therefore the second step, reflection, yields $a$.

If we analyze the symmetry elements of a molecule such as water (Fig. 3.9), we find that it has one $C_2$ axis, two $S_2$ planes, and of course $E$. This set of four symmetry operations generated by these elements is said to form a symmetry group, or point group. In the case of the water molecule, this set of four symmetry elements characterizes the point group $C_2v$. The assignment of a point group to a molecule is both a very simple labeling of a molecule, a shorthand description as it were, and a useful aid for probing the properties of the molecule.

The assignment of molecules to the appropriate point groups can be done on a purely formal, mathematical basis. Alternatively, most chemists quickly learn to classify molecules into the common point groups by inspection. The following approach is a combination of the two.

1. Groups with very high symmetry. These point groups may be defined by the large number of characteristic symmetry elements, but most readers will recognize them immediately as Platonic solids of high symmetry.
   a. Icosahedral, $I_h$.—The icosahedron (Fig. 3.10a), typified by the $B_{12}H_{12}^-$ ion (Fig. 3.10b), has six $C_5$ axes, ten $C_3$ axes, fifteen $C_2$ axes, fifteen mirror planes, and five $S_4$ axes.

11 The chief reason for pointing out these relationships is for systematization: All symmetry operations can be included in $C_n$ and $S_n$. Taken in the order in which they were introduced, $a = S_i$; $i = S_2$; $E = C_1$.

12 For example, the chemist may speak of the $D_4$ symmetry of the [FeCl$_4$]$^{2-}$ ion, the $D_{4h}$ symmetry of the [PtCl$_4$]$^{2-}$ ion, and the $C_4$ symmetry of the TeCl$_4$ molecule as alternative ways of describing the tetrahedral [PbCl$_4$]$^{2-}$ ion, the square planar [PtCl$_4$]$^{2-}$ ion, or the structure of the TeCl$_4$ molecule which is sometimes called a "butterfly" molecule.
What Is Inorganic Chemistry?

As was pointed out at the beginning of the chapter, many other subjects could have been chosen for the cover: the new high-temperature superconductors, metal cluster compounds, an optically active inorganic molecule, a bioinorganic enzyme (see how far inorganic chemistry has come from the days when it meant "non-living"?), or a crystal of photographer's hypo. Indeed, all of these have been used on the covers of recent inorganic textbooks (one reason why we chose something different), and all of them are as appropriate on the one hand, and as limited in scope on the other, as boggite. They will all be discussed in the following chapters. If there is one thought that you should take away with you after reading this chapter, and eventually this book, it is the amazing diversity of inorganic chemistry. It deals with 109 elements, each unique.

It is thus impossible in a single chapter to do more than scratch the surface of inorganic chemistry: Structure, reactivity, catalysis, thermodynamic stability, symmetry, experimental techniques, gas-phase, solution, and solid-state chemistry; they are all part of the process. However, it is hoped that some idea of the scope of the subject may have been formed. The following chapters in this book attempt to provide the reader with sufficient basic knowledge of the structure and reactivity of inorganic systems to ensure a more comprehensive understanding.

For a recent review of zeolite analysis, see Thomas, J. M. Sci. Amer. 1992, 266 (4), 112-118.

Fig. 1.6 Solid-state $^{13}$C NMR reveals the successive steps in the conversion of methanol to gasoline over zeolite ZSM-5. The methanol, consisting at 50 ppm, is first dehydrated to dimethyl ether (60 ppm). Subsequent carbon-carbon bond formation leads to a host of aliphatic (10 to 30 ppm) and aromatic (not shown) compounds. [Modified from Anderson, M. W.; Kilcawska, J. J. Am. Chem. Soc. 1990, 112, 10-16. Reproduced with permission.]
Figs. 3.2–3.7 that have C_3 axes? Note that it also has three C_2 axes, one through each of the carbonyl groups in the triangular plane that is perpendicular to the C_3 axis.

In contrast, tungsten hexacarbonyl (Fig. 3.7c) has a four-fold axis. In fact, it has three C_4 axes: (1) one running from top to bottom, (2) one running from left to right, (3) one running from front to back. (In addition, it has other rotation axes. Can you find them?)

A molecule may possess higher order rotational axes. Consider the eclipsed form of the molecule ferrocene (Fig. 3.8a), which has a C_5 axis through the iron atom and perpendicular to the cyclopentadienyl rings. Now consider the staggered form of ferrocene (Fig. 3.8b). Does it have a five-fold rotational axis? Next consider borazine (Fig. 3.8c). Does it have a C_6 axis?

Many molecules have more than one C_n axis. For example, staggered ferrocene has five C_2 axes, one of which lies in the plane of the paper. Staggered ferrocene also has five C_3 axes, though they are different from the ones in the staggered conformer (Fig. 3.8). In those cases in which more than one rotational axis is present, the one of highest order is termed the principal axis and is usually the z axis. Planes that contain the principal axis are termed vertical planes, σ_v, and a mirror plane perpendicular to the principal axis is called a horizontal plane, σ_h. For example, borazine (Fig. 3.2c) has three vertical planes (one is shown) and one horizontal plane (the plane of the molecule).

We have seen above that a C_3 operation (rotation by 360°) results in the same molecule that we started with. It is therefore an identity operation. The identity operation is denoted by E. It might appear that such an operation would be unimportant inasmuch as it would accomplish nothing. Nevertheless, it is included for mathematical completeness, and some useful relationships can be constructed using it. For example, we have seen that two consecutive C_3 operations about the same axis result in identity. We may therefore write: C_3 x C_3 = E, and likewise: C_3 x C_3 x C_3 = E. These may also be expressed as C_3^2 = E and C_3^3 = E.

1. Answer: SiF_4, PF_5, [CoF_6]^3-, NH_3, B_3N_3H_6, Fe(CO)_5, and W(CO)_6 all have one or more C_3 axes.
2. Answer: W(CO)_6 has three C_5 axes, four C_6 axes (through the octahedral faces), and six C_2 axes (through the octahedral edges).

Fig. 3.8 Molecules containing five-fold rotational axes: (a) eclipsed ferrocene, side and top view; (b) staggered ferrocene, side and top view. Each molecule has five C_5 axes, only one of which is shown. Upon rotation about the C_5 axis, the atoms interchanges: 1 → 2, 3, etc.
The Hydrogen Atom

The Schroedinger equation is solved for the hydrogen atom, it is found that
there are three characteristic quantum numbers \( n \), \( l \), and \( m_l \) (as expected for a three-
dimensional system). The allowed values for these quantum numbers and their relation
to the physical system will be discussed below, but for now they may be taken
as a set of three integers specifying a particular situation. Each solution found for a
different set of \( n \), \( l \), and \( m_l \) is called an eigenfunction and represents an orbital in the
hydrogen atom.

In order to plot the complete wave functions, one would in general require a
four-dimensional graph with coordinates for each of the three spatial dimensions
\( x, y, z \) or \( r, \theta, \phi \) and a fourth value, the wave function.

In order to circumvent this problem and also to make it easier to visualize the
actual distribution of electrons within the atom, it is common to break down the
wave function, \( \Psi \), into three parts, each of which is a function of but a single vari-
able. It is most convenient to use polar coordinates, so one obtains

\[
\Psi(r, \theta, \phi) = R(r) \cdot \Theta(\theta) \cdot \Phi(\phi)
\]

where \( R(r) \) gives the dependence of \( \Psi \) upon distance from the nucleus and \( \Theta \) and \( \Phi \) give the angular dependence.

The Radial Wave Function, \( R \)

The radial functions for the first three orbitals\(^1\) in the hydrogen atom are

\[
\begin{align*}
\text{\( n = 1 \), \( l = 0 \), \( m_l = 0 \)} & : R = \frac{2}{\sqrt{\pi}} \frac{Z}{a_0} e^{-Zr/a_0} & \text{1s orbital} \\
\text{\( n = 2 \), \( l = 0 \), \( m_l = 0 \)} & : R = \frac{1}{\sqrt{2\pi}} \frac{Z^2}{2a_0^2} \left( \frac{2 - Zr}{a_0} \right) e^{-Zr/2a_0} & \text{2s orbital} \\
\text{\( n = 2 \), \( l = 1 \), \( m_l = 0 \)} & : R = \frac{1}{\sqrt{3\pi}} \frac{Z^3}{3a_0^3} \left( \frac{2Zr}{a_0} - 1 \right) e^{-Zr/3a_0} & \text{2p orbital}
\end{align*}
\]

where \( Z \) is the nuclear charge, \( e \) is the base of natural logarithms, and \( a_0 \) is the radius
of the first Bohr orbit. According to the Bohr theory, this was an immutable radius,
but in wave mechanics it is simply the "most probable" radius for the electron to be
located. Its value, 52.9 pm, is determined by \( a_0 = h^2/4\pi m_e e^2 \), where \( h \) is Planck's
constant and \( m_e \) and \( e \) are the mass and charge of the electron, respectively. In hydrogen,
\( Z = 1 \), but similar orbitals may be constructed where \( Z > 1 \) for other elements.

For many-electron atoms, exact solutions of the wave equation are impossible to
obtain, and these "hydrogen-like" orbitals are often used as a first approximation.\(^2\)

Although the radial functions may appear formidable, the important aspects
may be made apparent by grouping the constants. For a given atom, \( Z \) will be
constant and may be combined with the other constants, resulting in considerable
simplification:

\[
\begin{align*}
\text{\( n = 1 \), \( l = 0 \), \( m_l = 0 \)} & : R = K_1 e^{-Zr/a_0} & \text{1s orbital} \\
\text{\( n = 2 \), \( l = 0 \), \( m_l = 0 \)} & : R = K_2 \left( \frac{2 - Zr}{a_0} \right) e^{-Zr/2a_0} & \text{2s orbital} \\
\text{\( n = 2 \), \( l = 1 \), \( m_l = 0 \)} & : R = K_3 \frac{Z^3}{3a_0^3} \left( 2Zr/a_0 - 1 \right) e^{-Zr/3a_0} & \text{2p orbital}
\end{align*}
\]

The most apparent feature of the radial wave functions is that they all repre-
sent an exponential "decay", and that (for \( n = 2 \) the decay is slower than for \( n = 1 \).
This may be generalized for all radial functions: Their decay takes the form \( e^{-Zr/a_0} \).
For this reason, the radius of the various orbitals (actually, the most probable radius) increases
with increasing \( n \). A second feature is the presence of a node in the \( 2s \) radial function.
At \( r = 2a_0/Z \), \( R = 0 \) and the value of the radial function changes from positive to
negative. Again, this may be generalized: \( s \) orbitals have \( n - 1 \) nodes, \( p \) orbitals have
\( n - 2 \) nodes, etc. The radial functions for the hydrogen 1s, 2s, and 2p orbitals are
shown in Fig. 2.1.

Because we are principally interested in the probability of finding electrons at
various points in space, we shall be more concerned with the squares of the radial
functions than with the functions themselves. It is the square of the wave function

---

1. The complete wave function in terms of the quantum numbers \( n \) and \( l \) are given by Pauling, L. The
Nature of the Chemical Bond; Cornell University: Ithaca, NY, 1960 (n = 1-6) and Porterfield, W. W.
Inorganic Chemistry: A Unified Approach; Addison-Wesley: Reading, MA, 1974 (n = 1-3).
2. The use of hydrogen-like orbitals for multielectronic atoms neglects electron-electron repulsion, and this
may often be a serious oversimplification (see pages 20-23).
The Mirror Plane, $\pi$

Most flowers, cut gems, pairs of gloves and shoes, and simple molecules have a plane or if it is possible to move in a straight line from the Center of Symmetry, $i$.

A molecule has a disulfide.

Symmetry of 1,2-dimethyl-3-phenylphosphine dibromide.

Fig. 3.3 The two-fold rotational axis in trans-dinitrogen difluoride. The two-fold axis is perpendicular to the plane of the paper and denoted by the symbol $C_2$.

Rotational Axis, $C_n$

If rotation of a molecule by $360°/n$ results in an indistinguishable configuration, the molecule is said to have an $n$-fold rotational axis. Consider trans-dinitrogen difluoride (Fig. 3.5). If we construct an axis perpendicular to the plane of the paper midway between the nitrogen atoms, we can rotate the molecule by $180°$ and obtain an identical configuration. Rotation by $180°$ is thus a symmetry operation.

The axis about which the rotation takes place is the symmetry element. In this case trans-dinitrogen difluoride is said to have a two-fold rotational axis. Note that if the operation is performed twice, all atoms are back in their initial positions.

Now consider cis-dinitrogen difluoride (Fig. 3.6). It possesses no axis perpendicular to the plane of the molecule that allows rotation (other than the trivial $360°$ one) and qualifies as a symmetry element. However, it is possible to draw an axis that lies in the plane of the molecule equidistant between the two nitrogen atoms and also equidistant between the two fluorine atoms. This is also a two-fold axis.

Rotational axes are denoted by the symbol $C_n$, representing the $n$-fold axis. Thus cis- and trans-dinitrogen difluoride each have a $C_2$ axis.

Note that SF$_6$ (Fig. 3.4a) has a three-fold axis, $C_3$. In fact, it has four of them, each lying along an $S-F$ bond. The single three-fold axis in ammonia may be somewhat less obvious (Fig. 3.7a). It lies on an imaginary line running through the center of the lone pair and equidistant from the three hydrogen atoms. If all the bond angles change, as from $107°$ in NH$_3$ to $102°$ in NF$_3$, does the symmetry change?

Note that iron pentacarbonyl (Fig. 3.7b) also has a $C_3$ axis. Are there any other molecules in

...
that provides the electron density or the probability of finding an electron at a point in space. There are two useful ways of doing this. The simplest is merely to square the functions plotted in Fig. 2.1. We could therefore square the numbers on the ordinates and plot the same curves except that the negative values become positive when squared (Fig. 2.2). While this seems very simple, it provides us with the relative electron density as a function of the radius. It is important to remember that for s orbitals, the maximum electron density is at the nucleus; all other orbitals have zero electron density at the nucleus.

A more common way of looking at the problem is to consider the atom to be composed of “layers” much like an onion and to examine the probability of finding the electron in the “layer” which extends from \( r \) to \( r + dr \), as shown in Fig. 2.3. The volume of the thin shell may be considered to be \( dV \). Now the volume of the sphere is

\[
V = \frac{4\pi r^3}{3}
\]

\[
dV = 4\pi r^2 dr
\]

\[
R^2 dV = 4\pi R^2 dr
\]

Consider the radial portion of the wave function for the 1s orbital as plotted in Fig. 2.1. When it is squared and multiplied by \( 4\pi r^2 \), we obtain the probability function shown in Fig. 2.4. The essential features of this function may be obtained qualitatively as follows:

1. At \( r = 0 \), \( 4\pi r^2 R^2 = 0 \); hence the value of the function at the nucleus must be zero.\(^3\)
2. At large values of \( r \), \( R \) approaches zero rapidly and hence \( 4\pi r^2 R^2 \) must approach zero.

\(^3\) Note that the mathematical function goes to zero because the volume of the incremental shell, \( dV \), goes to zero at \( r = 0 \). As we have seen, however, there is electron density at the nucleus for s orbitals.
Symmetry is a common phenomenon in the world around us. If Nature abhors a vacuum, it certainly seems to love symmetry! It is difficult not to overestimate the importance of symmetry in many aspects of science, not only chemistry. Just as the principle known as Occam's razor suggests that the simplest explanation for an observation is scientifically the best, so it is true that other things being equal, frequently the most symmetrical molecular structure is the "preferable" one. More important, the methods of analysis of symmetry allow simplified treatment of complex problems related to molecular structure.

Mathematical symmetry is a little more restrictive than is the meaning of the word in everyday usage. For example, some might say that flowers, diamonds, butterflies, snail shells, and paisley ties (Fig. 3.1) are all highly symmetrical because of the harmony and attractiveness of their forms and proportions, but the pattern of a paisley tie is not "balanced"; in mathematical language, it lacks symmetry elements. A flower, crystal, or molecule is said to have symmetry if it has two or more orientations in space that are indistinguishable, and the criteria for judging these are based on symmetry elements and symmetry operations.

A symmetry operation moves a molecule about an axis, a point, or a plane (the symmetry element) into a position indistinguishable from the original position. If there is a point in space that remains unchanged under all of the symmetry opera-

---

Fig. 3.1 The shapes and patterns of some pleasing designs found in nature or constructed as artifacts: (a) the flower of the black-eyed susan, *Rudbeckia hirta*; (b) the flower, stem, and leaves of the black-eyed susan; (c) a red cib, *Nepenthes nobilesformis*; (d) a cut diamond; (e) a paisley tie; (f) a snail shell, *Cepaea nemoralis*; (g) a monarch butterfly, *Danaus plexippus*; (h) a suspension bridge. Which are truly symmetrical?
Angular Wave Functions

3. In between, r and θ both have finite values, so there is a maximum in the plot of probability \(4\pi r^2 f^2\) as a function of r. This maximum occurs at \(r = a_0\), the value of the Bohr radius.

Similar probability functions (including the factor \(4\pi\)) for the 2s, 2p, 3s, 3p, and 3d orbitals are also shown in Fig. 2.4. Note that although the radial function for the 2s orbital is both positive \((r < 2a_0/\sqrt{2})\) and negative \((r > 2a_0/\sqrt{2})\), the probability function is everywhere positive (as of course it must be to have any physical meaning) as a result of the squaring operation.

The presence of a node in the wave function indicates a point in space at which the probability of finding the electron has gone to zero. This raises the interesting question, "How does the electron get from one side of the node to the other if it can never be found exactly at the node?" This is not a valid question as posed, since it presupposes our macroscopically prejudiced view that the electron is a particle. If we consider the electron to be a standing wave, no problem arises because it simultaneously exists on both sides of a node. Consider a vibrating string on an instrument such as a guitar. If the string is stopped at the twelfth fret the note will go up one octave because the wavelength has been shortened by one-half. Although it is experimentally difficult (a finger is not an infinitesimally small point!), it is possible to sound the same note on either half of the octave-stopped string. This vibration can be continuous through the node at the fret. In fact, on the open string, overtones occur at the higher harmonics such that nodes occur at various points along the string. Nodes are quite common to wave behavior, and conceptual problems arise only when we try to think of the electron as a "hard" particle with a definite position.

The presence of one or more nodes and maxima has any chemical effect? The answer depends upon the aspect of bonding in which we are interested. We shall see later that covalent bonding depends critically upon the overlap of orbitals. Conversely, if an orbital has a maximum in its radial wave function within a region with a node (minimum) in the wave function of a second atom, the overlap would be poor. However, in every case in which careful calculations have been made, it has been found that the nodes lie too close to the nucleus to affect the bonding appreciably.

The presence of nodes and small "subnodal maxima" does have a profound effect on the energy of electrons in different orbitals. An electron in an orbital with these subnodal maxima (particularly of orbitals with higher values of \(\ell\)) are said to be penetrating, that is, they have considerable electron density in the region of the nucleus. This is the fundamental reason for the ordering of the energy levels in polyatomic atoms: 1s, 2s, 2p, 3s, 3p, etc. (see pages 20-22).

The angular part of the wave function determines the shape of the electron cloud and varies depending upon the type of orbital involved (\(s, p, d, or f\)) and its orientation in space. However, for a given type of orbital, such as a or \(p\), the angular wave function is independent of the principal quantum number or energy level. Some typical angular functions are:

- For an \(s\) orbital, \(\phi = \frac{1}{\sqrt{2\pi a_0}}\) since it corresponds to the angular part of \(\psi_s^2\).
- The angular functions for the \(p_\ell\) orbitals are illustrated in Fig. 2.5. For an \(s\) orbital, \(\phi = 0\) is independent of angle and is of constant value. Hence this graph is circular or, more properly, in three dimensions--spherical. For the \(p_\ell\) orbital we obtain two tangent spheres. The \(p_x, p_y,\) and \(p_z\) orbitals are identical in shape but are oriented along the \(x, y,\) and \(z\) axes, respectively. We shall defer extensive treatment of the \(d\) orbitals (Chapter 11) and \(f\) orbitals (Chapter 14) until bond formation in coordination compounds is discussed, simply noting here that the basic angular function for \(d\) orbitals is four-leaved and that for \(f\) orbitals is six-leaved (see Fig. 2.9).

We are most interested in the probability of finding an electron, and so we shall wish to examine the function \(\psi^2\phi^2\) and \(\psi^2\). When the angular functions are squared, different orbitals change in different ways.

The meaning of Figs. 2.5 and 2.6 is easily misinterpreted. Neither one has any direct physical meaning. Both are graphs of mathematical functions, just as Figs. 2.2 and 2.4 are. Both may be used to obtain information about the probable distribution of electrons, but neither may in any way be regarded as a "picture" of an orbital. It is an unfortunate fact that fuzzy drawings of Figs. 2.5 or 2.6 are often presented as "orbitals." Now one can define an orbital in any way one wishes, corresponding to \(\psi, \psi^2, R, R^2, \psi\phi, \text{ or } \psi\phi^2\), but it should be realized that Figs. 2.2, 2.4, 2.5, and 2.6 are mathematical functions and drawing them fuzzy does not represent an atom.

Chemists tend to think in terms of electron densities, and hence \(\psi^2\) probably gives the best intuitive "picture" of an orbital. Methods of showing the total probability of finding an electron including both radial and angular probabilities are shown in Figs. 2.7-2.9. Although electron density may be shown either by shading (Fig. 2.7) or by contours of equal electron density (Figs. 2.8 and 2.9), only the latter method is quantitatively accurate.
2.9 The angular part of the wave function for the \( d_{xy} \) orbital is \( \sqrt{\frac{5}{4}} \sin \theta \sin 2\alpha \). Show that this expression corresponds to the \( d_{xy} \) orbital. The \( d_{xy} \) is actually a simplified way of representing the \( d_{x^2-y^2}, d_{xy}, d_{xz}, d_{yz} \) orbitals. Show that this corresponds to the angular function, \( 3\cos^2 \theta - 1 \).

2.10 Consider the following possible electron arrangements for a \( p^3 \) configuration:

Which of these represents the ground state? Which are excited states? Which are impossible states? In which configuration would exchange energy be maximized? In which configuration would coulombic repulsion be maximized?

2.11 The stabilization of a half-filled \( d \) shell is even more pronounced than that of the \( p \) subshell. Why?

2.12 Discuss the following question: Does an orbital exist if there is not an electron in it?

2.13 The Pauli exclusion principle forbids certain combinations of \( m_s \) and \( m_l \) in determining the term symbols for the states of the nitrogen atom. Consider an excited nitrogen atom in which the electronic configuration is \( 1s^2 2s^2 2p^3 \). What states now are possible?

2.14 Write out electronic configurations for free atoms of the following elements. Determine the number of unpaired electrons in the ground state.

- B
- N
- Mg
- V
- As
- Lu

2.15 Determine all of the term symbols for the following free atoms. Choose the ground state term in each case.

- B
- N
- Mg
- V
- As
- Lu

2.16 Write out the electronic configurations for the following ions. Determine the number of unpaired electrons in the ground state.

- Ti
- Mg
- Cu
- Pd
- Gd

2.17 Determine the ground state term symbols for each of the ions in Problem 2.16.

2.18 Clearly distinguish the following aspects of the structure of an atom and sketch the appropriate function for 1s, 2s, 2p, 3s, and 3p orbitals.

- a. radial wave function
- b. radial probability function
- c. angular wave function
- d. angular probability function

2.19 Using Slater's rules, calculate \( Z^* \) for the following electrons:

- a. a 3p electron in P
- b. a 4s electron in Co
- c. a 3d electron in Mn
- d. a valence electron in Mg

Compare the values of \( Z^* \) thus obtained with those of Clementi and Raimondi.

2.20 Which has the higher first ionization energy:
- Li or Cs?
- F or Br?
- Sc or Cu?
- Cu or Pt?

2.21 Plot the total ionization energies of Al as a function of \( n \) from \( n = 1 \) to \( n = 8 \). Explain the source of discontinuity in your curve.

2.22 a. Calculate the third ionization energy of lithium. [Hint: This requires no approximations or assumptions.]
- b. Calculate the first and second ionization energies of lithium using Slater's rules.
- c. Calculate the first and second ionization energies of lithium using the rules of Clementi and Raimondi.

2.23 Which is larger:
- K* or Cs*?
- La* or Lu*?
- Cl or Br?
- Ca* or Zn*?
- Cs or F?

2.24 Which has the highest electron affinity:
- Li or Cs?
- Li or F?
- Cs or F?
- F or Cl?
- Cl or Br?
- O or S?
- S or Se?

2.25 Note that Table 2.6 lists several molecules that have much higher electron affinities than fluorine (328.0 kJ mol\(^{-1}\)) or chlorine (349.0 kJ mol\(^{-1}\)). For example, consider PdF\(_4\) (772 kJ mol\(^{-1}\)). How can a molecule composed of six fluorine atoms and a metal (to be sure, not a very electropositive one) have a higher affinity for electrons than a fluorine atom?

2.26 The electronegativity of a group is determined by many other factors than simply its electron affinity. Nevertheless, look at the values in Table 2.6 and predict which the most electronegative groups are.

2.27 Which of the halogens, \( X_2 \), would you expect to be most likely to form a cation, \( X^+ \)? Discrete \( X^+ \) ions are not known in chemical compounds, but \( X_2^+ \), \( X^+ \), and \( X_2^+ \) are known. Why should the latter be more stable than \( X^+ \)?
The Structure of the Atom

The Hydrogen Atom

Fig. 2.7 (a) Pictorial representation of the electron density in a hydrogen-like 2p orbital compared with (b) the electron density contours for the hydrogen-like 2p orbital of carbon. Contour values are relative to the electron density maximum. The xy plane is a nodal surface. The signs (+ and —) refer to those of the original wave function. [The contour diagram is from Ogryzlo, E. A.; Porter, G. B. J. Chem. Educ. 1963, 40, 258. Reproduced with permission.]

Fig. 2.8 The electron density contours for the hydrogen-like 3p orbital of carbon. Contour values are relative to the electron density maximum. The xy plane and a sphere of radius 52 pm (dashed line) are nodal surfaces. The signs (+ and —) refer to those of the original wave function. [The contour diagram is from Ogryzlo, E. A.; Porter, G. B. J. Chem. Educ. 1963, 40, 256-261. Reproduced with permission.]

Fig. 2.9 Angular wave functions of s, p, d, and f orbitals illustrating gerade and ungerade symmetry: (a) s orbital, gerade; (b) p orbital, ungerade; (c) pictorial representation of symmetry of p orbital; (d) d<sub>xz</sub> orbital, gerade; (e) pictorial representation of symmetry of d<sub>xz</sub> orbital; (f) d<sub>yz</sub> orbital, gerade; (g) f<sub>z</sub> orbital, ungerade.

Since $\Theta^2P^2$ is termed an angular probability function, the question may properly be asked what its true meaning is, if not a "picture" of electron distribution. Like any other graph, it simply plots the value of a function $\Theta^2P^2$ versus the variable $\Theta$ or $\theta$. If one chooses an angle $\Theta$, the probability that the electron will be found in that direction (summed over all distances) is proportional to the magnitude of the vector connecting the origin with the functional plot at that angle.

Symmetry of Orbitals

In Fig. 2.9 are shown sketches of the angular parts of the wave functions for s, p, d, and f orbitals. The signs in the lobes represent the sign of the wave function in those directions. For example, in the $p_z$ orbital, for $\Theta = 90^\circ$, $\cos \Theta = 0$ and for $90^\circ < \Theta < 270^\circ$, $\cos \Theta$ is negative. The signs of the wave functions are very important when considering the overlap of two bonding orbitals. It is customary to speak of the symmetry of orbitals as gerade or ungerade. These German words meaning even and uneven refer to the operation shown in the sketches—rotation about the center.

If one moves from any point A to the equivalent point B on the opposite side of the
Table 2.6
Electron affinities of molecules

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Experimental (kJ mol⁻¹)</th>
<th>Molecule</th>
<th>Experimental (kJ mol⁻¹)</th>
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<td>732</td>
<td>OCN</td>
<td>348</td>
</tr>
<tr>
<td>C₆H₅CH₃</td>
<td>283</td>
<td>SH₃</td>
<td>140</td>
</tr>
<tr>
<td>C₆H₅(CH₂)₂</td>
<td>165</td>
<td>PH₃</td>
<td>150</td>
</tr>
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<td>100</td>
<td>PiF₅</td>
<td>160</td>
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<td>PiF₆</td>
<td>770</td>
</tr>
<tr>
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<tr>
<td>O₄C₂H₄</td>
<td>104</td>
<td>UF₅</td>
<td>540</td>
</tr>
</tbody>
</table>


# Uncertainty is approximately ±20 except for numbers given to three significant digits.

2.1 Calculate the r value in pm at which a radial node will appear for the 2s orbital of the hydrogen atom.

2.2 Which quantum numbers reveal information about the shape, energy, orientation, and size of orbitals?

2.3 How many orbitals are possible for n = 4? Which of these may be described as valence orbitals?

2.4 How many radial nodes do 3s, 4s, 5d and 6f orbitals exhibit? How many angular nodes?

2.5 Make a photocopy of Fig. 2.6. Draw two lines, one along the z axis, and one at a 45° angle away from the z axis. Along one of these lines measure the distance from the origin (nucleus) to each contour line and plot the value of the contour line at that distance (r). Do this for all contours on both lines. Compare your drawing with Fig. 2.4.

2.6 Determine the maximum number of electrons that can exist in a completely filled n = 5 level. Give four possible quantum numbers for a 5f electron of the hydrogen atom.

2.7 The signs of the unsquared wave functions are usually shown in plots of the squared functions. Why do you think this practice exists?

2.8 Sometimes 3p orbitals are drawn as shown below.
center the sign of the wave function does not change, the orbital is said to be gerade.

The s orbital is a trivial case in which the sign of the angular wave function is everywhere the same. The d orbitals (only two of which are shown here) are also gerade.

The p orbitals, however, are unsymmetrical with respect to inversion and the sign changes on going from A to B; hence the symmetry isungerade. Likewise, f orbitals areungerade. Another way of referring to the symmetry properties of these orbitals is to say that s and d orbitals have a center of symmetry, and that p and f orbitals do not. In addition to symmetry with respect to inversion about the center, orbitals have other symmetry properties with respect to other symmetry operations. These will be discussed in Chapter 3.

It should be noted that most textbooks, including this one, generally portray the symmetry of orbitals as in Fig. 2.9a-g with wave functions plotted and the signs marked. However, an exceedingly common practice in the original literature of both inorganic and organic chemistry is to indicate the signs of the wave functions by the shading of stylized orbitals. Fig. 2.9c indicates the symmetry of a p orbital and 2.9c a d orbital by this convention.

Attention should be called to a rather confusing practice that chemists commonly use. In Figs. 2.7 and 2.8 it will be noted that small plus and minus signs appear. Although the figure refers to the probability of finding the electron and thus must be everywhere positive, the signs + and − refer to the sign of the original wave function, \( \psi \), in these regions of space. In Fig. 2.8, for example, in addition to the inversion resulting from theungerade p orbital, there is a second node (actually a spherical nodal surface) at a distance of \( \sqrt{2} a_0 \) resulting from the radial wave function. Although this practice may seem confusing, it is useful and hence has been accepted. The \( \psi^2 \) plot is useful in attempting to visualize the physical "picture" of the atom, but the sign of \( \psi \) is important with respect to bonding.\(^5\)

### Energies of Orbitals

The energy levels of the hydrogen atom are found to be determined solely by the principal quantum number, and their relationship is the same as found for a Bohr atom:

\[
E_n = -\frac{2\pi^2\hbar^2}{m_e^2 h^2} \left(\frac{1}{n^2}\right) \tag{2.5}
\]

where \( m \) is the mass of the electron, \( e \) is the electronic charge, \( n \) is the principal quantum number, and \( h \) is Planck's constant. Quantization of energy and angular momentum were introduced as assumptions by Bohr, but they follow naturally from the wave treatment. The quantum number \( n \) may have any positive, integral value from one to infinity:

\[ n = 1, 2, 3, 4, \ldots, \infty \]

The lowest (most negative) energy corresponds to the minimum value of \( n \) (\( n = 1 \)) and the energies increase (become less negative) with increasing \( n \) until the continuum is reached (\( n = \infty \)). Here the electron is no longer bound to the atom and thus is no longer quantized, but may have any amount of kinetic energy.

The allowed values of \( l \) range from zero to \( n - 1 \):

\[ l = 0, 1, 2, 3, \ldots, n - 1 \]


---

The quantum number \( l \) is a measure of the orbital angular momentum of the electron and determines the "shape" of the orbital. The types of orbitals are designated by the letters s, p, d, f, g, \ldots; corresponding to the values of \( l = 0, 1, 2, 3, 4, \ldots \).

The first four letters originate in spectroscopic notation (see page 26) and the remainder follow alphabetically. In the previous section we have seen the various angular wave functions and the resulting distribution of electrons. The nature of the angular wave function is determined by the value of the quantum number \( l \).

The number of equivalent ways that orbitals can be oriented in space is equal to \( 2l + 1 \). In the absence of an electric or magnetic field these orientations are degenerate; that is, they are identical in energy. Consider, for example, the p orbital. It is possible to have a p orbital in which the maximum electron density lies on the x-axis; this is the \( \psi \)-plane. Application of a magnetic field splits the degeneracy of the set of three p orbitals. The magnetic quantum number, \( m_l \), is related to the component of angular momentum along a chosen axis—for example, the x-axis—and determines the orientation of the orbital in space. Values of \( m_l \) range from \(-l \to +l\):

\[ m_l = -l, -l + 1, \ldots, 0, +1, +2, \ldots, +l \]

Thus for \( l = 1 \), \( m_l = -1, 0, +1 \), and there are three p orbitals possible, \( p_x \), \( p_y \), and \( p_z \). Similarly, for \( l = 2 \) (d orbitals) \( m_l = -2, -1, 0, +1, +2 \), and for \( l = 3 \) (f orbitals) \( m_l = -3, -2, -1, 0, +1, +2, +3 \).

It is an interesting fact that just as the single s orbital is spherically symmetric, the summation of electron density of a set of three p orbitals, five d orbitals, or seven f orbitals is also spherical (Kronecker's theorem). Thus, although it might appear as though an atom such as neon with a filled set of s and p orbitals would have a "lumpy" electron cloud, the total probability distribution is perfectly spherical.

From the above rules we may obtain the allowed values of \( n, l, \) and \( m_l \). We have seen previously (page 10) that a set of particular values for these three quantum numbers determines an eigenfunction or orbital for the hydrogen atom. The possible orbitals are therefore:

\[ n = 1 \quad l = 0 \quad m_l = 0 \quad 1s \text{ orbital} \]

\[ n = 2 \quad l = 0 \quad m_l = 0 \quad 2s \text{ orbital} \]

\[ n = 2 \quad l = 1 \quad m_l = -1, 0, +1 \quad 2p_{x,y,z} \text{ orbitals} \]

\[ n = 3 \quad l = 0 \quad m_l = 0 \quad 3s \text{ orbital} \]

\[ n = 3 \quad l = 1 \quad m_l = -1, 0, +1 \quad 3p_{x,y,z} \text{ orbitals} \]

\[ n = 4 \quad l = 2 \quad m_l = -2, -1, 0, +1, +2 \quad 4d_{x,y,z} \text{ orbitals} \]

\[ n = 4 \quad l = 0 \quad m_l = 0 \quad 4s \text{ orbital} \]

We can now summarize the relation between the quantum numbers \( n, l, \) and \( m_l \) and the physical pictures of electron distribution in orbitals by a few simple rules.\(^6\)

\(^6\) Although the \( p, d, \) and \( f \) orbitals correspond to \( n = 0 \), there is no similar on-to-one correspondence for the other orbitals and other values of \( n \). The functions are complex for \( m \neq 0 \) and must be formed into new, linear combinations for the real \( p, d, \) and \( f \) orbitals. See Morse, W. I., Physical Chemistry, 4th ed.; Freeman: San Francisco, 1990; p 610. Figgis, B. N., Introduction to Liquids, Fields, Wiley: New York, 1966, pp 9-15.

\(^7\) These orbitals are sketched and discussed further in Chapter 11.
Electron Affinity

Electron affinity is conventionally defined as the energy released when an electron is added to the valence shell of an atom. Unfortunately, this is in contradistinction to the universal thermodynamic convention that enthalpies of exothermic reactions shall be assigned negative signs. Since it seems impossible to overthrow the electron affinity convention at this late date without undue confusion, one can adopt one of two viewpoints to minimize confusion. One is to let the electron affinities of the most active nonmetals be positive, even though in thermodynamic calculations the enthalpies are negative:

\[ F + e^- \rightarrow F^- \quad EA = +328 \text{ kJ mol}^{-1} \quad \Delta H = -328 \text{ kJ mol}^{-1} \]

A slightly different approach is to consider the electron affinities of the atoms to be the same as the ionization energies of the anions. Now the positive electron affinity corresponds to an endothermic reaction:

\[ F^- + e^- \rightarrow F + e^- \quad IE = -328 \text{ kJ mol}^{-1} \quad \Delta H = +328 \text{ kJ mol}^{-1} \]

This second approach has the added benefit of calling attention to the very close relationship between electron affinity and ionization potential. In fact, when the ionization energies and electron affinities of atoms are plotted, a smooth curve results and the function may be described rather accurately by the quadratic formula:

\[ E = aq + bq^2 \] (2.17)

where \( E \) is the total energy of the ion (\( \Sigma IQ \) or \( \Sigma EA \)) and \( q \) is the ionic charge. See Fig. 2.13.

It may readily be seen that whereas the acceptance of electrons by active nonmetals is initially exothermic, the atoms become “saturated” relatively quickly, the energy reaches a minimum, and further addition of electrons is endothermic. In fact, from the trend along the 3d series mentioned above. Although this trend is not responsible for the effect (as discussed previously), it does give an indication. It thus appears that as the atomic number goes up, and hence as \( Z^* \) increases, the energy levels approach more closely to those in a hydrogen atom, namely, all levels having the same principal quantum number are degenerate and lie below those of the next quantum number. Now the effective nuclear charge in the ion increases markedly because of the net ionic charge and the reduced shielding. It is not unreasonable to suppose, then, that the formation of a dipositive ion accomplishes more than the ionization of the atom (for example, core electrons are scarcely differentiated energetically according to type of orbital)—they closely approach the hydrogenic degeneracy.


Actually, a more accurate expression is a polynomial of the type \( E = aq + bq^2 + cq^3 + dq^4 \). The constants \( a \) and \( b \), however, are small, and Fig. 2.17 is a good approximation. See Eckardt, R. F.; Margrave, J. L. J. Am. Chem. Soc. 1964, 86, 3547.


should be emphasized that these rules are no substitute for a thorough understanding of the previous discussion, but merely serve as handy guides to recall some of the relations.

1. Within the hydrogen atom, the lower the value of \( n \), the more stable will be the orbital. For the hydrogen atom, the energy depends only upon \( n \); for atoms with more than one electron the quantum number \( l \) is important as well.

2. The type of orbital is determined by the \( l \) quantum number:
   - \( l = 0 \): s orbitals
   - \( l = 1 \): p orbitals
   - \( l = 2 \): d orbitals
   - \( l = 3 \): f orbitals
   - \( l \geq 4 \): g orbitals, etc.

3. There are \( 2l + 1 \) orbitals of each type, that is, one \( s \), three \( p \), five \( d \), and seven \( f \) orbitals, etc., per set. This is also equal to the number of values that \( m \) may assume for a given value of \( l \), since \( m \) determines the orientation of orbitals, and obviously the number of orbitals must be equal to the number of ways in which they are oriented.

4. There are \( n \) types of orbitals in the \( n \)th energy level, for example, the third energy level has \( s, p, \) and \( d \) orbitals.

5. There are \( n - l - 1 \) nodes in the radial distribution functions of all orbitals, for example, the 3s orbital has two nodes, the 4d orbitals each have one.

6. There are nodal surfaces in the angular distribution functions of all orbitals, for example, \( s \) orbitals have none, \( d \) orbitals have two.

---

### The Polyelectronic Atom

With the exception of Unsöld's theorem, above, everything discussed thus far has dealt only with the neutral hydrogen atom, the only atom for which the Schrödinger equation can be solved exactly. This treatment can be extended readily to one-electron ions isoelectronic with hydrogen, such as \( \text{He}^+, \text{Li}^{2+}, \) and \( \text{Be}^{3+} \), by using the appropriate value of the nuclear charge, \( Z \). The next simplest atom, helium, consists of a nucleus and two electrons. We thus have three interactions: the attraction of electron 1 for the nucleus, the attraction of electron 2 for the nucleus, and the repulsion between electrons 1 and 2. This is an example of the classic three-body problem in physics and cannot be solved exactly. We can, however, approximate a solution to a high degree of accuracy using successive approximations. For simple atoms such as helium this is not too difficult, but for heavier atoms the number of interactions which must be considered rises at an alarming rate and the calculations become extremely laborious. A number of methods of approximation have been used, but we shall not explore them here beyond describing in conceptual terms one of the more accurate methods. It is referred to as the Hartree-Fock method, after the men who developed it, or as the self-consistent field (SCF) method. It consists of (1) assuming a reasonable wave function for each of the electrons in an atom except one, (2) calculating the effect which the field of the nucleus and the remainder of the electrons exert on the chosen electron, and (3) calculating a wave function for the last electron, including the effects of the field of the other electrons. A different electron is then chosen, and using the field resulting from the other electrons (including the contribution from the improved wave function of the formerly chosen electron), an improved wave function for the second electron is calculated. This process is continued until the wave functions for all of the electrons have been improved, and the cycle is then started over to improve further the wave function of the first electron in terms of the field resulting from the improved wave functions of the other electrons. The cycle is repeated as many times as necessary until a negligible change takes place in improving the wave functions. At this point it may be said that the wave functions are self-consistent and are a reasonably accurate description of the atom.

Such calculations indicate that orbitals in atoms other than hydrogen do not differ in any radical way from the hydrogen orbitals previously discussed. The principal difference lies in the consequence of the increased nuclear charge—all the orbitals are somewhat contracted. It is common to call such orbitals which have been adjusted by an appropriate nuclear charge hydrogen-like orbitals. Within a given major energy level it is found that the energy of these orbitals increases in the order \( s < p < d < f \). For the higher energy levels these differences are sufficiently pronounced that a staggering of orbitals may result, such as \( 6s < 5d < 4f \), etc. The energy of a given orbital depends on the nuclear charge (atomic number) and different types of orbitals are affected to different degrees. Thus there is no single ordering of energies for all orbitals which will be universally correct for all elements. Nevertheless, the order \( 1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5d < 6f \) is found to be extremely useful. This complete order is correct for a single element; yet, paradoxically, with respect to placement of the inert gases or valence electrons, it is remarkably accurate for all elements. For example, the valence electron in potassium must choose between the 3d and 4s orbitals, and as predicted by this series it is found in the 4s orbital. The above ordering should be assumed to be only a rough guide to the filling of energy levels (see "The Aufbau principle", page 23). In many cases the orbitals are very similar in energy and slight changes in atomic structure can invert two levels and change the order of filling. Nevertheless, the above series is a useful guide to the building up of electronic structure if it is realized that exceptions may occur. A useful mnemonic diagram was suggested by Moeller (Fig. 2.10). To recall the order of filling, merely follow the arrows and the numbers from one orbital to the next.

As expected from our experience with a particle in a box, three quantum numbers are necessary to describe the spatial distribution of electrons in atoms. To describe an electron in an atom completely, a fourth quantum number, \( m_s \), called the spin quantum number must be specified. This is because every electron has associated with it a magnetic moment which is quantized in one of two possible orientations: parallel or opposed to an applied magnetic field. The magnitude of the magnetic moment is given by the expression

\[
\mu = 2.00 \times 10^{-24} \text{emu} \text{Bohr}
\]

---

The electrons that are lost on ionization are those that lie at highest energies and therefore require the least energy to remove. One might expect, therefore, that electrons would be lost on ionization in the reverse order in which orbitals were filled (see "The Aufbau Principle"). There is a tendency for this to be true. However, there are some very important exceptions, notably in the transition elements, which are responsible for the characteristic chemistry of these elements. In general, transition elements react as follows:

\[
\text{M}^{2+} + 2e^- \rightarrow \text{M}^{0} + 2\text{e}^- \\
\text{M}^{3+} + 3\text{e}^- \rightarrow \text{M}^{0} + 3\text{e}^- \\
\text{M}^{4+} + 4\text{e}^- \rightarrow \text{M}^{0} + 4\text{e}^- \
\]

**Table 2.4**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Molecule</th>
<th>Molecule</th>
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<tbody>
<tr>
<td>CH₄</td>
<td>NH₃</td>
<td>NO₂</td>
</tr>
<tr>
<td>0.949 (eV)</td>
<td>9.84</td>
<td>8.13</td>
</tr>
<tr>
<td>CH₃F</td>
<td>NO</td>
<td>CO₂</td>
</tr>
<tr>
<td>0.729</td>
<td>7.56</td>
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</tr>
<tr>
<td>CN</td>
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<td>OH</td>
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<td>1.350</td>
<td>14.09</td>
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<tr>
<td>CO</td>
<td>F₂</td>
<td>CF₃</td>
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<tr>
<td>1.252</td>
<td>14.01</td>
<td>13.00</td>
</tr>
<tr>
<td>C₂F₅</td>
<td>CS₂</td>
<td>SiCl₄</td>
</tr>
<tr>
<td>0.806</td>
<td>8.89</td>
<td>15.09</td>
</tr>
<tr>
<td>N₂O</td>
<td>F₂</td>
<td>O₂</td>
</tr>
<tr>
<td>1.503</td>
<td>15.58</td>
<td>15.99</td>
</tr>
</tbody>
</table>

The ionization energies of a few groups are known (Table 2.4). Although not generally as useful as atomic values, they can be used in Born-Haber calculations (see Chapter 4) involving polyatomic cations, such as NO⁺ and O₂⁺. They also provide a rough estimate of the electron-donating or -withdrawing tendencies of groups.

For many purposes, that given by Koopmans' theorem is adequate: If the nth orbital is the highest orbital used to describe the ground-state wave function of an atom X, then the energy of orbital n is approximated by the ionization energy of the atom. These energies can be calculated by the self-consistent-field method described previously (see page 20). These calculations have been made and much has been written concerning their interpretation. The seeming contradiction presented by the ground state of the atom and the ground state of the ions results from the fact that it is the total energy of the atom (ion) that is important, not the energy of the electronic configuration of Cu. If the relative energies of the 3d and 4s levels are examined, it is found that they lie very close together and that the energy of the 3d level decreases with increasing atomic number. This is often advanced as the explanation for the electronic configuration of Cu. If the 3d level has dropped below the 4s level, then the ground state must be 3d⁶4s². Nevertheless, this can have no effect on the phenomena that we are investigating, because the difference in configuration between ground state of the neutral atom and the ionic state is the same. Because all of the transition metals in the first series (with exception of Cr and Cu) have a 3d⁶4s² ground state for the neutral atom and a stable 3d⁶4s⁰ state for the dipositive ion, the source of our problem must be sought in the difference between atom and ion, not in trends along the series.

Before the question can be answered adequately, it is necessary to define what is meant by "orbital energy". For most purposes, that given by Koopmans' theorem is adequate. If the nth orbital is the highest orbital used to describe the ground-state wave function of an atom X, then the energy of orbital n is approximated by the ionization energy of the atom. These energies can be calculated by the self-consistent-field method described previously (see page 20). These calculations have been made and much has been written concerning their interpretation. The seeming contradiction presented by the ground state of the atom and the ground state of the ions results from the fact that it is the total energy of the atom (ion) that is important, not the energy of the electronic configuration of Cu. If the relative energies of the 3d and 4s levels are examined, it is found that they lie very close together and that the energy of the 3d level decreases with increasing atomic number. This is often advanced as the explanation for the electronic configuration of Cu. If the 3d level has dropped below the 4s level, then the ground state must be 3d⁶4s². Nevertheless, this can have no effect on the phenomena that we are investigating, because the difference in configuration between ground state of the neutral atom and the ionic state is the same. Because all of the transition metals in the first series (with exception of Cr and Cu) have a 3d⁶4s² ground state for the neutral atom and a stable 3d⁶4s⁰ state for the dipositive ion, the source of our problem must be sought in the difference between atom and ion, not in trends along the series.
reaching consequences in chemistry. For our present discussion the principle may be stated as follows: In a given atom no two electrons may have all four quantum numbers identical. This means that in a given orbital specified by \( n, l, m_s \) and \( m_l \), a maximum of two electrons may exist (\( m_s = \pm \frac{1}{2} \) and \( m_l = \pm \frac{1}{2} \)).

We can now add Rule 7 to those given on page 20:

7. Each orbital can contain two electrons, corresponding to the two allowed values of \( m_s = \pm \frac{1}{2} \).

The Aufbau Principle

The electron configuration, or distribution of electrons among orbitals, may be determined by application of the Pauli principle and the ordering of energy levels suggested above. The method of determining the appropriate electron configuration of minimum energy (the ground state) makes use of the aufbau principle, or “building up” of atoms one step at a time. Protons are added to the nucleus and electrons are added to orbitals to build up the desired atom. It should be emphasized that this is only a formalism for arriving at the desired electron configuration, but an exceedingly useful one.

The quantum numbers \( n, l, m_s \) in various permutations describe the possible orbitals of an atom. These may be arranged according to their energies. The ground state for the hydrogen atom will be the one with the electron in the lowest orbital, the 1s. The spin of the electron may be of either orientation with neither preferred. We would thus expect a random distribution of spins; indeed, if a stream of hydrogen atoms were introduced into a magnetic field, half would be deflected in one direction, the other half in the opposite direction. Thus the four quantum numbers \( (n, l, m_s, m_l) \) for a hydrogen atom are \( (1, 0, 0, \pm 1) \). For the helium atom we can start with a hydrogen atom and add a proton to the nucleus and a second electron. The first three quantum numbers of this second electron will be identical to those from a hydrogen atom (i.e., the electron will also seek the lowest possible energy, the 1s orbital), but the spin must be opposed to that of the first electron. So the quantum numbers for the helium atom will be \( (1, 0, 0, \pm 1) \) and \( (1, 0, 0, \mp 1) \). For the lithium atom we can start with a hydrogen atom and add a proton to the nucleus and a third electron. The first three quantum numbers of this third electron will be identical to those from a hydrogen atom (i.e., the electron will also seek the lowest possible energy, the 1s orbital), but the spin must be opposed to that of the first electron. So the quantum numbers for the two electrons in a helium atom are \( (1, 0, 0, \pm 1) \) and \( (1, 0, 0, \mp 1) \). The 1s orbital is now filled, and the addition of a third electron to form a lithium atom requires that the 2s orbital, the next lowest in energy, be used. The electron configurations of the first five elements together with the quantum numbers of the last electron are:

\[
\begin{align*}
H & = 1s^1 \\
\text{He} & = 1s^2 \\
\text{Li} & = 1s^22s^2 \\
\text{Be} & = 1s^22s^2 \\
\text{B} & = 1s^22s^22p^1
\end{align*}
\]

This procedure may be continued, one electron at a time, until the entire list of elements has been covered. A complete list of electron configurations of the elements

---

\( ^{12} \) The \( m_s \) values for the unpaired electron in \( H, Li, \) and \( B \) are, of course, undetermined and may be either + or -1. It is merely necessary that the values for the second electron entering a 1s orbital in \( H \) and \( Be \) be opposite to the first. Likewise, the last electron in boron may enter the 2p, 3s, or 3p, orbital, all equal in energy, and so the \( m_s \) value given above is arbitrary.
Table 23

<table>
<thead>
<tr>
<th></th>
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<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes:
- Electron affinity values are calculated from the data in the reference.
- Personal communication.


Personal communication.
is given in Table 2.1. It will be seen that there are only a few differences between these configurations obtained experimentally and a similar table which might be constructed on the basis of the Aufbau principle. In every case in which an exception occurs the energy levels involved are exceedingly close together and factors not accounted for in the above discussion invert the energy levels. For example, the (n — 1)l and n levels tend to lie very close together when these levels are filling, with the latter slightly lower in energy. If some special stability arises, such as a filled or half-filled subshell (see page 27 and Chapter II), the most stable arrangement may not be the configuration obtained experimentally and a similar table which might be constructed on the basis of the Aufbau principle. In every case in which an exception occurs the energy levels involved are exceedingly close together and factors not accounted for in the above discussion invert the energy levels. For example, the (n — 1)l and n levels tend to lie very close together when these levels are filling, with the latter slightly lower in energy. If some special stability arises, such as a filled or half-filled subshell (see page 27 and Chapter II), the most stable arrangement may not be

Table 2.1 (Continued)

Electron configurations of the elements

<table>
<thead>
<tr>
<th>Z</th>
<th>Element</th>
<th>Electron configuration</th>
<th>Z</th>
<th>Element</th>
<th>Electron configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>64</td>
<td>Pm</td>
<td>[Xe]6s2[5d10]4f3</td>
<td>83</td>
<td>B</td>
<td>[Ar]4s2[3d10]4p6</td>
</tr>
<tr>
<td>65</td>
<td>Sm</td>
<td>[Xe]6s2[5d10]4f4</td>
<td>84</td>
<td>Bi</td>
<td>[Ar]4s2[3d10]4p6[5s2]</td>
</tr>
<tr>
<td>68</td>
<td>Tb</td>
<td>[Xe]6s2[5d10]4f7</td>
<td>87</td>
<td>Fr</td>
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<td>69</td>
<td>Dy</td>
<td>[Xe]6s2[5d10]4f8</td>
<td>88</td>
<td>Ra</td>
<td>[Ar]4s2[3d10]4p6[5s2][5p2][5d2][6s2][6p2]</td>
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<td>89</td>
<td>Ac</td>
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</tr>
<tr>
<td>71</td>
<td>Er</td>
<td>[Xe]6s2[5d10]4f10</td>
<td>90</td>
<td>Th</td>
<td>[Ar]4s2[3d10]4p6[5s2][5p2][5d2][6s2][6p2][6d2][7s2]</td>
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<tr>
<td>72</td>
<td>Tm</td>
<td>[Xe]6s2[5d10]4f11</td>
<td>91</td>
<td>Pa</td>
<td>[Ar]4s2[3d10]4p6[5s2][5p2][5d2][6s2][6p2][6d2][7s2][7p2]</td>
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<td>73</td>
<td>Yb</td>
<td>[Xe]6s2[5d10]4f12</td>
<td>92</td>
<td>U</td>
<td>[Ar]4s2[3d10]4p6[5s2][5p2][5d2][6s2][6p2][6d2][7s2][7p2][7d2]</td>
</tr>
<tr>
<td>74</td>
<td>Lu</td>
<td>[Xe]6s2[5d10]4f13</td>
<td>93</td>
<td>Np</td>
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<td>75</td>
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<td>[Xe]6s2[5d10]4f14</td>
<td>94</td>
<td>Pu</td>
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<tr>
<td>76</td>
<td>Ta</td>
<td>[Xe]6s2[5d10]4f15</td>
<td>95</td>
<td>Am</td>
<td>[Ar]4s2[3d10]4p6[5s2][5p2][5d2][6s2][6p2][6d2][7s2][7p2][7d2][8s2][8p2][8d2]</td>
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<tr>
<td>77</td>
<td>W</td>
<td>[Xe]6s2[5d10]4f16</td>
<td>96</td>
<td>Cm</td>
<td>[Ar]4s2[3d10]4p6[5s2][5p2][5d2][6s2][6p2][6d2][7s2][7p2][7d2][8s2][8p2][8d2][9s2]</td>
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<tr>
<td>78</td>
<td>Re</td>
<td>[Xe]6s2[5d10]4f17</td>
<td>97</td>
<td>Bk</td>
<td>[Ar]4s2[3d10]4p6[5s2][5p2][5d2][6s2][6p2][6d2][7s2][7p2][7d2][8s2][8p2][8d2][9s2][9p2]</td>
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<tr>
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<td>Os</td>
<td>[Xe]6s2[5d10]4f18</td>
<td>98</td>
<td>Cf</td>
<td>[Ar]4s2[3d10]4p6[5s2][5p2][5d2][6s2][6p2][6d2][7s2][7p2][7d2][8s2][8p2][8d2][9s2][9p2][9d2]</td>
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<td>[Xe]6s2[5d10]4f19</td>
<td>99</td>
<td>Es</td>
<td>[Ar]4s2[3d10]4p6[5s2][5p2][5d2][6s2][6p2][6d2][7s2][7p2][7d2][8s2][8p2][8d2][9s2][9p2][9d2][10s2]</td>
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<tr>
<td>81</td>
<td>Pt</td>
<td>[Xe]6s2[5d10]4f20</td>
<td>100</td>
<td>Fm</td>
<td>[Ar]4s2[3d10]4p6[5s2][5p2][5d2][6s2][6p2][6d2][7s2][7p2][7d2][8s2][8p2][8d2][9s2][9p2][9d2][10s2][10p2]</td>
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<tr>
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<td>Au</td>
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<td>101</td>
<td>Md</td>
<td>[Ar]4s2[3d10]4p6[5s2][5p2][5d2][6s2][6p2][6d2][7s2][7p2][7d2][8s2][8p2][8d2][9s2][9p2][9d2][10s2][10p2][10d2]</td>
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<tr>
<td>83</td>
<td>Hg</td>
<td>[Xe]6s2[5d10]4f22</td>
<td>102</td>
<td>No</td>
<td>[Ar]4s2[3d10]4p6[5s2][5p2][5d2][6s2][6p2][6d2][7s2][7p2][7d2][8s2][8p2][8d2][9s2][9p2][9d2][10s2][10p2][10d2][11s2]</td>
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<tr>
<td>84</td>
<td>Tl</td>
<td>[Xe]6s2[5d10]4f23</td>
<td>103</td>
<td>Lr</td>
<td>[Ar]4s2[3d10]4p6[5s2][5p2][5d2][6s2][6p2][6d2][7s2][7p2][7d2][8s2][8p2][8d2][9s2][9p2][9d2][10s2][10p2][10d2][11s2][11p2]</td>
</tr>
<tr>
<td>85</td>
<td>Pb</td>
<td>[Xe]6s2[5d10]4f24</td>
<td>104</td>
<td>Rf</td>
<td>[Ar]4s2[3d10]4p6[5s2][5p2][5d2][6s2][6p2][6d2][7s2][7p2][7d2][8s2][8p2][8d2][9s2][9p2][9d2][10s2][10p2][10d2][11s2][11p2][11d2]</td>
</tr>
</tbody>
</table>


** Predicted configuration.
be useful now to discuss trends in atomic sizes without becoming too specific at the present time about the actual sizes involved.

As we have seen from the radial distribution functions, the most probable radius tends to increase with increasing n. Countering this tendency is the effect of increasing effective nuclear charge, which tends to contract the orbitals. From these opposing forces we obtain the following results:

1. Atoms in a given family tend to increase in size from one period (= horizontal row of the periodic chart) to the next. Because of shielding, Z* increases very slowly from one period to the next. For example, using Slater's rules we obtain the following values for Z*:

   | H | Li | Be | B | C | N | O | F | Ne |
---|---|----|----|---|---|---|---|---|----|
| 1.00 | 1.279 | 1.912 | 2.576 | 2.421 | 4.117 | 4.886 | 6.367 | 5.858 |

2. Within a given series, the principal quantum number n does not change. [Even in the "long" series in which the filling may be in the order n = (n − 1f, sf, ...), the outermost electrons are always in the nth level.] The effective nuclear charge increases steadily, however, since electrons added to the valence shell shield each other very ineffectively. For the second series:

   | Li | Be | B | C | N | O | F | Ne |
---|----|---|---|---|---|---|---|----|
| 1.3 | 1.95 | 2.60 | 3.25 | 3.90 | 4.55 | 5.20 | 5.85 |

As a result there is a steady contraction from left to right. The net effect of the top-to-bottom and the left-to-right trends is a discontinuous variation in atomic size. There is a steady contraction with increasing atomic number until there is an increase in the principal quantum number. This causes an abrupt increase in size followed by a further decrease.

Ionization Energy

The energy necessary to remove an electron from an isolated atom in the gas phase is the ionization energy (often called ionization potential) for that atom. It is the energy difference between the highest occupied energy level and that corresponding to n = ∞, that is, complete removal. It is possible to remove more than one electron, and the succeeding ionization energies are the second, third, fourth, etc. Ionization energies are always endothermic and thus are always assigned a positive value in accord with common thermodynamic convention (see Table 2.3). The various ionization energies of an atom are related to each other by a polynomial equation, which will be discussed in detail later in this chapter.

For the nontransition elements (alkali and alkaline earth metals and the non-metals) there are fairly simple trends with respect to ionization energy and position in the periodic chart. Within a given family, increasing n tends to cause reduced ionization energy because of the combined effects of size and shielding. The transition and post-transition elements show some anomalies in this regard, which will be discussed in Chapters 14 and 18. Within a given series there is a general tendency for the ionization energy to increase with increase in atomic number. This is a result of the tendency for Z* to increase progressing from left to right in the periodic chart. There are two other factors which prevent this increase from being monotonous.

One is the change in type of orbital which occurs as one goes from Group 1A (1s orbital) to Group 1B (2s orbital) to Group 2B (2p orbital). The second is the exchange energy between electrons of like spin. This stabilizes a system of parallel electron spins because electrons having the same spin tend to avoid each other as a result of the Pauli exclusion principle. The electronic repulsions between electrons are thus reduced.

We have seen previously that this tends to maximize the number of unpaired electrons (Hund's principle of maximum multiplicity) and also accounts for the "anomalous" behavior of Cu and Cr. It also tends to make it more difficult to remove the electron from the nitrogen atom than would otherwise be the case. As a result of this stabilization, the ionization energy of nitrogen is greater than that of oxygen (see Fig. 2.12).
Although the *aufbau* principle and the ordering of orbitals given previously may be used reliably to determine electron configurations, it must again be emphasized that the device is a formalism and may lead to serious error if overextended. For example, in the atoms of the elements potassium, calcium, and scandium the 4s level is lower in energy than the 3d level. This is not true for heavier elements or for charged ions. The energies of the various orbitals are sensitive to changes in nuclear charge and to the occupancy of other orbitals by electrons (see "Shielding", page 30), and this prevents the designation of an absolute ordering of orbital energies. It happens that the ordering suggested by Fig. 2.10 is reasonably accurate when dealing with orbitals corresponding to the valence shell of an atom; that is, the energies 3d > 4s and 5p > 4d are correct for elements potassium and yttrium, for example, but not necessarily elsewhere.

It is convenient to be able to specify the energy, angular momentum, and spin multiplicity of an atom by a symbolic representation. For example, for the hydrogen atom we may define \( S, P, D, F \) states, depending upon whether the single electron occupies an \( s, p, d, f \) orbital. The ground state of hydrogen, \( 1s^1 \), is an \( S \) state; a hydrogen atom excited to a \( 2p^1 \) configuration is in an \( F \) state, etc. For polyatomic electrons, an atom in a \( P \) state has the same total angular momentum (for all electrons) as a hydrogen atom in a \( P \) state. Corresponding to states \( S, P, D, F \), etc., are quantum numbers \( L = 0, 1, 2, 3, 4, \ldots \) which parallel the \( l \) values for \( s, p, d, f \) orbitals.\(^{12}\) Likewise, there is quantum number \( S \) (not to be confused with the \( S \) state just mentioned) that is the summation of all the electronic spins. For a closed shell or subshell, obviously \( S = 0 \), since all electrons are paired. Somewhat less obviously, under these conditions \( L = 0 \), since all of the orbital momenta cancel. This greatly simplifies working with states and term symbols.

The chemist frequently uses a concept known as multiplicity, originally derived from the number of lines shown in a spectrum. It is related to the number of unpaired electrons and, in general, is given by the expression \( 2S + 1 \). Thus, if \( S = 0 \), the multiplicity is one and the state is called a singlet; if \( S = 1 \), the multiplicity is two and the state is a doublet; \( S = 1 \) is a triplet; etc. Hund's rule of maximum multiplicity states that the ground state of an atom will be the one having the greatest multiplicity (i.e., the greatest value of \( S \)). Consider a carbon atom \( 1s^2 2s^2 2p^2 \). We may ignore the closed \( 1s^2 \) and \( 2s^2 \). The two \( 2p \) electrons may be paired (\( S = 0 \)) or have parallel spins in different orbitals (\( S = 1 \)). Hund's rule predicts that the latter will be the ground state; that is, a triplet state. It happens precisely in this state \( L = 1 \), so we may say that the ground state of carbon is \( 2p^2 \) (previously named "triplet-\( 2p \)"). The \( 1s^2 2s^2 2p^2 \) is said to be the term symbol.

It is convenient for many purposes to draw "box diagrams" of electron configurations in which boxes represent individual orbitals, and electrons and their spins are indicated by arrows:

\[
\begin{array}{ccc}
1s^2 & 2s^2 & 2p^2 \\
\uparrow & \uparrow & \uparrow \\
1 & 1 & T
\end{array}
\]

\(^{12}\) This is the reverse of the historical process. \( S, P, D, F \) states were observed spectroscopically and named after sharp, principal, diffuse, and fundamental characteristics of the spectra. Later the symbols \( s, p, d, f \) were applied to orbitals. The methods for assigning the various possible values of \( L \) and the determination of term symbols, as well as the general topic of the coupling of orbital angular momenta and electron angular momenta, are given in Appendix C.

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Such devices can be very useful for bookkeeping, providing pigashowes in which to place electrons. However, the reader is warned that they can be misleading if improperly used, especially with respect to term symbols.

Traditionally, Hund's rule has been explained by assuming that there is less repulsion between electrons in the high-spin state, stabilizing it. Yet we have seen that electrons having the same spin are highly correlated and actually repel each other more than electrons of opposite spin (page 22). However, because electrons of parallel spin avoid each other, they shield each other from the nucleus less and the electron-nucleus attraction is greater and dominates. The overall energy is lowered.

The extra stability of parallel-spin configurations is given by the exchange energy:

\[
E_{ex} = \sum \frac{N(N-1)}{2} K
\]

where \( N \) is the number of electrons having parallel spins. Because the exchange energy is a quadratic function of \( N \), it rises rapidly as the number of parallel spins increases: \( 0 = \frac{1}{2} (N-1)^2 \), \( 1 = \frac{1}{2} (N-2)^2 \), \( 6 = \frac{1}{2} (N-3)^2 \). Since the number of parallel spins is maximized for filled and half-filled subshells, the exchange energy is responsible for the so-called "special stability" of these configurations.\(^{13}\)

For chemists working with several elements, the periodic chart of the elements is so indispensable that one is apt to forget that, far from being divinely inspired, it resulted from the hard work of countless chemists. True, there is a quasimathematical basis for the periodicity of the elements, as we shall see shortly. But the inspiration of such scientists as Mendeleev and the perspiration of a host of nineteenth-century chemists provided the chemist with the benefits of the periodic table about half a century before the existence of the electron was proved! The confidence that Mendeleev had in his chart, and his predictions based on it, make fascinating reading.\(^{14}\)

The common long form of the periodic chart (Fig. 2.11) may be considered a graphic portrayal of the rules of atomic structure given previously. The arrangement of the atoms follows naturally from the *aufbau* principle. The various groups of the chart may be classified as follows:

1. The "s" block elements: Groups IA and II A (Columns I and 2), the alkali and alkaline earth metals. These elements are also sometimes called the "light metals." They are characterized by an electron configuration of \( ns^1 \) or \( ns^2 \) over a core with a noble gas configuration.

2. The "p" block elements: Groups 13-18 (Columns 3-12), the transition metals. Characteristically, atoms of these elements in their ground states have electron configurations that are filling d orbitals.\(^{15}\) For example, the first transition series proceeds from \( Sc(3d^1) \) to \( Zn(3d^{10}) \). Each of these ten elements stands at the head of a family of homologues (e.g., the chromium family, VII B).

---


\(^{13}\) There are problems with any simple definition of "transition metals." See the discussion under "Shielding."
3. All of the other electrons in the (ns, np) group, shield the valence electron to an extent of 0.35 each.26
4. All electrons in the n - 1 shell shield to an extent of 0.85 each.
5. All electrons n - 2 or lower shield completely; that is, their contribution is 1.00 each.

When the electron being shielded is in an nd or nf group, rules 2 and 3 are the same but rules 4 and 5 become:

6. All electrons in groups lying to the left of the nd or nf group contribute 1.00.

Examples

1. Consider the valence electron in the atom ,N = 1s22s22p3. Grouping of the orbitals gives (1s)2(2s, 2p). S = (2 x 0.85) + (4 x 0.35) = 3.10. Z* = Z - S = 7.0 - 3.1 = 3.9.
2. Consider the valence (4s) electron in the atom ,Zn. The grouped electron configuration is (1s)2(2s, 2p)3(3s, 3p)3(3d)10(4s). S = (10 x 1.00) + (18 x 0.85) + (1 x 0.35) = 25.65. Z* = 4.35.
3. Consider a 3d electron in Zn. The grouping is as in example 2, but the shielding is S = (18 x 1.00) + (9 x 0.35) = 21.15. Z* = 8.85.

It can be seen that the rules are an attempt to generalize and to quantify these aspects of the radial distributions discussed previously. For example, d and f electrons are shielded more effectively (S = 1.00) than s and p electrons (S = 0.85) by the electrons lying immediately below them. On the other hand, Slater's rules assume that all electrons, s, p, d, or f, shield electrons lying above them equally well (in computing shielding the nature of the shielding electron is ignored). This is not quite true, as we have seen above and will tend to some error. For example, in the Ga atom (= 3s23p13d104s24p1) the rules imply that the 4p electron is shielded as effectively by the 3d electrons as by the 3s and 3p electrons, contrary to Fig. 2.4.

Slater formulated these rules in proposing a set of orbitals—for use in quantum mechanical calculations. Slater orbitals are basically hydrogen-like but differ in two important respects:

1. They contain no nodes. This simplifies them considerably but of course makes them less accurate.
2. They make use of Z* in place of Z, and for heavier atoms, n is replaced by n*, where for n = 4, n* = 4.7; n = 5, n* = 4.9; n = 6, n* = 4.2. The difference between n and n* is referred to as the quantum defect.

To remove the difficulties and inaccuracies in the simplified Slater treatment of shielding, Clementi and Raimondi27 have obtained effective nuclear charges from self-consistent field wave functions for atoms from hydrogen to krypton and have generalized these into a set of rules for calculating the shielding of any electron. The shielding which an electron in the n*th energy level and lth orbital (Slater) experiences is given by:

$$S_{l,n*} = 0.3(N_{l,n*} - 1) + 0.0072(N_{l-2,n*} + N_{l-2,n*}) + 0.0158(N_{l-3,n*} + N_{l-3,n*})$$

(2.9)

where

$$Z_{l,n*} = 1.7208 + 0.3601(N_{l-2,n*} - 1 + N_{l-2,n*}) + 0.2062(N_{l-3,n*} + N_{l-3,n*})$$

(2.10)

$$S_{l-n*} = 2.5878 + 0.332(N_{l-n*} - 1) - 0.0732N_{l-n*} - 0.0156(N_{l-n*} + N_{l-n*}) + 0.008N_{l-n*} + 0.0085N_{l-n*}$$

(2.11)

$$Z_{l-n*} = 8.4927 + 0.2501(N_{l-n*} - 1 + N_{l-n*}) + 0.0776N_{l-n*} + 0.3352N_{l-n*} + 0.1978N_{l-n*}$$

(2.12)

$$S_{l-5,n*} = 9.5345 + 0.2903(N_{l-5,n*} - 1) + 0.0526N_{l-5,n*} + 0.2359N_{l-5,n*} + 0.1458N_{l-5,n*}$$

(2.13)

$$Z_{l-5,n*} = 15.50 + 0.0731(N_{l-5,n*} - 1) + 0.8433N_{l-5,n*} + 0.0867N_{l-5,n*}$$

(2.14)

$$S_{l-6,n*} = 12.3934 + 0.2903(N_{l-6,n*} - 1) - 0.1065N_{l-6,n*}$$

(2.15)

$$Z_{l-6,n*} = 21.78 + 0.2905(N_{l-6,n*} - 1)$$

(2.16)

where Nl,n* represents the number of electrons in the n* orbital. For the examples given above, the effective nuclear charges obtained are Z2s = 3.756, Z2p = 5.065, and Z3p = 13.987. The shielding rules of Clementi and Raimondi explicitly account for penetration of outer orbital electrons. They are thus more realistic than Slater's rules, at the expense, however, of more complex computation with a larger number of parameters. If accuracy greater than that afforded by Slater's rules is necessary, it would appear that direct application of the effective nuclear charge from the SCF wave functions is not only simple but also accurate. Such values are listed in Table 2.2. With the accurate values of Table 2.2 available, the chief justification of "rules", whether Slater's or those of Clementi and Raimondi, is the insight they provide into the phenomenon of shielding.

The Sizes of Atoms

Atomic size is at best a rather nebulous quantity since an atom can have no well-defined boundary similar to that of a billiard ball. In order to answer the question, "How big is an atom?" one must first pose the questions, "How are we going to measure the atom?" and "How hard are we going to push?" If we measure the size of a xenon atom resting in the relatively relaxed situation obtained in solid xenon, we might expect to get a different value than if the measurement is made through violent collisions. A sodium ion should be compressed more if it is tightly bound in a crystal lattice (e.g., NaF) than if it is loosely solvated by molecules of low polarity. The question, "How big is an atom?" one must first pose the questions, "How are we going to measure it?" and "How hard are we going to push?" If we measure the size of a xenon atom resting in the relatively relaxed situation obtained in solid xenon, we might expect to get a different value than if the measurement is made through violent collisions.

26 Except for the 1s orbital for which a value of 0.30 seems to work better.
The "p" block elements: The nonmetals and posttransition metals, Groups III A to VIIIA (Columns 13 to 18). This block of elements contains six families corresponding to the maximum occupancy of six electrons in a set of p orbitals. The classification between metals and nonmetals is imprecise, principally because the distinction between metal and nonmetal is somewhat arbitrary, though usually associated with a "stair-step" dividing line running from boron to satatium. All these elements (except He) share the feature of filling p orbitals, the noble gases (VIIIA and 18) having a completely filled set of p orbitals.

3. The "f" block elements: Lanthanide and actinide series. These two series often appear with a * or † in Group III B (3), but these elements do not belong to that family. (Note that the transition metals do not belong to group II A (2), which they follow.) The most common oxidation state for the lanthanides and actinides is +3, and in an almost opposite sense. Some chemists would define transition metals strictly as those elements whose ground state atoms have partially filled d orbitals. This excludes zinc from the first transition series. One must admit that zinc does have several properties that distinguish it from "typical" transition metal behavior. It forms a single oxidation state, Zn^2+, which is neither paramagnetic nor colored and which forms rather weak complexes for its small size, etc. If we so exclude zinc, do we also exclude Cu^2+, which is isoelectronic with Zn^2+ and metallic copper, which also has a filled 3d^10 configuration? More importantly, if we exclude zinc and its congeners, cadmium and mercury, from the transition metals, then to be logically consistent we must exclude the noble gases from the nonmetals. Some chemists might favor this, but the point is made in Chapter 17 that the separation of the noble gases from the halogens, which are in some ways similar, impeded noble gas chemistry. Finally, to be internally logical, lutecium would have to be removed from the lanthanides and lawrencium from the actinides. Likewise, the designation of groups as "A" or "B" is purely arbitrary. Assignment of all of the transition metals to "B" groups has an internal consistency as well as historical precedent. Unfortunately, some periodic charts have used "A" and "B" in an almost opposite sense. In addition, as a historical carryover from the older "short form" chart, the iron, cobalt, and nickel families were lumped under the non-descript "VIII". This state of confusion led the IUPAC to recommend that the groups be numbered as shown in Table 2.1. The periodic chart may thus be used to derive the electron configuration of an element as readily as use of the rules given above. It should be quite apparent, however, that the chart can give us back only the chemical knowledge that we have used in composing it; it is not a source of knowledge in itself. It is useful in portraying and correlating the information that has been obtained with regard to electron configurations and other atomic properties.

It is possible to trace the aufbau principle simply by following the periodic chart. Consider the elements from Cs (Z = 55) to Rn (Z = 86). In the elements Cs and Ba the electrons enter (and fill) the 6s level. The next electron enters the 5d level, and La (Z = 57) may be considered a transition element. In the elements Ce through Lu the electrons are added to the 4f levels and these elements are lanthanide or inner transition elements. After the 4f level is filled with Lu, the next electrons continue to fill the 5d orbitals (the transition elements Hf to Hg). Finally, the 6p level is filled in the elements Tl to Rn, in accord with Table 2.1. The periodic chart may thus be used to derive the electron configuration of an element as readily as use of the rules given above. It should be quite apparent, however, that the chart can give us back only the chemical knowledge that we have used in composing it; it is not a source of knowledge in itself. It is useful in portraying and correlating the information that has been obtained with regard to electron configurations and other atomic properties.

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Shielding

The energy of an electron in an atom is a function of $Z$. Since the nuclear charge increases more rapidly than the principal quantum number, it would continually increase with increasing atomic number. This is not so, as can be might be led to expect that the energy necessary to remove an electron from an atom within a similar vein, suggestions have been made that all transactinide elements be named by a system that translates the atomic number into a latinated name with a three-letter symbol that is a one-to-one letter equivalent of the atomic number. Within this scheme, ratherdium ($Z = 104$) would become unnilquadium, Unq.

IUPAC labels is the best compromise at present (Fig. 2.11). However, the IUPAC calls these "temporarily names" to be used until a suitable name can be agreed upon, which, it is hoped, will be chosen in the time-honoured manner.

The energy of an electron in an atom is a function of $Z^{1/2}$. Since the nuclear charge ($Z$ atomic number) increases more rapidly than the principal quantum number, one might be led to expect that the energy necessary to remove an electron from an atom would continually increase with increasing atomic number. This is not so, as can be shown by comparing hydrogen ($Z = 1$) with lithium ($Z = 3$). The ionization energies are $1312 \text{ kJ mol}^{-1}$ (H) and $520 \text{ kJ mol}^{-1}$ (Li). The ionization energy of lithium is lower for two reasons: (1) The average radius of a 2s electron is greater than that of a 1s electron (see Fig. 2.4); (2) the 2s electron in lithium is repelled by the inner core 1s electrons, so that the former is more easily removed than if the core were not there. Another way of treating this inner core repulsion is to view it as "shielding" or "screening" of the nucleus by the inner electrons, so that the valence electron actually "sees" only part of the total charge. Thus, the ionization energy for lithium corresponds to an effective nuclear charge of between one and two units. The radial probability functions for hydrogen-like orbitals have been discussed previously (Fig. 2.4).

The bulk of the electron density of the 1s orbital lies between the nucleus and the bulk of the 2s density. The laws of electrostatics state that when a test charge is outside of a "cage" of charge such as that represented by the 1s electrons, the potential is much less than that due to the presence of one node and an intranodal maximum in the 3p orbital. Although the 3p orbitals are "smaller" in the sense that the most probable radius decreases in the order 3s > 3p > 3d, the presence of one node and an intranodal maximum in the 3p orbital causes them to be affected more by the nucleus. Hence the energies of these orbitals lie 3d > 3p > 3s as we have seen in filling the various energy levels previously.

In order to estimate the extent of shielding, a set of empirical rules has been proposed by Slater. It should be realized that these rules are simplified generalizations based upon the average behavior of the various electrons. Although the electronic energies estimated by Slater's rules are often not very accurate, they permit simple estimates to be made and will be found useful in understanding related topics such as atomic size and electronegativity.

To calculate the shielding constant for an electron in an np or an orbital:

1. Write out the electronic configuration of the element in the following order and groupings: $(1s)^2 (2s, 2p)$ $(3s, 3p)$ $(4s, 4p)$ $(5s, 5p)$, etc.
2. In any group to the right of the $(ns, np)$ group contribute nothing to the shielding constant.

where S is the shielding or screening constant.

25 If this is numbered 1-32, immediately the same problem as before arises through simultaneous usage of 1-18 and 1-32 charts. Does column (I) refer to F, Cl, Br, and I, or to Na and Kr? (See Jensen, W. B. Chem. Eng. News 1937, 1, 673.) 2-15 Strong arguments can be made for extending the A-B system to an A-B-C system. A logarithmic form is the use of a step-pyramid. (See Jensen, W. B. Comp. Math. Appl. 1964, 15, 471-513.) Such a chart makes the logarithm small. A = "main group elements"; B = "transition elements"; C = "inner transition elements" (= lanthanides and actinides). However, this means accepting the North American conventions with regard to A and B, which may not be politically practical. And indeed, are going to look somewhat at any future use of A and B. Perhaps internal inclusion of these elements is not the end of the story if the "superpseud" idea discussed in Chapter 14 are ever discovered, a fifty column chart could follow. The step pyramid would accommodate this possibility with the addition of one more, "D" layer.


27 The reason for proposing a change, supposedly only temporary, in the traditional way of naming elements i.e., giving that option and honor to the discoverer is a result of two important factors: (1) There should be some provisional way of discussing elements that are so yet undiscovered. The atomic number does not exist simultaneously. (2) There is an intense national rivalry and chauvinism in the discovery of these elements, an inability to respect claimed discoveries, and the fact that the nickel seems to have left the area of science and is now one of politics. Perhaps the current presence of plutonium and independent European laboratories will resolve this issue. See also Chapter 14.
The presence of one or more bis(4-tert-butylypyridine)osmyl groups provides "handles" to break the pseudospherical symmetry of the C$_{60}$ molecules and anchor them in the crystal. The X-ray crystal structure of the one-to-one adduct was readily accomplished. This allowed the authors to say:

"The crystal structure [Fig. 3.34] confirms the soccer ball-like arrangement of carbon atoms in C$_{60}$ by clearly showing the 32 faces of the carbon cluster composed of 20 six-membered rings fused with 12 five-membered rings. The low-temperature phase, unlike that at room temperature, is ordered and thus fusion..."

A phase change for C$_{60}$ occurs at 249 K (face-centered cubic to simple cubic). Buckminsterfullerene has a high electron affinity. Treatment with up to six moles of an alkali metal such as potassium or rubidium gives products

\[ nM + C_{60} \rightarrow M_nC_{60} \]  

which show metallic conductivity. If only three moles of potassium or rubidium are allowed to react, the products consist of K$_3$C$_{60}$ and Rb$_3$C$_{60}$ which become superconducting at temperatures below 18 K and 30 K, respectively.\(^{60}\) These compounds have a face-centered cubic unit cell with a close-packed array of C atoms, with M$^+$ ions in the tetrahedral and octahedral holes (see Chapter 4). At present it does not appear that these superconductors will prove competitive with the cuprate high-temperature superconductors (Chapter 7) because of their much higher critical temperature and the fact that they are quite susceptible to oxidation.

Buckminsterfullerene, C$_{60}$, appears to be the first of a large number of allotropes of fullerene-like fullerenes: C$_{60}$ is already fairly well known—it probably has the shape of a rugby ball—and other C$_{n}$ molecules with $n = 76, 84, 90, 94$ have been isolated. Even larger molecules with $n$ equal to 240 and even 420 have been suggested.\(^{51}\)

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**Problems**

3.1 Assign the molecules in Figs. 3.2, 3.4, and 3.7 to their appropriate point groups.

3.2 Assign the molecules in Figs. 3.5, 3.6, and 3.8 to their appropriate point groups.

3.3 Assign the following molecules to their appropriate point groups.

- a. cyclopropane
- b. SO$_2$
- c. CO$_2$
- d. B$_3$H$_6$
- e. P$_4$
- f. C$_3$C=C=CCl
- g. BF$_3$
- h. PH$_3$
- i. $\text{I}_2$SCl$_2$
- j. OSCl$_2$
- k. $\text{H}_2$O

3.4 Assign the following to their appropriate point groups.

- a. tris(oxalato)chromium(III)
- b. tris(carbonato)cobalt(III)
- c. tris(glycinato)cobalt(I)
- d. $\text{B}=\text{B}$
- e. $\text{H}^+\text{P}-\text{P}^-$
- f. $\text{C}=\text{C}^-\text{C}^-\text{C}^-$
- g. $\text{Cl}^-\text{C}^-\text{Cl}^-$
- h. $\text{O}^-$
- i. $\text{S}^-$
- j. $\text{O}_2^-$
- k. $\text{H}_2$O

3.5 Groups with $I_a$, $T_d$, $T_h$, $C_{3v}$, and $C_i$ symmetries were assigned in the text by inspection. Take the molecules given as illustrations of these symmetries (Figs. 3.3 and 3.11) and run them through the flowchart (Fig. 3.16) to assign their proper point groups.

3.6 Although most molecules in point groups $I_a$, $T_d$, $T_h$, $C_{3v}$, and $C_i$ may be assigned by inspection, some appear unusual. Consider the cubic symmetry of cubane, C$_{68}$. To
Instead of silicon or germanium with four valence electrons (to yield a filled band of \(4 + 4 = 8\) electrons on band formation), we can form a compound from gallium (three valence electrons) and arsenic (five valence electrons) to yield gallium arsenide with a filled valence band. In general, however, the \(\Delta E\) for the band gap will differ from those of elemental semiconductors. The band gap will increase as the tendency for electrons to become more and more localized on atoms increases, and thus it is a function of the electronegativities of the constituents (Fig. 7.25). Note that conductivity is a continuous property ranging from metallic conductance (Sn) through elemental semiconductors (Ge, Si), compound semiconductors (GaAs, CdS) to insulators, both elemental (diamond, C) and compounds (NaCl).

Consider a pure crystal of germanium. Like silicon it will have a low intrinsic conductivity at low temperatures. If we now dope some gallium atoms into this crystal, we shall have formed holes because each gallium atom contributes only three electrons rather than the requisite four to fill the band. These holes can conduct electricity by the process discussed above. By controlling the amount of gallium impurity, we can control the number of carriers.

Thinking only in terms of electrons or holes that are completely free to move suggests that there would be no energy gap in a gallium-doped germanium semiconductor. However, note that gallium lies to the left of germanium in the periodic table and is more electropositive; it thus tends to keep the positive hole. (Alternatively, germanium is more electronegative, and the electron tends to stay on the germanium atoms rather than flow into the hole on the gallium atom.) This electronegativity effect creates an energy gap, as shown more graphically in Fig. 7.26. The electronic energy levels for gallium lie above the corresponding ones for germanium and thus above the germanium valence band. Providing a small ionization energy, \(\Delta E\), generates the holes for semiconduction. The resulting system is called an acceptor (since gallium can accept an electron) or \(p\)-type (\(p\) = positive holes) semiconductor.

In an exactly analogous but opposite manner, doping germanium with arsenic (five valence electrons) results in an excess of electrons and a donor (the arsenic donates the fifth electron) or \(n\)-type (\(n\) = negative electrons) semiconductor. The conduction can be viewed in terms of an energy diagram in which the electrons can be removed from the impurity arsenic atoms to the conduction band of the semiconductor (Fig. 7.27).
3.7 Find the symmetry elements, if any, in the objects shown in Fig. 3.1.

3.8 In the discussion of crystallography, translational symmetry was likened to moving ducks and blinking eyes. Extend this discussion to the action of a strobe light blinking $t$ times per second relative to the following.

a. ducks moving with a certain linear velocity

b. a spoked wheel spinning at a certain angular velocity

3.9 Why does SF$_4$ have $C_2$ symmetry rather than $C_4^*$? (See Fig. 6.4).

3.10 Find all of the symmetry elements in an octahedron.

3.11 Tris(2-aminoethoxo)cobalt(III) (Fig. 3.12b) was assigned $C_3$ symmetry, but the methylene groups of the ligand were not drawn out explicitly. Does consideration of these groups change the symmetry? Discuss.

3.12 Gauc/H$_2$O$_2$ has $C_2$ symmetry. What are the symmetries of the eclipsed (cis) conformation and the anti (trans) conformation?

3.13 On page 64 the argument is made that a molecule with a center of symmetry, $i$, cannot have a molecular dipole moment. Prove this same rule using a molecule with a center of symmetry and summing up the individual bond moments.

3.14 Meso molecules such as R,S-1,2-dichloro-1,2-difluorocyclohexane are usually cited as achiral because they possess a mirror plane (when in the perfectly eclipsed conformation) and thus have no optical activity. What is the symmetry of this conformer? In other conformations? Discuss why meso molecules show no optical activity.

3.15 Which of the following molecules will have dipole moments?

3.16 What are the symmetries of the normal modes of vibration of these molecules?
The Solid State

7. Intrinsic and Photoexcited Semiconductors

Intrinsic and Photoexcited Semiconductors

For every electron excited to the antibonding conduction band, there will remain behind a hole, or vacancy, in the valence band. The electrons in both the valence band and the conductive band will be free to move under a potential by the process shown in Fig. 7.23, but since the number of electrons (conduction band) and holes (valence band) is limited, only a limited shift in occupancy from left-bound states to right-bound states can occur and the conductivity is not high as in a metal. This phenomenon, known as intrinsic semiconduction, is the basis of thermistors (temperature-sensitive resistors).

An alternative picture of the conductivity of the electrons and holes in intrinsic semiconductors is to consider the electrons in the conduction band as migrating, as expected, toward the positive potential, and to consider the holes as discrete, positive charges migrating in the opposite direction. Although electrons are responsible for conduction in both cases, the hole formalism represents a convenient physical picture.

If, instead of thermal excitation, a photon of light excites an electron from the valence band to the conduction band, the same situation of electron and hole carriers obtains, and one observes the phenomenon of photoconductivity, useful in photocells and similar devices.

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Fig. 7.22 Effect of an electric field on the energy levels in a metal: (a) no field, no net flow of electrons; (b) field applied, net flow of electrons to the right.

The metal is conducting electricity, if the band is completely filled (Fig. 7.23), there is no possibility of transfer of electrons and, despite the presence of a potential, equal numbers of electrons flow either way; therefore, the net current is zero and the material is an insulator.

All insulators will have a filled valence band plus a number of completely empty bands at higher energies, which arise from the higher-energy atomic orbitals. For example, the silicon atom will have core electrons in essentially atomic orbitals $1s^2$, $2s^2$, and $2p^2$, and a valence band composed of the $3s$ and $3p$ orbitals. Then there will be empty orbitals arising out of combinations of $3d$, $4s$, $4p$, and higher atomic orbitals. If the temperature is sufficiently high, some electrons will be excited thermally from the valence band to the lowest-lying empty band, termed the conduction band (Fig. 7.24). The number excited will be determined by the Boltzmann distribution as a function of temperature and band gap, $\Delta E$. Before discussing the source of the magnitude of the energy gap, let us note typical band-gap and conductivity values for insulators (diamond, C), semiconductors (Si, Ge), and an "almost metal," gray tin.

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Van Vlack, L. H. *Elements of Materials Science and Engineering*, 5th ed.; Addison-Wesley: Reading, MA, 1985, p. 332. Gray tin has the same structure as diamond. Metallic tin is called white tin and has a distorted octahedral environment about each tin atom. It conducts electricity like other metals.
3.27 Fig. 3.35 shows removal of B from octahedral \( \text{AB}_6 \) to give square pyramidal \( \text{AB}_5 \) and loss of a second B to give seesaw \( \text{AB}_4 \). Suppose that instead of the geometries shown, the \( \text{AB}_6 \) microcrystal to give a trigonal antiprismatic structure and \( \text{AB}_4 \) assumed a square planar shape. What orbital symmetries and degeneracies would occur for these two cases?

3.28 Consider the following \( \text{AB}_n \) molecules and determine the symmetries and degeneracies of the \( x, p, \) and \( d \) orbitals on A in each.

- a. \( \text{AB}_6 \) (cube)
- b. \( \text{AB}_6 \) (square plane)
- c. \( \text{AB}_5 \) (trigonal pyramid)
- d. \( \text{AB}_5 \) (trigonal plane)
- e. \( \text{AB}_4 \) (T-shape)
- f. \( \text{AB}_4 \) (rectangular plane)

3.29 For each of the following molecules, determine what atomic orbitals on the central atom are allowed by symmetry to be used in the construction of sigma hybrid orbitals.

- a. \( \text{NH}_3 \) (trigonal pyramid)
- b. \( \text{BF}_3 \) (trigonal plane)
- c. \( \text{SF}_4 \) (octahedron)
- d. \( \text{PF}_3 \) (trigonal bipyramidal)

3.30 A chemist isolated an unknown transition metal complex with a formula of \( \text{AB}_6 \). Five potential structures were considered, belonging to point groups \( D_4^h \), \( D_{4h} \), \( D_{3h} \), and \( D_2h \). Spectroscopic studies led to the conclusion that the \( p \) orbitals originating on A in the complex were completely nondegenerate. Sketch a structural formula that is consistent with each of the five point group assignments and decide which structures can be eliminated on the basis of the experimental results.

3.31 What atomic orbitals on carbon in the planar \( \text{CO}_2^- \) anion could be used (on the basis of symmetry) to construct in-plane and out-of-plane \( \pi \) bonds? First answer the question by thinking about the orientations of the orbitals relative to the geometry of the ion; then answer it by using reducible representations and the appropriate character table.

3.32 What is the symmetry of buckminsterfullerene? Is a geodesic dome the same as a segment of buckminsterfullerene? What is the symmetry of the bis(4-r-butylpyridine)osmyl derivative of buckminsterfullerene (Fig. 3.34)? Do you expect it to be chiral? To have a dipole moment? To be soluble in benzene?

3.33 Flow many \( ^1\text{C} \) NMR signals do you expect to see for \( \text{C}_6\text{H}_{10} \)? How many for \( \text{C}_6\text{H}_4 \)?

3.34 Look up carbon–carbon bond lengths (single, double, and aromatic) in an organic chemistry textbook and compare with the bond lengths in buckyball. What can you conclude about the bonding in buckyball?

3.35 Depending upon the conditions, reactant ratios, etc., the product of Eq. 3.2 consists of (1) a toluene-soluble fraction that gives a single, sharp chromatographic peak for a material that analyzes \( \text{C}_{22}\text{O}_5\text{O}_{10}(\text{NC}_3\text{H}_7\text{C}_6\text{H}_{15})_2 \), and yields the structure shown in Fig. 3.34, and (2) a precipitate that analyzes as \( \text{C}_{26}\text{O}_{10}(\text{NC}_3\text{H}_7\text{C}_6\text{H}_{15})_2 \). What is the significance of a single \( \text{C}_{24}\text{H}_{30}\text{O}_{10}\text{N}_{10}\text{C}_{30}\text{H}_{45}\text{F}_{15} \) derivative (1) of buckminsterfullerene? When (2) is analyzed chromatographically, five peaks are observed. Discuss.

3.36 It has been suggested that if the potassium (or rubidium) atoms in the \( \text{M}_2\text{C}_{60} \) superconductors could somehow be placed inside the buckyballs, they would be protected, and thus these superconductors would not be susceptible to oxidation. Comment.

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germanium, compounds between these elements, such as gallium arsenide, or various
nonstoichiometric or defect structures. In electrical properties they fall between
conductors and nonconductors (insulators).

**Band Theory**

In order to understand the bonding and properties of an infinite array of atoms of a
metallic element in a crystal, we should first examine what happens when a small
number of metal atoms interact. For simplicity we shall examine the lithium atom,
since it has but a single valence electron, 2s¹, but the principles may be extended to
transition and posttransition metals as well. When two wave functions interact, one of
the resultant wave functions is raised in energy and one is lowered. This is discussed
for the hydrogen molecule in Chapter 5. Similarly, interaction between two 2s orbitals
of two lithium atoms would provide the bonding σ energy level and the antibonding σ*
energy level shown in Fig. 7.19. Interaction of n lithium atoms will result in n energy
levels, some bonding and some antibonding (Fig. 7.20). A mole of lithium metal will
provide an Avogadro's number (N) of closely spaced energy levels (the aggregate is
termed a band), the more stable of which are bonding and the less stable, antibonding.20
Since each lithium atom has one electron and the number of energy levels is
equal to the number of lithium atoms, half of the energy levels will be filled whether
there are two, a dozen, or N lithium atoms. Thus, in the metal the band will be half
filled (Fig. 7.21), with the most stable half of the energy levels doubly occupied and the
least stable, upper half empty. The preceding statement is true only for absolute zero.
At all real temperatures the Boltzmann distribution21 together with the closely spaced
energy levels in the band will ensure a large number of half-filled energy levels, and so

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20 The levels near the center of the band are essentially nonbonding.
21 In the Boltzmann distribution, the population of higher energy states will be related to the value of
the expression e⁻E/kT where e is the base of natural logarithms, E is the energy of the higher state,
κ is Boltzmann’s constant, and T is the absolute temperature.
The authors stated that "[The structure] has space group $P_I$. Owing to the strongly scattering $Sb$ atoms, the $H$ atoms . . . could not be definitely localized . . . The $H_3F_3$ ion . . . is located on a symmetry center of the space group and therefore has [a or b? Choose one.] conformation." Discuss how the correct conformation, a or b, can be chosen by symmetry arguments even if the hydrogen atoms cannot be located.

3.43 Fig. 3.38 is a stereoview of the unit cell of Fe(CO)$_4$(b'-PPh$_2$CH$_2$CH$_2$PPh$_2$) which crystallizes in the monoclinic space group $P2_1/c$. Find the symmetry elements of the unit cell. [Hint: Find three easily recognized atoms in the Fe(CO)$_4$(b'-PPh$_2$CH$_2$CH$_2$PPh$_2$) molecule and connect corresponding atoms in the four molecules in the unit cell with tie lines. Think about the relation of the intersection of these tie lines and the symmetry elements.]
tain composition. It was first thought to be "β-alumina," a polymorph of the common γ-alumina, $\text{Al}_2\text{O}_3$. Its actual composition is close to the stoichiometric $\text{Na}_2\text{Al}_2\text{O}_3$ ($= \text{Na}_2\text{O} - 1/2 \text{Al}_2\text{O}_3$), but there is always an excess of sodium, as, for example, $\text{Na}_2\text{Fe}_{11}\text{Al}_{19}\text{O}_{44}$. The structure is closely related to spinel, with 50 of the 58 atoms in the unit cell arranged in exactly the same position as in the spinel structure. In fact, sodium beta alumina may be thought of as infinite sandwiches composed of slices of spinel structure with a filling of sodium ions. It is the presence of the sodium between the spinel-like layers that provides the high conductivity of sodium beta alumina. The $\text{Al} - \text{O} - \text{Al}$ linkages between layers act like pillars in a parking garage (Fig. 7.17) and keep the layers far enough apart that the sodium ions can move readily, yielding conductivities as high as $0.030 \Omega^{-1}\text{cm}^{-1}$. There is a related structure called sodium β" alumina with the layers held farther apart and with even higher conductivities of up to $0.18 \Omega^{-1}\text{cm}^{-1}$.

There are many potential uses for solid electrolytes, but perhaps the most attractive is in batteries. Recall that a battery consists of two very reactive substances (the more so, the better), one a reducing agent and one an oxidizing agent (see Chapter 10 for a discussion of inorganic electrochemistry). To prevent them from reacting directly, these reactants must be separated by a substance that is unreactive towards both, and which is an electrolytic conductor but an electronic insulator. Generally (as in the lead storage battery, the dry cell, and the nickel alkaline battery), solutions of electrolytes in water serve the last purpose, but in most common batteries this reduces the weight efficiency of the battery at the expense of reactants. The attractiveness of solid electrolytes is that they might provide more efficient batteries.

Consider the battery in Fig. 7.18. The sodium beta alumina barrier allows sodium ions formed at the anode to flow across to the sulfur compartment, where, together with the reduction products of the sulfur, it forms a solution of sodium trisulfide in the sulfur. The latter is held at 300 °C to keep it molten. The sodium beta alumina also acts like an electronic insulator to prevent short circuits, and it is inert toward both sodium and sulfur. The reaction is reversible. At the present state of development, when compared with lead storage cells, batteries of this sort develop twice the power on a volume basis or four times the power on a weight basis.

Because some of the properties of solids that contain no ionic bonds may be conveniently compared with those of ionic solids, it is useful to include them here despite the fact that this chapter deals primarily with ionic compounds.

We may classify solids broadly into three types based on their electrical conductivity. Metals conduct electricity very well. In contrast, insulators do not. Insulators may consist of discrete small molecules, such as phosphorus trioxide, in which the energy necessary to ionize an electron from one molecule and transfer it to a second is too great to be effected under ordinary potentials. We have seen that most ionic solids are nonconductors. Finally, solids that contain infinite covalent bonding such as diamond and quartz are usually good insulators (but see Problem 7.5).

The third type of solid comprises the group known as semiconductors. These are either elements on the borderline between metals and nonmetals, such as silicon and...
4

Bonding Models in
Inorganic Chemistry:

1. Ionic Compounds

Structure and bonding lie at the heart of modern inorganic chemistry. It is not too much to say that the renaissance of inorganic chemistry following World War II was concurrent with the development of a myriad of spectroscopic methods of structure determination. Methods of rationalizing and predicting structures soon followed. In this and following chapters we shall encounter methods of explaining and predicting the bonding in a variety of compounds.

The Ionic Bond

Although there is no sharp boundary between ionic bonding and covalent bonding, it is convenient to consider each of these as a separate entity before attempting to discuss molecules and lattices, in which both are important. Furthermore, because the purely ionic bond may be described with a simple electrostatic model, it is advantageous to discuss it first. The simplicity of the electrostatic model has caused chemists to think of many solids as systems of ions. We shall see that this view needs some modification, and there are, of course, many solids, ranging from diamond to metals, which require alternative theories of bonding.

Properties of Ionic Substances

Several properties distinguish ionic compounds from covalent compounds. These may be related rather simply to the crystal structure of ionic compounds, namely, a lattice composed of positive and negative ions in such a way that the attractive forces between oppositely charged ions are maximized and the repulsive forces between ions of the same charge are minimized. Before discussing some of the possible geometries, a few simple properties of ionic compounds may be mentioned.1

1. Ionic compounds tend to have very low electrical conductivities as solids but conduct electricity quite well when melted. This conductivity is attributed to the presence of ions, atoms charged either positively or negatively, which are free to move under the influence of an electric field. In the solid, the ions are bound tightly in the lattice and are not free to migrate and carry electrical current. It should be noted that we have no absolute proof of the existence of ions in solid sodium chloride, for example, though our best evidence will be discussed later in this chapter (pages 111-113). The fact that ions are found when sodium chloride is melted or dissolved in water does not prove that they existed in the solid crystal. However, their existence in the solid is usually assumed, since the properties of these materials may readily be interpreted in terms of electrostatic attractions.

2. Ionic compounds tend to have high melting points. Ionic bonds usually are quite strong and they are omnidirectional. The second point is quite important, since ignoring it could lead one to conclude that ionic bonding was much stronger than covalent bonding—which is not the case. We shall see that substances containing strong, multidirectional covalent bonds, such as diamond, also have very high melting points. The high melting point of sodium chloride, for example, results from the strong electrostatic attractions between the sodium cations and the chloride anions, and from the lattice structure, in which each sodium ion attracts six chloride ions, each of which in turn attracts six sodium ions, etc., throughout the crystal. This relation between bonding, structure, and the physical properties of substances will be discussed at greater length in Chapter 8.

3. Ionic compounds usually are very hard but brittle substances. The hardness of ionic substances follows naturally from the argument presented above, except in this case we are relating the multivalent attractions between the ions with mechanical separation rather than separation through thermal energy. The tendency toward brittleness results from the nature of ionic bonding. If one can apply sufficient force to displace the ions slightly (e.g., the length of one-half of the unit cell in NaCl), the formerly attractive forces become repulsive as anion-anion and cation-cation contacts occur; hence the crystal flies apart. This accounts for the well-known cleavage properties of many minerals.

4. Ionic compounds are often soluble in polar solvents with high permittivities (dielectric constants). The energy of interaction of two charged particles is given by

\[ U = \frac{q^+ q^-}{4\pi \varepsilon_0 r} \]

where \( q^+ \) and \( q^- \) are the charges, \( r \) is the distance of separation, and \( \varepsilon_0 \) is the permittivity of the medium. The permittivity of a vacuum, \( \varepsilon_0 \), is 8.85 \times 10^{-12} \text{ C}^2 \text{ m}^{-1} \text{ J}^{-1}. For common polar solvents, however, the permittivity values are considerably higher. For example, the permittivity is 7.25 \times 10^{-8} \text{ C}^2 \text{ m}^{-1} \text{ J}^{-1} for water, 2.9 \times 10^{-10} \text{ C}^2 \text{ m}^{-1} \text{ J}^{-1} for acetonitrile, and 2.2 \times 10^{-19} \text{ C}^2 \text{ m}^{-1} \text{ J}^{-1} for ammonia, giving relative permittivities of 82 \( \varepsilon_0 \) (H_2O), 33 \( \varepsilon_0 \) (CH_3CN), and 25 \( \varepsilon_0 \) (NH_3). Since the permittivity of ammonia is 25 times that of a vacuum, the attraction between ions dissolved in ammonia, for example, is only 4% as great as in the absence of solvent. For solvents with higher permittivities the effect is even more pronounced.

Another way of looking at this phenomenon is to consider the interaction between the dipole moments of the polar solvent and the ions. Such solvation will provide considerable energy to offset the otherwise unfavorable energetic of breaking up the crystal lattice (see Chapter 8).

1 Some very interesting ionic compounds prove to be exceptions to these rules. They are discussed in Chapter 7.
Conductivity in Ionic Solids

Conductivity by Ion Migration

1. Vacancy mechanism. If there is a vacancy in a lattice, it may be possible for an adjacent ion of the type that is missing, normally a cation, to migrate into it, the difficulty of migration being related to the sizes of the migrating ion and the ions that surround it and tend to impede it.

2. Interstitial mechanism. As we have seen with regard to Frenkel defects, if an ion is small enough (again, usually a cation), it can occupy an interstitial site, such as a tetrahedral hole in an octahedral lattice. It may then move to other interstitial sites.

3. Interstitialcy mechanism. This mechanism is a combination of the two above. It is a concerted mechanism, with one ion moving into an interstitial site and another ion moving into the vacancy thus created. These three mechanisms are shown in Fig. 7.15.

In purely ionic compounds, the conductivity from these mechanisms is intrinsic and relates only to the entropy-driven Boltzmann distribution; the conductivity will thus increase with increase in temperature. Because the number of defects is quite limited, the conductivities are low, of the order of $10^{-6}$ $\Omega^{-1}$ cm$^{-1}$. In addition, extrinsic vacancies will be induced by ions of different charge (see page 264). There exist, however, a few ionic compounds that as solids have conductivities several orders of magnitude higher. One of the first to be studied and the one with the highest room-temperature conductivity, $0.27$ $\Omega^{-1}$ cm$^{-1}$, is rubidium silver iodide, RbAgI$_5$.

Another solid electrolyte that may lead to important practical applications is sodium beta alumina. Its unusual name comes from a misidentification and an uncer-
Occurrence of Ionic Bonding

Simple ionic compounds form only between very active metallic elements and very active nonmetals. Two important requisites are that the ionization energy to form the cation, and the electron affinity to form the anion, must be energetically favorable. This does not mean that these two reactions must be exothermic (see impossibility—see Problem 4.13), but means, rather, that they must not cost too much energy. Thus the requirements for ionic bonding are (1) the atoms of one element must be able to lose one or two (rarely three) electrons without undue energy input and (2) the atoms of the other element must be able to accept one or two electrons (almost never three) without undue energy input. This restricts ionic bonding to compounds between the most active metals: Groups IA(1), IIA(2), part of IIIA(3) and some lower oxidation states of the transition metals (forming cations), and the most active nonmetals: Groups VIIA(17), VIA(16), and nitrogen (forming anions). All covalent energies are endothermic, but for the metals named above they are not prohibitively so. For these elements, electron affinities are exothermic only for the halogens, but they are not excessively endothermic for the chalcogens and nitrogen.

Before discussing the energetics of lattice formation, it will be instructive to examine some of the most common arrangements of ions in crystals. Although only a few of the many possible arrangements are discussed, they indicate some of the possibilities available for the formation of lattices. We shall return to the subject of structure after some basic principles have been developed.

The first four structures described below contain equal numbers of cations and anions, that is, the 1:1 and 2:2 salts. Most simple ionic compounds with such formulations crystallize in one of these four structures. They differ principally in the coordination number, that is, the number of counterions grouped about a given ion, in these examples four, six, and eight.

The sodium chloride structure. Sodium chloride crystallizes in a face-centered cubic structure (Fig. 4.1a). To visualize the face-centered arrangement, consider only the sodium ions or the chloride ions this will require extensions of the sketch of the lattice. Eight sodium ions form the corners of a cube and six more are centered on the faces of the cube. The chloride ions are similarly arranged, so that the sodium chloride lattice consists of two interpenetrating face-centered cubic lattices. The coordination number (C.N.) of both ions in the sodium chloride lattice is 6, that is, there are six chloride ions about each sodium ion and six sodium ions about each chloride ion.

Sodium chloride crystallizes in the cubic space group FmOHm (see Table 3.7). That is, it is face-centered, has a three-fold axis, and has two mirror planes of different class. If there is one C3 axis, however, three others must exist, and the presence of two different mirror planes requires seven others. In fact, this compact symmetry label is enough to tell us that all elements of symmetry found in an octahedron are present. Thus, the Schoenflies equivalent of FmOHm is O3.

The sodium chloride structure is adopted by most of the alkali metal halides: All of the lithium, sodium, potassium, and rubidium halides plus cesium fluoride. It is also found in the oxides of magnesium, calcium, strontium, barium, and cadmium.

The cesium chloride structure. Cesium chloride crystallizes in the cubic arrangement shown in Fig. 4.1b. The cesium or chloride ions occupy the eight corners of the cube and the counterion occupies the center of the cube. Again,
Schottky defect (cation vacancy) induced and balanced by the presence of a higher valence cation. [Hannay, N. B. Solid State Chemistry; Prentice-Hall: Englewood Cliffs, NJ, 1967. Reproduced with permission.]

Amount of cadmium chloride, the Cd$^{2+}$ ion fits easily into the silver chloride lattice (cf. ionic radii, Table 4.4). The dipositive charge necessitates a vacancy to balance the change in charge (Fig. 7.11). Closely related is the concept of "controlled valency," in which a differently charged, stable cation is introduced into a compound of a transition metal. Because the latter has a variable oxidation state, balance is achieved by gain or loss of electrons by the transition metal. For example, consider Fig. 7.12. Stoichiometric nickel(II) oxide, like aqueous solutions containing the Ni$^{2+}$ ion, is pale green. Doping it with a little Li$_2$O causes a few of the cation sites to be occupied by Li$^+$ instead of Ni$^{2+}$. This induces a few Ni$^{2+}$ ions to lose electrons and become Ni$^{3+}$ ions, thus preserving the electrical neutrality of the crystal. The properties of the NiO change drastically: The color changes to gray-black, and the former insulator (to be expected of an ionic crystal, see Chapter 4), is now a semiconductor.

A rather similar effect can occur with the formation of nonstoichiometric compounds. For example, copper(I) sulfide may not have the exact ratio of 2:1 expected from the formula, Cu$_2$S. Some of the Cu$^+$ ions may be absent if they are compensated by an equivalent number of Cu$^{2+}$ ions. Since both Cu$^+$ and Cu$^{2+}$ ions are stable, it is possible to obtain stoichiometries ranging from the ideal to Cu$_{2-x}$S$_x$. If the "vacancy" is not a true vacancy but contains a trapped electron at that site, the imperfection is called an $F$ center. For example, if a small amount of sodium metal is doped into a sodium chloride crystal, the crystal energy causes the sodium to ionize to Na$^+$ + e$^-$ and the electron occupies a site that would otherwise be filled by a chloride ion (Fig. 7.13). The resulting trapped electron can absorb light in the visible region and the compound is colored ($F$ = Ger. Farbe, color). The material may be considered a nonstoichiometric compound, Na$_{1-x}$Cl$_x$, or as a dilute solution of "sodium electrode." If the missing ion has not been completely removed as in a Schottky defect, but only displaced to a nearby interstitial site, the result is called a Frenkel defect (Fig. 7.14). The vacancy and corresponding interstitial ion may be caused by a cation or an anion, but because the cation is generally smaller than the anion, it will usually be easier to fit a cation into an interstitial hole other than the one in which it belongs. For the same reason, although it is theoretically possible to have both interstitial cations and anions at the same time, at least one will ordinarily be energetically unfavorable because of size.

Semiconductors are discussed on pp 274-276 of this chapter.

13 See Chapter 10 for solutions of sodium chloride in liquid ammonia.

14 Where $S$ is small with respect to $I$.

we must consider a lattice composed either of the cesium ions or of the chloride ions, both of which have simple cubic symmetry. The coordination number of both ions in cesium chloride is 8; that is, there are eight anions about each cation and eight cations about each anion. The space group is \( \text{Pm}3\text{m} \). The lattice is primitive, but otherwise the symmetry elements are the same as in NaCl.

Among the alkali halides, the cesium chloride structure is found only in CCl, CsBr, and CsI at ordinary pressures, but all of the alkali halides except the salts of lithium can be forced into the CsCl structure at higher pressures. It is also adopted by the ammonium halides (except \( \text{NH}_4 \text{F} \), \( \text{TCI} \), \( \text{TIBr} \), \( \text{TCN} \), \( \text{CSNH} \), \( \text{CaCN} \), \( \text{CsSH} \), \( \text{CsSeH} \), and \( \text{CsNH}_2 \)).

The zinc bleund and wurtzite structures. Zinc sulfide crystallizes in two distinct lattices: hexagonal wurtzite (Fig. 4.2a) and cubic zinc blende (Fig. 4.2b). We shall not elaborate upon them now (see page 121), but simply note that in both the coordination number is 4 for both cations and anions. The space groups are \( \text{P6}3\text{mc} \) and \( \text{F4}3\text{m} \). Can you tell which is which?

Many divalent metal oxides and sulfides such as \( \text{BeO}, \text{ZnO}, \text{BeS}, \text{MnS}, \text{ZnS}, \text{CdS}, \) and \( \text{HgS} \) adopt the zinc blende or wurtzite structures, or occasionally both. Other compounds with these structures include \( \text{AgI}, \text{NH}_4\text{F}, \) and SiC.

All the following structures have twice as many anions as cations (1:2 structures), thus the coordination number of the cation must be twice that of the anion: 8, 6, 3, 4, 2, etc. The inverse structures are also known where the cations outnumber the anions by two to one.

The fluorite structure. Calcium fluoride crystallizes in the fluorite structure, cubic \( \text{Fm}3\text{m} \) (Fig. 4.3). The coordination numbers are 8 for the cation (eight fluoride ions form a cube about each calcium ion) and 4 for the anion (four \( \text{Ca}^{\text{2+}} \) ions tetrahedrally arranged about each \( \text{F}^{-} \) ion).

Many difluorides and dioxides are found with the fluorite structure. Examples are the fluorides of Ca, Sr, Ba, Cd, Hg, and Pb, and the dioxides of Zr, Hf, and some lanthanides and actinides. If the numbers and positions of the cations and anions are reversed, one obtains the antifluorite structure which is adopted by the oxides and the sulfides of Li, Na, K, and Rb.

The rutile structure. Titanium dioxide crystallizes in three crystal forms at atmospheric pressure: anatase, brookite, and rutile (Fig. 4.4a). Only the last (tetragonal \( \text{P}4\text{2}2\text{lmnm} \)) will be considered here. The coordination numbers are 6 for the cation (six oxide anions arranged approximately octahedrally about the titanium ions) and 3 for the anion (three titanium ions trigonally about the oxide ions). The rutile structure is also found in the dioxides of Cr, Mn, Ge, Ru, Rh, Sn, Os, Ir, Pt, and Pb.

The \( \beta \)-cristobalite structure. Silicon dioxide crystallizes in several forms (some of which are stabilized by foreign atoms). One is \( \beta \)-cristobalite (Fig. 4.4b), which is related to zinc blende (Fig. 4.2b) having a silicon atom where every zinc and sulfur atom is in zinc blende, and with oxygen atoms between the silicon atoms. Other compounds adopting the \( \beta \)-cristobalite structure are \( \text{BeF}_2, \text{ZnCl}_2, \) \( \text{SiO}_2 \) at high pressures, and \( \text{BeOH}_2 \) and \( \text{ZnOH}_2 \), although the latter are distorted by hydrogen bonding. Another form of \( \text{SiO}_2 \), tridymite, is related to the

---

*The structure of \( \beta \)-cristobalite has been determined several times over the past 60 years, but crystal disorder has led to uncertainty in the space group assignments (Hyde, B. G.; Andersson, S. Inorganic Crystal Structures; Wiley: New York, 1998; pp 395-399).
There is no simple explanation for the precise arrangement of all of the layered structures. But certainly the forces involved are complex, often subtle, and a hard-sphere ionic model will not come close to accounting for them. As Adams has pointed out:

"... ionic theory is a good starting point for getting some general guidance on the relative importance of factors such as size and coordination arrangement and is very important in energetics, but for anything beyond this we must use the concepts and language of modern valence theory and talk in terms of orbital overlap and band structure. Ionic theory is still valuable. . . . [now about three-fourths of a century]... it is still heavily overemphasized; so far as detailed considerations of crystal structure are considered it is time it was interred."

These are the words of someone devoted to the details of solid state chemistry, and they may be a bit overstated for the student merely wishing a general knowledge of inorganic solids, but they are well taken, and certainly all of the interesting subtleties of structure will be found to rise out of forces other than the electrostatics of hard spheres. We shall examine these more closely later in this chapter.

It was noted in Chapter 4 that the Madelung constant of a structure may be expressed in various ways. The way that is conceptually simplest in terms of the Born-Lande equation is the simple geometric factor, $A$, such that when combined with the true ionic charges, $Z^+$ and $Z^-$, the correct electrostatic energy is formulated. It was noted that some workers have favored using another constant, $A'$, combined with the highest common factor of $Z^+$ and $Z^-$, $Z_0$.

Further insight into the stability of predominantly ionic compounds can be gained by inspection of the reduced Madelung constant, $A^{-1}$. The reduced Madelung constant is closely related to the derivation of the Koppinski equation given earlier (Chapter 4). Templeton showed that if the lattice energy of a compound $M^+_nX^-_m$ is formulated as:

$$\hat{U}_0 = \frac{1.389 \times 10^{12} \text{ J mol}^{-1} \text{ pm}^{3} \cdot Z^+Z^-A'(m+1)}{2x}$$  \hspace{1cm} (7.2)

then all Madelung constants reduce to a value of about 1.7 (Table 7.1). The usefulness of this viewpoint is that it indicates that despite the wide variety of ionic sizes, compound formulations, and structures, there is basically an upper limit to lattice energy set by the constraints of geometry; inefficient structures may be somewhat below it (though not far); there will always be an alternative structure near the limit; and even efficient structures may never rise above it.

Table 7.1: A comparison of Madelung constants

<table>
<thead>
<tr>
<th>Compound</th>
<th>Geometric factor, $A$</th>
<th>Conventional factor, $A'$</th>
<th>Reduced factor, $A^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlCl$_3$</td>
<td>4.172</td>
<td>25.031</td>
<td>1.68</td>
</tr>
<tr>
<td>CaF$_2$</td>
<td>2.519</td>
<td>5.039</td>
<td>1.68</td>
</tr>
<tr>
<td>CdCl$_2$</td>
<td>2.264</td>
<td>4.499</td>
<td>1.50</td>
</tr>
<tr>
<td>CdF$_2$</td>
<td>2.192</td>
<td>4.383</td>
<td>1.46</td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>1.763</td>
<td>1.753</td>
<td>1.76</td>
</tr>
<tr>
<td>NaCl</td>
<td>1.748</td>
<td>1.748</td>
<td>1.75</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>2.288</td>
<td>4.597</td>
<td>1.47</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>2.408</td>
<td>4.816</td>
<td>1.60</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>1.641</td>
<td>1.641</td>
<td>1.64</td>
</tr>
<tr>
<td>ZnO</td>
<td>1.638</td>
<td>1.638</td>
<td>1.64</td>
</tr>
</tbody>
</table>

* Exact values depend upon details of structure.
* Cristobalite.
* Rutile.
* Wurtzite.
* Zinc Blende.

Imperfections in Crystals

To this point the discussion of crystals has implicitly assumed that the crystals were perfect. Obviously, a perfect crystal will maximize the cation-anion interactions and minimize the cation-cation and anion-anion repulsions, and this is the source of the very strong driving force that causes gaseous sodium chloride, for example, to condense to the solid phase. In understanding this condensation, however, it suffers a loss of entropy from the random gas to the highly ordered solid. This entropy-entropy antagonism is largely resolved in favor of the enthalpy because of the tremendous crystal energies involved, but the entropy factor will always result in equilibrium defects at all temperatures above absolute zero.

The simplest type of defect is called the Schottky or Schottky-Wagner defect. It is simply the absence of an atom or ion from a lattice site. An ionic crystal, electrical neutrality requires that the missing charge be balanced in some way. The simplest way is for the missing cation, for example, to be balanced by another Schottky defect, a missing anion, elsewhere (Fig. 7.10).

Alternatively, the missing ion can be balanced by the presence of an impurity ion of higher charge. For example, if a crystal of silver chloride is "doped" with a small...
Fig. 4.4 Crystal structures of two more 1:2 compounds; oxygen is the larger circle in both:
(a) unit cell of rutile, TiO₂, tetragonal, space group P4₃/mmm; (b) unit cell of β-cristobalite.

wurtzite structure in the same way that β-cristobalite is related to zinc blende. The coordination numbers in β-cristobalite and tridymite are 4 for silicon and 2 for oxygen.

The calcite and aragonite structures. Almost all of the discussion in this chapter is of compounds containing simple cations and anions. Nevertheless, most of the principles developed here are applicable to crystals containing polyatomic cations or anions, though often the situation is more complicated. Examples of two structures containing the carbonate ion, CO₃²⁻, are calcite (Fig. 4.5a) and aragonite (Fig. 4.5b). Both are calcium carbonate. In addition MgCO₃, FeCO₃, LiNO₃, NaNO₃, LaB₂O₄, and YB₂O₃ have the calcite structure (rhombohedral R₃₃). The coordination number of the metal ion is 6. Larger metal ions adopt the aragonite structure (orthorhombic Pcmn) with nine oxygen atoms about the metal ion. Examples are, in addition to calcium carbonate, SrCO₃, KNO₃, and LaBO₃.

Fig. 4.5 Crystal structures of two forms of calcium carbonate: (a) unit cell of calcite, rhombohedral, space group R₃₃; (b) unit cell of aragonite, orthorhombic, space group Pcmn. Circles in decreasing order of size are oxygen, calcium, and carbon. [From Ladd, M. F. C. Structure and Bonding in Solid State Chemistry, Wiley: New York, 1979. Reproduced with permission.]

Lattice Energy

The energy of the crystal lattice of an ionic compound is the energy released when ions come together from infinite separation to form a crystal:

\[
M^+ + X^- \rightarrow MX \quad (4.2)
\]

It may be treated adequately by a simple electrostatic model. Although we shall include non-electrostatic energies, such as the repulsions of closed shells, and more sophisticated treatments include such factors as dispersion forces and zero-point energy, simple electrostatics accounts for about 90% of the bonding energies. The theoretical treatment of the ionic lattice energy was initiated by Born and Landé, and a simple equation for predicting lattice energies bears their names. The derivation follows.
Layered Structures

should expect for a complex such as \([\text{RhF}_6]^{7-}\). Bridging halide ions are well known in coordination compounds. Furthermore, according to Fajans' rules, we should be suspicious of an ionic structure containing a cation with a +5 charge.

Sanderson\(^8\) went so far as to say that even crystals such as alkali halides should be considered as infinite coordination polymers with each cation surrounded by an octahedral coordination sphere of six halide ions, which in turn bridge to five more alkali metal atoms. Although this point of view is probably of considerable use when discussing transition metal compounds, most chemists would not extend it to all ionic lattices.

This brings us to a class of compounds too often overlooked in the discussion of simple ionic compounds: the transition metal halides. In general, these compounds (except fluorides) crystallize in structures that are hard to reconcile with the structures of simple ionic compounds seen previously (Figs. 4.1-4.3). For example, consider the cadmium iodide structure (Fig. 7.8). It is true that the cadmium atoms occupy octahedral holes in a hexagonal closest packed structure of iodine atoms, but in a definite layered structure that can be described accurately only in terms of covalent bonding and infinite layer molecules.

Layered structures form in some ways, an awkward bridge between simple compounds with a high degree of ionicity (for which NaCl seems always to be the prototype), less ionic compounds with considerable covalency but similar structure (both AgCl and AgBr have the NaCl structure), and solids such as HgCl and AlF\(_3\) wherein the presence of discrete molecules seems apparent. A schematic illustrating the relationships among some of these structures in terms of size and electronic structure might look like this:

![Schematic illustration](image)

In the CdI\(_2\) structure, octahedral sites between every other pair of ccp layers of iodine atoms are occupied by cadmium atoms; CdCl\(_2\) has cadmium in octahedral sites between ccp layers. Actually, matters can get much more complicated than that. There are three different CdI\(_2\) structures with varied layers. To indicate the potential complexity without going into the details of the several possibilities, the structure of one form of CdBrI will be mentioned: It has a twelve-layer repeating unit of halide ions, ABCBCABABCAC, surely long-range order of a fairly high degree.

We have seen (Problem 4.1) that the change in stoichiometry from CsCl to CaF\(_2\) can be accommodated readily in the simple cubic system by merely "omitting" every other metal ion; the resulting fluorite structure is highly symmetrical and quite stable. This is not the case when covalency becomes important. Fig. 7.9 illustrates this well: Although the CdCl\(_2\) structure can be readily related to the NaCl structure, the omission of alternate cations is not such as to leave a structure with the same high symmetry. The 3-D cubic symmetry has been transformed into a 2-D layer symmetry.

---

Consider the energy of an ion pair, \( M^+ \), \( X^- \), separated by a distance \( r \). The electrostatic energy of attraction is obtained from Coulomb’s law:

\[
E_C = \frac{Z^+ Z^- e^2}{4\pi\varepsilon_0 r}
\]

Since one of the charges is negative, the energy is negative (with respect to the energy at infinite separation) and becomes increasingly so as the interionic distance decreases. Figure 4.6 shows the coulombic energy of an ion pair (dotted line). Because it is common to express \( Z^+ \) and \( Z^- \) as multiples of the electronic charge, \( e = 1.6 \times 10^{-19} \) coulomb, we may write:

\[
E_C = \frac{Z^+ Z^- e^2}{4\pi\varepsilon_0 r}
\]

Now in the crystal lattice there will be more interactions than the simple one in an ion pair. In the sodium chloride lattice, for example, there are attractions to the six nearest neighbors of opposite charge, repulsions by the twelve next nearest neighbors of like charge, etc. The summation of all of these geometrical interactions is known as the Madelung constant, \( A \). The energy of a pair of ions in the crystal is then:

\[
E_C = \frac{A Z^+ Z^- e^2}{4\pi\varepsilon_0 r}
\]

The evaluation of the Madelung constant for a particular lattice is straightforward. Consider the sodium ion (\( \oplus \)) at the center of the cube in Fig. 4.7. Its nearest neighbors are the six face-centered chloride ions (\( \bullet \)), each at a characteristic distance determined by the size of the ions involved. The next nearest neighbors are the twelve sodium ions (\( \bigcirc \)) centered on the edges of that unit cell (cf. Fig. 4.4a inverted). The distance of these repelling ions can be related to the first distance by simple geometry, as can the distance of eight chloride ions in the next shell (those at the corners of the cube). If this process is followed until every ion in the crystal is included, the

\[\text{Madelung constant, } A, \text{ may be obtained from the summation of all interactions. The first three terms for the interactions described above are:}\]

\[
A = 6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} \ldots
\]

Fortunately, the Madelung constant may be obtained mathematically from a converging series, and there are computer programs that converge rapidly. However, we need not delve into these procedures, but may simply employ the values obtained by other workers (Table 4.1). The value of the Madelung constant is determined

\begin{table}[h]
\centering
\caption{Madelung constants of some common crystal lattices}
\begin{tabular}{|l|c|c|c|}
\hline
Structure & Coordination number & Geometrical factor, \( A \) & Conventional factor, \( A^* \) \\
\hline
Sodium chloride & 6:6 & 1.74756 & 1.74756 \\
Cesium chloride & 8:8 & 1.78267 & 1.78267 \\
Zinc blende & 4:4 & 1.63006 & 1.63006 \\
Wurtzite & 4:4 & 1.64432 & 1.64432 \\
Fluorite & 8:4 & 2.1939 & 5.03878 \\
Rutile & 6:3 & 2.498 & 4.816 \\
\( \beta \)-Cristobalite & 4:2 & 2.291 & 4.587 \\
Corundum & 6:4 & 4.1719 & 25.0312 \\
\hline
\end{tabular}
\end{table}

* Use \( Z^+ = \text{highest common factor}. \\
* Exact values depend upon details of structure.
In the usual discussion of Fajans’ rules as given in Chapter 4, emphasis is placed on physical properties such as melting points, solubility, etc. The possible effects of covalency on structure were also mentioned with regard to the fact that sp³ bonding in HgS could favor the tetrahedral zinc sulfide structure (Chapter 4). Therefore in moving from an empirical structure field map to a semiempirical model (or semi-theoretical, depending upon the viewpoint), we may take other factors into account. For example, we have previously seen that covalent character might be expected to cause a switch from coordination number 6 to coordination number 4. Therefore, we might attempt to bring in covalent corrections to improve a purely mechanical or radius ratio approach. There are two factors that increase covalency: (1) Small differences in electronegativity produce highly covalent bonds; (2) other things being equal, smaller atoms form stronger covalent bonds than larger atoms (see Chapter 9).

To incorporate these two variables, Pearson⁵ has plotted the principal quantum number, \( n \) (a rough indicator of size), versus a function of electronegativity difference (\( \Delta \chi \)) and radius ratio, \( r_+/r_- \), and has shown that compounds with coordination number 4 segregate quite well from those with coordination number 6.

More recently, Shankar and Parr⁴ have designed structure stability diagrams in which the compounds are plotted according to electronegativity and hardness (Fig. 7.6). When the data are presented in this way, the compounds segregate quite well by structure and coordination number. The slope of any line passing through the origin is given by:

\[
m = \frac{a_m - a_h}{b_m + b_h}
\]

(7.1)

This is the simplest expression for charge (ionicity) in the Mulliken-Jaffe system with electronegativity equalization (see Eq. 5.85). The boundary lines in Fig. 7.6 radiate more or less from the origin with the slope of \( m \) from Eq. 7.1. We may thus infer that each represents a line of constant ionicity that is responsible for the changeover from one structure type to the next.

Other workers have developed the ideas presented here to increased levels of understanding. However, often increased precision is purchased at the expense of simplicity.

Because coordination compounds are usually considered to be covalently bonded, to a first approximation (see Chapter 11), extended complex structures in the solid can readily be related to them. Consider, for example, rhodium pentafluoride. Obviously, it could be considered as an ionic structure, \( \text{Rh}^{5+}F_{-5}^- \), and indeed the crystal structure consists, in part, of \( \text{RhF}_5 \) complexes with rhodium in octahedral holes. However, closer inspection of the structure reveals that it consists of tetrameric units, \( \text{Rh}_4\text{F}_{22}^- \) that are distinct from one another (Fig. 7.7). The environment about each rhodium atom, an octahedron of six fluorine atoms, is what we

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5 Hardness is a property of an atom or ion approximately inversely proportional to its polarizability. It is useful in solid-state discussions. See Chapter 9.
6 For discussions of the prediction of the structures of solids, starting with the material presented here and going far beyond, see Bardell, J. K. In Structure and Bonding in Crystals; O’Keeffe, M.; Navrotsky, A., Eds.; Academic: New York, 1981; Vol. 1, Chapter 11; Adv. Chem. Phys. 1982, 40, 47.
only by the geometry of the lattice and is independent of ionic radius and charge. Unfortunately, previous workers have often incorporated ionic charge into the value which they used for the Madelung constant. The practice appears to have arisen from a desire to consider the energy of a "molecule" such as $MX_2$:

$$E = -\frac{A Z^+ Z^- e^4}{4\pi\varepsilon_0 r^3}$$  \hspace{1cm} (4.7)

where $A = 2.4$ and $Z^+$ is the highest common factor of $Z^+$ and $Z^-$ (1 for NaCl, CaF$_2$, and Al$_2$O$_3$; 2 for MgO, TiO$_2$, and ReO$_3$, etc.). We could ignore this confusing practice and use the geometric Madelung constant, $A$, only, except that values reported in the literature are almost invariably given in terms of Eq. 4.7. Values for both $A$ and $\frac{A}{A}$ are given in Table 4.1, and the reader may readily confirm that use of either Eq. 4.5 or 4.7 yields identical results.

Returning to Eq. 4.5 we see that unless there is a repulsion energy to balance the attractive coulombic energy, no stable lattice can result. The attractive energy becomes infinite at infinitesimally small distances. Ions are, of course, not point charges but consist of electron clouds which repel each other at very close distances. This repulsion is shown by the dashed line in Fig. 4.6. It is negligible at large distances but increases very rapidly as the ions approach each other closely.

Born suggested that this repulsive energy could be expressed by

$$E_R = \frac{B}{r^9}$$  \hspace{1cm} (4.8)

where $B$ is a constant. Experimentally, information on the Born exponent, $n$, may be obtained from compressibility data, because the latter measure the resistance which the ions exhibit when forced to approach each other more closely. The total energy for a mole of the crystal lattice containing an Avogadro's number, $N$, of units is

$$U = E_a + E_F = \frac{A N Z^+ Z^- e^4}{4\pi\varepsilon_0} + \frac{N B}{r}$$  \hspace{1cm} (4.9)

The total lattice energy is shown by the solid line in Fig. 4.6. The minimum in the curve, corresponding to the equilibrium situation, may be found readily:

$$\frac{dU}{dr} = 0 = -\frac{A N Z^+ Z^- e^2}{4\pi\varepsilon_0 r^{10}} - \frac{n N B}{r^{10}}$$  \hspace{1cm} (4.10)

Physically this corresponds to equating the force of electrostatic attraction with the repulsive forces between the ions. It is now possible to evaluate the constant $B$ and remove it from Eq. 4.9. Since we have fixed the energy at the minimum, we shall use

$$U_0$$ and $r_0$ to represent this energy and the equilibrium distance. From Eq. 4.10:

$$B = \frac{A N Z^+ Z^- e^2}{4\pi\varepsilon_0 n^2}$$  \hspace{1cm} (4.11)

$$U_0 = \frac{A Z^+ Z^- e^2}{4\pi\varepsilon_0} + \frac{A N Z^+ Z^- e^2}{4\pi\varepsilon_0 n^2}$$  \hspace{1cm} (4.12)

$$U_0 = \frac{A N Z^+ Z^- e^2}{4\pi\varepsilon_0} \left(1 - \frac{1}{n^2}\right)$$  \hspace{1cm} (4.13)

This is the Born-Lande equation for the lattice energy of an ionic compound. As we shall see, it is quite successful in predicting accurate values, although it omits certain energy factors to be discussed below. It requires only a knowledge of the crystal structure (in order to choose the correct value for $A$) and the interionic distance, $r_0$, both of which are readily available from X-ray diffraction studies.

The Born exponent depends upon the type of ion involved, with larger ions having relatively higher electron densities and hence larger values of $n$. For most calculations the generalized values suggested by Pauling (see Table 4.2) are sufficiently accurate for ions with the electron configurations shown.

The use of Eq. 4.13 to predict the lattice energy of an ionic compound may be illustrated as follows. For sodium chloride the various factors are

- $A = 1.74756$ (Table 4.1)
- $N = 6.022 \times 10^{23}$ ion pairs mol$^{-1}$, Avogadro’s number
- $Z^+ = +1$, the charge of the Na$^+$ ion
- $Z^- = -1$, the charge of the Cl$^-$ ion
- $e = 1.60218 \times 10^{-19}$ C, the charge on the electron (Appendix B)
- $\pi = 3.14159$
- $s_0 = 8.854188 \times 10^{-12}$ C$^2$ J$^{-1}$ m$^{-1}$ (Appendix B)
- $r_0 = 2.814 \times 10^{-10}$ m, the experimental value. If this is not available, it may be estimated as $2.83 \times 10^{-10}$ m, the sum of radii of Na$^+$ and Cl$^-$ (Table 4.4).
- $n = 8$, the average of the values for Na$^+$ and Cl$^-$ (Table 4.2).

Performing the arithmetic, we obtain $U_0 = -755$ kJ mol$^{-1}$, which may be compared with the best experimental value (Table 4.3) of $-770$ kJ mol$^{-1}$. We may feel confident in the Born-Lande equation where we have no experimental values.

As long as we do not neglect to understand each of the factors in the Born-Lande equation (4.13), we can simplify the calculations. It should be realized that only the variables in the Born-Lande equation are the charges on the ions, the interatomic distance, the Madelung constant, and the value of $n$. Equation 4.13 may thus be simplified with no loss of accuracy by grouping the constants to give:

---

but three spinels—sodium molybdate, sodium tungstate, and silver molybdate—fall well outside their field.

Once we have established the fields shown in Fig. 7.4, we can use the map as follows: If we discover a new mineral with $r_A = 90$ pm and $r_B = 30$ pm, we should expect it to have the same structure as the mineral olivine, $(Mg,Fe)_2SiO_4$, but we should not be too surprised if it turned out to be isomorphous with hibernite, $Na_2SiO_4$.

A second structure field map is shown in Fig. 7.5. This is a much more ambitious and generalized undertaking, since the oxidation states for species $A$ range from $+1$ to $+4$ and for $B$ from $+2$ to $+6$, with $X = O$ or $F$. By combining such a large number of compounds and somewhat oversimplifying the resultant diagram, we lose some accuracy in predictability, but we gain in the knowledge that a large and diverse set of compounds can be understood in terms of such simple parameters as relative sizes.

It may be noted in passing that although by far the largest amount of work on crystal structures has been done in terms of the ordering of cations in a closest packed structure of anions, this is not the only viewpoint. As is often the case in inorganic chemistry, it is usually possible and often profitable to turn the model around 180°, so to speak. Thus interesting insights can be gained by considering the alternative—placing the emphasis on the arrangements of cations.

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**Fig. 7.3** Structure of an olivine, Mg$_2$SiO$_4$, portrayed three ways. Left: Discrete SiO$_4$ tetrahedra and Mg$^{2+}$ ions. Center: Network of Mg—O illustrating the extended structure. The Si atoms have been omitted for clarity. Right: Mg$^{2+}$ ions in a hep array of oxide ions. The Si atoms have been omitted. Can you find the tetrahedral holes that they occupy? [Modified from Wells, A. F. Structural Inorganic Chemistry, 5th ed.; Clarendon: Oxford, 1984. Reproduced with permission.]

**Fig. 7.4** Structure field map for $A_2B_2O_4$ compounds as a function of cation size. Note that only the more common structures are plotted. Each point on this plot represents at least one compound having the indicated structure and size of cations $A(r_A)$ and $B(r_B)$. [From Muller, O.; Roy, R. The Major Ternary Structural Families; Springer-Verlag: New York, 1974. Reproduced with permission.]

**Fig. 7.5** Composite structure field map for $ABX_4$ structures, $X = F$ or $O$. [From Muller, O.; Roy, R. The Major Ternary Structural Families; Springer-Verlag: New York, 1974. Reproduced with permission.]
The Born—Haber Cycle

The Born—Haber cycle is a thermodynamic cycle that allows the calculation of various properties of solids, such as lattice energies and enthalpies of atomization. It is based on the principle of Hess's law, which states that the enthalpy change for a reaction is independent of the pathway taken. The cycle involves the following steps:

1. The dissociation of the elements into their constituent atoms, each in its ground electronic state, to form the gaseous monatomic ions.
2. The formation of the gaseous diatomic molecules from the monatomic ions.
3. The formation of the ionic solid from the gaseous diatomic molecules.
4. The sublimation of the solid to form the gaseous diatomic molecules.
5. The dissociation of the gaseous diatomic molecules into their constituent monatomic ions.

The enthalpy change for each step can be written as:

$$\Delta H_{\text{dissociation}} + \Delta H_{\text{formation}} + \Delta H_{\text{sublimation}} = \Delta H_{\text{atom}} + \Delta H_{\text{ion}} + \Delta H_{\text{gas}}$$

Where

- $\Delta H_{\text{dissociation}}$ is the enthalpy of atomization of the solid.
- $\Delta H_{\text{formation}}$ is the enthalpy of formation of the solid.
- $\Delta H_{\text{sublimation}}$ is the enthalpy of sublimation.
- $\Delta H_{\text{atom}}$ is the enthalpy of atomization of the elements.
- $\Delta H_{\text{ion}}$ is the enthalpy of ionization of the elements.
- $\Delta H_{\text{gas}}$ is the enthalpy of the gaseous diatomic molecules.

The Born—Haber cycle is depicted as a series of summation and separation steps in Fig. 4.8.

Uses of Born—Haber-Type Calculations

The Born—Haber cycle can be used to calculate various properties of solids, such as lattice energies, enthalpies of atomization, and ionization energies. These calculations are important in understanding the electronic and chemical bonding in solids, as well as in predicting the stability and reactivity of various compounds.
Fig. 7.2 Geometric relationships and interconversions (1-16) among various molecules and lattices (a-i): A "real" sulfur hexafluoride molecule (a) is transformed (1) into a space-filling model (b), which is transformed (2) into a "stick-and-ball" model (c) of SF₆. The SF₆ molecule is symmetrically identical (3) to the hypothetical [NaC¹°I₅]⁻ ion (d), which is a portion (4) of the NaCl lattice (e), which may be depicted (5) by the unit cell of NaCl shown as a "see through" lattice (f), or depicted (6) as a space-filling model (g). The unit cell (f,g) may also be depicted (6') with fractional atoms to show the actual number of atoms per unit cell (h). The unit cell (7) is part of the extended lattice (i). Removal of the chloride ion nearest the viewer (8) reveals an underlying triangular set of three sodium ions lying on top of a triangular set of six chloride ions (j). Removal of these three sodium ions and six chloride ions (9) reveals a triangle of ten sodium ions lying on top of a triangle of fifteen chloride ions (k). The fifteen chloride ions form (10) a closest packed array of ions (l). Compare (k) with Figs. 4.12 and 4.14. Taking (11) a portion (m) of the previous array provides (12) a tetrahedral hole (n) or (13) an octahedral hole (o) depending upon the covering atoms. Adding a second closest packed layer of three ions forms (13) an octahedral hole. There is a C₃ axis perpendicular to the plane of the paper (marked A). Addition (14) of geometric lines shows the octahedral symmetry (p), and the structure may be converted (15) into an octahedron (q) as in SF₆ which is identical to the stick-and-ball octahedral model (c) seen previously. Likewise the formation of a tetrahedral hole can be shown (12) by addition of one atom on top to give a tetrahedral space-filling model (n) which, in turn may be converted (16) to a "real" molecule of electron clouds (r).
Most of the enthalpies associated with steps in the cycle can be estimated, to a greater or less accuracy, by experimental methods. The lattice energy, however, is almost always obtained theoretically rather than from experimental measurement. It might be supposed that the "enthalpy of dissociation" of a lattice could be measured in the same way as the enthalpy of atomization of a metal or nonmetal, that is, by heating the crystal and determining how much energy is necessary to dissociate it into ions. Unfortunately, this is experimentally very difficult. When a crystal sublimes we can use the cycle to help obtain information on any other step in the cycle for this reason it is necessary to use Eq. 4.13 or some more accurate version of it. We might be supposed that the "enthalpy of dissociation" of a lattice could be measured into ions. Unfortunately, this is experimentally very difficult. When a crystal sublimes we can use the cycle to help obtain information on any other step in the cycle for this reason it is necessary to use Eq. 4.13 or some more accurate version of it. We can then use the Born-Haber cycle to check the accuracy of our predictions if we can obtain accurate data on every other step in the cycle. Values computed from the Born-Haber cycle are compared with those predicted by Eq. 4.13 and its modifications in Table 4.3.

Once we have convinced ourselves that we are justified in using theoretical values for \( \Delta U_i \), we can use the cycle to help obtain information on any other step in the cycle which is experimentally difficult to measure. For many years electron affinities were obtained almost exclusively by this method since accurate estimates were difficult to obtain by direct experiment.

Finally, it is possible to predict the heats of formation of a new and previously unknown compound. Reasonably good estimates of enthalpies of atomization, ionization energies, and electron affinities are now available for most elements. It is then necessary to make some good guesses as to the most probable lattice structure, including interatomic distances and geometry. The interatomic distance can be estimated with the aid of tables of ionic radii. Sometimes it is also possible to predict the geometry (in order to know the correct Madelung constant) from a knowledge of the bond radii. For example, consider the hypothetical sodium dichloride, NaCl2+. Because of the +2 charge on the sodium ion, we might expect the lattice energy to be considerably larger than that of NaCl, adding to the stability of the compound. But if all the terms are evaluated, it is found that the increased energy necessary to ionize sodium to Na2+ is more than that which is returned by the increased lattice energy. We can make a very rough calculation assuming that the interatomic distance in NaCl2 is the same as in NaCl166 and that

Table 4.3

<table>
<thead>
<tr>
<th>Salt</th>
<th>Experimental (Born-Haber cycle)</th>
<th>Simple model (Eq. 4.13)</th>
<th>&quot;Best values&quot;*</th>
<th>Kapustinskii approximation†</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>1034</td>
<td>1008</td>
<td>1033</td>
<td>927.7</td>
</tr>
<tr>
<td>LiCl</td>
<td>840.1</td>
<td>811.3</td>
<td>845.2</td>
<td>807.7</td>
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<td>LiF</td>
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<td>766.1</td>
<td>797.9</td>
<td>792.9</td>
</tr>
<tr>
<td>LiCl</td>
<td>718.4</td>
<td>708.4</td>
<td>739.3</td>
<td>713.0</td>
</tr>
<tr>
<td>NaF</td>
<td>914.2</td>
<td>902.0</td>
<td>915.0</td>
<td>884.9</td>
</tr>
<tr>
<td>NaCl</td>
<td>770.3</td>
<td>755.2</td>
<td>777.8</td>
<td>752.9</td>
</tr>
<tr>
<td>NaBr</td>
<td>728.4</td>
<td>718.8</td>
<td>739.3</td>
<td>713.4</td>
</tr>
<tr>
<td>NaI</td>
<td>680.7</td>
<td>663.2</td>
<td>692.0</td>
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</tr>
<tr>
<td>KF</td>
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<td>797.5</td>
<td>813.4</td>
<td>788.7</td>
</tr>
<tr>
<td>KCl</td>
<td>701.2</td>
<td>676.5</td>
<td>708.8</td>
<td>680.7</td>
</tr>
<tr>
<td>KBr</td>
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<td>659.8</td>
<td>679.5</td>
<td>674.9</td>
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<td>640.2</td>
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<td>777.8</td>
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<td>661.5</td>
<td>685.2</td>
<td>661.9</td>
</tr>
<tr>
<td>RbBr</td>
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<td>636.4</td>
<td>659.0</td>
<td>626.3</td>
</tr>
<tr>
<td>RbI</td>
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<td>622.2</td>
<td>589.9</td>
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<tr>
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<td>742.0</td>
<td>774.7</td>
<td>713.0</td>
</tr>
<tr>
<td>CsCl</td>
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<td>672.6</td>
<td>693.3</td>
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</tr>
<tr>
<td>CsBr</td>
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<td>599.6</td>
<td>632.2</td>
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</tr>
<tr>
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<td>568.2</td>
<td>601.2</td>
<td>563.6</td>
</tr>
</tbody>
</table>

* Calculated using a modified Born equation with corrections for polarization effects, repulsion between nearest and next nearest neighbors, and zero-point energy (Kapustinskii, D. J. Chem. Phys. 1955, 21, 1646-1651; ibid., 1961, 39, 2189).
† See Eq. 4.20.

A/B models in Inorganic Chemistry: 1. Ionic Compounds
Chapter 7

The Solid State

In previous chapters we have seen how simple bonding models (the electrostatic one for ionic compounds, various theories of covalent bonding, partial ionic and covalent character, etc.) can be applied to the chemical and physical properties of compounds of interest to the inorganic chemist. Of course, there are other important factors such as dipole moments and van der Waals forces that influence these properties, and we shall encounter them later. In this chapter we shall examine examples of the solids held together by ionic or covalent bonds or mixtures of the two. Crystals held together by predominantly ionic forces (e.g., magnesium oxide, which has the NaCl structure, see Fig. 4.1) and those held together by purely covalent forces (e.g., diamond, see Fig. 7.1) are surprisingly similar in their physical properties. Both types of crystals are mechanically strong and hard, are insulators, and have very high melting points (MgO = 2852 °C, diamond = 3550 °C). Neither type is soluble in most solvents. The conspicuous difference between the two types of crystals is that there are a few solvents of high permittivity that will dissolve some ionic compounds (water is most notable, but see Chapter 10). The second difference is that these solutions as well as the molten ionic compounds conduct electricity, but that is not a property of the solid itself.

The Structures of Complex Solids

Chapter 4 considered the topic of simple ionic compounds such as NaCl, CsCl, CaF$_2$, etc., as well as the concepts of tetrahedral and octahedral holes in closest packed lattices, the idea of efficiency in packing, and the radius ratio rule. Chapters 5 and 6 discussed covalent bonding and the structure of molecules. These ideas are summarized and illustrated in Fig. 7.2 (carefully correlate the parts and processes in the figure and legend). In addition, the drawings in this figure should be of help in visualizing various structures by showing the different methods used by chemists to depict atoms and ions.

Given the difficulties and exceptions that we have seen with the radius ratio rule, we might despair that any predictive power was available to the inorganic chemist studying complex crystal structures. If simple M$^+$$X^-$ compounds violate the radius ratio rules as often as they do (see Fig. 4.18), how is the geochemist to deal in a rational way with the structures of minerals like olivine (Mg$_2$SiO$_4$), spinel (MgAl$_2$O$_4$), and other silicates and aluminosilicates containing a variety of metal ions? These minerals form most of the earth's crust and mantle (see Chapter 16). In addition to being important minerals, some of these compounds are important in the laboratory as well. The class of compounds called spinels played an important early role in the development of crystal field theory (see Chapter 11). The current interest of interest in high-temperature superconductors centers on mixed metal oxides with structures similar to the mineral perovskite (see page 285).

There are various ways of looking at structures of this sort. One may formulate them as silicate anions with isolated tetrahedra or linked into rings, chains, sheets, etc. This viewpoint will be pursued further in Chapter 16. Alternatively, one can view them as closest packed structures, in the case of olivine as Si$^{4+}$ ions occupying tetrahedral holes and Mg$^{2+}$ ions (or Fe$^{2+}$ ions by isomorphous replacement) in octahedral holes in a hexagonal closest packed array of oxide ions (Fig. 7.3). But considering the difficulties encountered with the radius ratio approach, one may well ask: "Is it possible to make accurate predictions?" Fortunately, the answer is "Yes."

The chief difficulty with the radius ratio approach is that it is based purely on geometric considerations, not chemical ones. If we include chemical factors, such as partial covalency, our predictive power is considerably enhanced. There are several approaches to the problem, but only two will be mentioned here. The simplest is a purely empirical approach, and like so many methods in inorganic chemistry its strength lies in its experimental basis: Possible unknown errors and hidden factors are built into and accommodated by it. One takes a list of known structures of a given general formula, say A$_2$BO$_4$ (where A is a metal and B is a higher valent metal or nonmetal). The radii of A and B are plotted against each other along two coordinate axes. This is the graphical equivalent of looking at arithmetic radius ratios. In the resultant structure field map (Fig. 7.4) it is found that similar structures cluster together. The olivines cluster around 90 pm for A ($r_{A^{2+}} = 86$ pm, $r_{B^{2+}} = 92$ pm) and 40 pm for B ($r_{B^{2+}} = 40$ pm). In contrast, the spinels cluster around $r_{A^{2+}} = 60-90$ pm ($r_{A^{2+}} = 68$ pm).

A structure field map is remarkably accurate. That exceptions do occur, usually on the borders of the fields, should not be surprising. Serious errors are relatively rare,
it would crystallize in the fluorite structure with a Madelung constant of $A = 2.52$. The lattice energy is then $U_{L} = -2180$ kJ mol$^{-1}$. The summation of Born-Haber terms is

$U_{L} = -2180$
$\Delta H_{\text{IK}} = +108$
$\Delta H_{\text{IE}} = +496$
$\Delta H_{\text{EA}} = +4562$
$\Delta H_{\text{zc}} = +342$
$\Delta H_{f} = -2550$ kJ mol$^{-1}$

Although the estimation of $U_{L}$ by our crude approximation may be off by 10–20%, it cannot be in error by over 100%, or 2500 kJ mol$^{-1}$. Hence we can see why NaCl does not exist. The extra stabilization of the lattice is insufficient to compensate for it cannot be in error by over 100%, or 2500 kJ mol$^{-1}$. Hence we can see why NaCl does not exist. The extra stabilization of the lattice is insufficient to compensate for the very large second ionization energy.

A slightly different problem arises when we consider the lower oxidation states of metals. We know that CaF$_2$ is stable. Why not CaF as well? Assuming that CaF would crystallize in the same geometry as KF and that the internuclear distance would be about the same, we can calculate a lattice energy for CaF, $U_{L} = -795$ kJ mol$^{-1}$. The terms in the Born-Haber cycle are

$U_{L} = -795$
$\Delta H_{\text{IK}} = +176$
$\Delta H_{\text{IE}} = +590$
$\Delta H_{\text{EA}} = +328$
$\Delta H_{\text{zc}} = +79$
$\Delta H_{f} = -276$ kJ mol$^{-1}$

An enthalpy of formation of $-276$ kJ mol$^{-1}$, though not large, is perfectly acceptable because it is about the same as that of LiI, for example. Why does CaF not exist? Because if we were able to prepare it, it would spontaneously disproportionate into CaF$_2$ and Ca exothermically.$^{15}$

$$2\text{CaF} \rightarrow \text{CaF}_2 + \text{Ca} \quad (4.18)$$

An examination of the ionic compounds of the main group elements would show that all of the ions present have electronic configurations that are isoelectronic with noble gases, hence the supposed "stability of noble gas configurations". But what type of stability? It is true that the halogens are from 295 to 350 kJ mol$^{-1}$ lower in energy as halide ions than as free atoms. But the formation of the F$^-$, S$^{2-}$, N$^-$, Li$^+$, Na$^+$, Mg$^{2+}$, and Ca$^{2+}$ ions is endothermic by 250 to 2200 kJ mol$^{-1}$. Even though these ions possess noble gas configurations, they represent higher energy states than the free atoms. The "stability" of noble gas configurations is meaningless unless one considers the stabilization of the ionic lattice. For the main group elements the noble gas configuration is that which maximizes the gain from high charges (and large lattice energies) while holding the cost (in terms of ionization potential-electron affinity energies) as low as possible. This is shown graphically in Fig. 4.9. Although the second ionization energy for a metal is always larger than the first, and the third larger than the second, the increase is moderate except when a noble gas configuration is broken. Then the ionization energy increases markedly because the electron is being removed from the $n - 1$ shell. Below this limit the lattice energy increases faster with oxidation state than does the ionization energy, so that the most stable oxidation state is the one that maximizes the charge without breaking the noble gas configuration. This is why aluminum always exists as Al$^{3+}$ when in ionic crystals despite the fact that it costs 5140 kJ mol$^{-1}$ to remove three electrons from the atom.

For transition metals, all ions lost on ionization are either ns or (n - 1)d electrons which, as we have seen, are very similar in energy. Hence there are no abrupt increases in ionization energy, only the more gradual change accumulating from loss of electrons to form higher Z$^+$, and these will be compensated by higher lattice energies. Consider, for example, CuCl and CuCl$_2$. We may calculate (cf. Prob.

\[\text{Ag} = \text{CaF}_2 + \text{Ca}\]

\[2\Delta H_f = -550 \quad \Delta H_f = -1220 \quad \Delta H_f = 0 \quad \Delta H_f = -670 \text{ kJ mol}^{-1}\]

Fig. 4.9 Energies of free cations and of ionic compounds as a function of the oxidation state of the cation. Top: Lines represent the ionization energy necessary to form the +1, +2, +3, and +4 cations of sodium, magnesium, and aluminum. Note that although the ionization energy increases most sharply when a noble gas configuration is "broken," isolated cations are always less stable in higher oxidation states. Bottom: Lines represent the sum of ionization energy and ionic bonding energy for hypothetical molecules $\text{MX}$, $\text{MX}_2$, $\text{MX}_3$, and $\text{MX}_4$ in which the interionic distance, $r_{\text{ij}}$, has been arbitrarily set at 200 pm. Note that the most stable compounds (identified by arrow) are $\text{NaX}$, $\text{MgX}_2$, and $\text{AlX}_3$. (All of these molecules will be stabilized additionally by a small extent by the electron affinity of X).

---

$^{15}$ The direction of chemical reaction will be determined by the free energy, $\Delta G$, not the enthalpy, $\Delta H$. However, in the present reaction the entropy term, $\Delta S$, is apt to be comparatively small and since $\Delta G = \Delta H - T \Delta S$, the free energy will be dominated by the enthalpy at moderate temperatures.
angle decreases. Bond angles for \( \text{NO}_2 \), \( \text{NO}_3 \), and \( \text{NO}_4 \) are 109°, 134°, and 116°, respectively. Account for this trend.

6.29 How many sets of symmetry equivalent atoms are found in the following molecules?

- a. \( \text{ClF}_2 \)
- b. \( \text{SF}_4 \)
- c. \( \text{Fe(CO)}_5 \)
- d. \( \text{MnO}_7 \)
- e. \( \text{B}^3\text{H}_9 \)
- f. \( \text{naphthalene, C}_{10}\text{H}_{14} \)
- g. \( \text{CO}_3^2^- \)
- h. \( \text{AB}_6 \)

6.30 Figures 6.10 and 6.11 illustrate unobserved but possible structures for \( \text{SF}_4 \) and \( \text{ICl}_7^- \). Assign point group symmetries to these hypothetical structures. Would the difference in symmetry affect the spectroscopic properties?

6.31 On page 235 the statement is made that there are other symmetry operations which exist that illustrate the equivalence of the bridging bromo groups. Give an example.

6.32 Atoms of molecules which are chemically nonequivalent are also magnetically nonequivalent and will, in general, give rise to different NMR chemical shifts. Sometimes atoms may be chemically equivalent, but at the same time be magnetically nonequivalent. Atoms are magnetically equivalent if they couple equally to all other atoms in the molecule. For example, in methane each of the four hydrogen atoms couples to the carbon and to each other in exactly the same way and they are therefore magnetically equivalent (as well as chemically equivalent). In \( \text{CO}_3^2^- \), however, one of the three oxygen atoms trans to hydrogen couples to a different atom which is cis. As a result, even though the two oxygen atoms are chemically (symmetry) equivalent, they are magnetically nonequivalent, as are the two hydrogen atoms. In NMR terms, we would say that the \( \text{CO}_3^2^- \) has an \( \text{AA'XX'} \) rather than an \( \text{A'X}'X \) spin system, and that its NMR spectrum would reflect that complexity. Refer to Problem 6.29 and determine which atoms of each molecule or ion are magnetically equivalent.

6.33 The structures of all of the mixed \( \text{X} = 1-5 \text{ClFClF}_n \) chlorofluorophosphancs \( \text{MX}_n(\text{PCI}F_n^-) \) and \( \text{chlorofluoroarsanes}(\text{AsCl}F_n^-) \) have recently been determined. Before reading the experimental results, predict these structures.

6.34 Methyl- and trifluoromethylsulfur chloride were fluorinated with silver difluoride.

\[
\text{CH}_3\text{SCl} + 2\text{AgF} \rightarrow \text{CH}_3\text{S} + 2\text{AgCl} + 2\text{F}_2
\]

Elemental analysis of the products gave:

1. \( C = 13.2\%, H = 2.8\%, S = 30.8\%, F = 54.3\% \)
2. \( C = 7.0\%, S = 26.2\%, F = 72.2\% \)

Predict the molecular structures of the products as completely as possible. Name the products according to IUPAC nomenclature.

6.35 In the opening paragraph of Chapter 3 the statement was made that "frequently the most symmetrical molecular structure is the 'preferable' one." But in that same chapter we saw that \( \text{XeF}_4 \) is square planar, not tetrahedral, which some theoreticians had argued for because of the higher symmetry of the latter. Other exceptions have been discussed in this chapter. Rationalize these apparent paradoxes.

6.36 The original investigators of the diazirine compound shown in Fig. 6.22 claim that the following features can be found in that figure:

(a) bent bonds in the \( \text{C}—\text{N}—\text{N} \) triangle;
(b) the \( \text{N}—\text{N}—\text{N} \) double bond;
(c) the greater electronegativity of nitrogen compared with carbon;
(d) the presence of lone pairs on the nitrogen atoms;
(e) the absence of \( \text{C}_2^\infty \) symmetry in the electron density of the diazirine ring, nor should such symmetry be expected. Note the difference of an order of magnitude between the contours in (a) and (b).

Confirm each of these observations.

60 In IUPAC nomenclature, a "phosphane" is normally a derivative of what we ordinarily call "phosphine." \( \text{PH}_3 \). Pentavalent derivatives of the hypothetical \( \text{PH}_5 \) (phosphane) are labeled \( \text{As}_5 \).

61 Similarly, derivatives of \( \text{H}_3\text{S} \) would be sulfanes, and the tetravalent and hexavalent derivatives would be labeled \( \text{As}_4 \) and \( \text{As}_6 \), respectively.


63 The authors did not report elemental analyses, but they are given here (calculated on the basis of the empirical formulas) to aid in the solution of this problem.
In the same way that Fig. 4.9 was sketched with "average" values to illustrate the stability of compounds with noble gas configurations, we can simply Eq. 4.14 further by inserting some "average" values. It must be clearly understood that this is merely clearing away some of the numerical shrubbery to lay out the picture of the chemical forest in clearer detail. Let us assume that we are studying compounds M \( ^{\text{2+}}X^{2-} \) with an internuclear distance of about 200 pm. Of course, \( Z^+ = Z^- = 1 \). To be as general as possible, let's use an average value of \( A = 2 \), which is not too inaccurate for present purposes (about 20\% error) for NaCl, CuCl, CaF\(_2\), TiO\(_2\), and both ZnS structures. Equation 4.14 reduces to

\[
U_0 = -1400 \text{kJ mol}^{-1} = -330 \text{ kcal mol}^{-1} = -14 \text{ eV}
\]  

This approximation is somewhat high for most compounds chiefly because an internuclear distance of 200 pm is too small for most compounds. But it has the useful aspect of requiring that only the coefficients of Eq. 4.14 be remembered. Furthermore, it allows some simple predictions to be made without involving the detailed calculation of the above example. For example, can we make a "rule of thumb" to predict when a compound M \( ^{\text{2+}}X^{2-} \) will be readily oxidized to M \( ^{\text{3+}}2X \)? Using Eq. 4.14, we predict that the lattice energy will double, or increase by one- to one-and-a-half MJ mol\(^{-1}\), upon conversion to MX\(_2\). By far the major energy that has to be paid to accomplish this change is IE\(_1\), of the metal. While a thorough examination of all of the energy terms is necessary for a careful analysis of the situation, we are led to believe that if the additional cost of ionization is less than about 1.3--1.5 MJ mol\(^{-1}\) (13--15 eV) for the higher oxidation state, it may well be stable, too. In the case of copper, given above, we have

\[
\text{IE}_1 = 0.75 \text{ MJ mol}^{-1} \quad \text{IE}_2 = 2.0 \text{ MJ mol}^{-1} \quad \text{IE}_3 = 3.5 \text{ MJ mol}^{-1}
\]

Our rule of thumb follows the more careful calculations above and predicts that both Cu(I) and Cu(II) compounds will be stable and, furthermore, it also works where data are not available for a more careful analysis. Cu(II) compounds are predicted to be unstable or marginally stable (Chapter 14).

On the other hand, if the succeeding ionization energies are too near each other, as was the case for IE\(_1\) and IE\(_2\) of calcium above:

\[
\text{IE}_1 = 0.66 \text{ MJ mol}^{-1} \quad \text{IE}_2 = 1.3 \text{ MJ mol}^{-1}
\]

then the lower oxidation state (Ca\(_{\text{2+}}\)) is unstable because it is too readily oxidized to Ca\(_{\text{3+}}\). Of course, Ca\(_{\text{2+}}\) is unavailable because it is too prohibitively expensive.

Ahrens, who was the first to point out this rule of thumb, contrasted the behavior of titanium:

\[
\text{IE}_1 = 0.66 \text{ MJ mol}^{-1} \quad \text{IE}_2 = 1.3 \text{ MJ mol}^{-1}
\]

with that of zirconium:

\[
\text{IE}_1 = 0.66 \text{ MJ mol}^{-1} \quad \text{IE}_2 = 3.3 \text{ MJ mol}^{-1}
\]

The differences between the successive oxidation states for titanium are just sufficient to allow marginally stable Ti(II) and Ti(III) oxidation states in addition to Ti(IV). The corresponding lower oxidation states are uncommon for zirconium whose chemistry is dominated by Zr(IV).

Of intermediate accuracy between the rough rule of thumb given above and the precise Born-Lande equation is a suggestion made by Kapustinskii. He noted that the Madelung constant, the internuclear distance, and the empirical formula of a compound are all interrelated. He has suggested that in the absence of knowledge of crystal structure (and hence of the appropriate Madelung constant) a reasonable estimation of the lattice energy can be obtained from the equation:

\[
U_0 = 210,200 \text{eV} \frac{Z^+ Z^-}{r_0} \left(1 - \frac{34.5}{r_0} \right) \text{ (kJ mol}^{-1}\text{)}
\]  

where \( v \) is the number of ions per "molecule" of the compound and \( r_0 \) is estimated as 98\% of the experimental value, comparing favorably with that obtained from Eq. 4.13. Of course, the usefulness of Eq. 4.20 lies not in its prediction of the average ionization energies but in the ability to make simple rules for predicting the stability of compounds.
6.18 Suggest the most likely stereochemistry of the phosphinate ester resulting from ethanolysis of the following compound:

\[ \text{CH}_3\text{P(O)}\text{OCH}_2\text{C}_6\text{H}_5\]

6.19 Predict the geometries of (CH\textsubscript{3})\textsubscript{3}P(C\textsubscript{CF\textsubscript{3}}\textsubscript{3})\textsubscript{3} and (CH\textsubscript{3})\textsubscript{2}P(C\textsubscript{CF\textsubscript{3}}\textsubscript{3})\textsubscript{2}. Do you expect these molecules to undergo pseudorotation? Explain. (See The, K. K.; Cavell, R. G. Chem. Commun. 1975, 716.)

6.20 In an sp\textsuperscript{3} hybridized phosphorus atom in a TBP molecule, will the atom have a greater electronegativity when bonding through equatorial or axial orbitals? Explain.

6.21 Earlier (page 212) it was stated that the repulsive effects of a lone pair and a doubly bonded oxygen atom in VSEPR theory were very similar. Discuss qualitative and quantitative differences that you feel should exist. (See Christe K. O.; Oberhammer, H. Inorg. Chem. 1981, 20, 296.)

6.22 Predict and say as much as you can about the probable structure of solid InCl. Be careful! (Refer to Chapter 47 on solids.)

6.23 Consider Fig. 6.32, which is an electron density contour map of the sodium cyanide crystal. Interpret this diagram in terms of everything that you know about the structure of solid sodium cyanide.

**Fig. 6.31** Square pyramidal dioxo-A'-phosphane with five- and four-membered rings. [From Howard, J. A.; Russell, D.; Trippett, S. Chem. Commun. 1973, 856-857. Reproduced with permission.]

6.24 Identify the symmetry elements and operations in the molecules and ions shown in the figures listed below. Determine the appropriate point group for each molecule and ion.

a. 6.4  b. 6.5  c. 6.6  
d. 6.7  e. 6.8  f. 6.10  
g. 6.11  h. 6.18

6.25 Calculate the hybridization of the carbon and nitrogen atoms in Fig. 6.27.

6.26 Considering the molecular orbital diagrams for carbon monoxide (Fig. 5.20) and the discussion concerning hybridization and energy (pages 225-227), predict whether the carbon monoxide molecule will be more basic (i.e., will donate electrons more readily) or more acidic (will accept electrons more readily) and form the stronger, direct covalent bond.

6.27 Consult the molecular orbital diagram in Fig. 6.16 and predict whether OH\textsubscript{2} will be linear or bent. What would you predict for the excited state configuration, 2\textitalics\alpha\beta\beta\alpha? 

6.28 Refer to the molecular orbital diagram for NO\textsubscript{2} in Fig. 5.31. Walsh diagrams, similar to those in Fig. 6.16, predict that the HOMO (\(\tilde{\alpha}_3\)) becomes more stable as the O—N—O bond...
lattice energy of sodium chloride, which is well known and provides a check on its accuracy, but in giving reasonably accurate estimates for compounds that are not well known (see Problem 4.24).

In summary, in addition to allowing simple calculations of the energetics of ionic compounds, the Born-Haber cycle provides insight into the energetic factors operating. Furthermore, it is an excellent example of the application of thermodynamic methods to inorganic chemistry and serves as a model for other, similar calculations not only for solids, but also for reactions in solution and in the gas phase.

Factors Affecting the Radii of Ions

The determination of the sizes of ions has been a fundamental problem in inorganic chemistry for many years. Many indirect methods have been suggested for approximating the internuclear distance between two ions, relatively easy to obtain, into ionic radii. Although these have been ingenious and provide insight into atomic properties, they are no longer necessary.

When an X-ray crystallographer determines the structure of a compound such as NaCl (Fig. 4.1a), usually only the spacing of ions is determined, because the repeated spacings of the atoms diffract the X rays as the grooves on a phonograph record. However, if very careful measurements are made, accurate maps of electron density can be constructed since, after all, it is the electrons of the individual atoms that scatter the X rays. The result is Fig. 4.10. One may now appreciate the interatomic distance in NaCl, 281 pm, using the minimum in electron density as the operational definition of "where one ion stops and the other starts".

Although not many simple ionic compounds have been studied with the requisite accuracy to provide data on ionic radii, there are enough to provide a basis for a complete set of ionic radii. Such a set has been provided in the crystal radii of Shannon and Prewitt.\(^{19}\) Values of these radii are given in Table 4.4.

A comparison of the values given in Table 4.4 allows one to make some conclusions regarding the various factors that affect ionic size. We have already seen that progressing to the right in a periodic series should cause a decrease in size. If the ionic charge remains constant, as in the +3 lanthanide cations, the decrease is smooth and moderate. Progressing across the main group metals, however, the ionic charge is increasing as well, which causes a precipitous drop in cationic radii: Na\(^+\) (116 pm), Mg\(^{2+}\) (69.5 pm), Al\(^{3+}\) (67.5 pm). In the same way, for a given metal, increasing oxidation state causes a shrinkage in size, not only because the ion becomes smaller as it loses electron density, but also because the increasing cationic charge pulls the anions closer in. This change can be illustrated by comparing the bond lengths in the complex anions FeCl\(_2^-\) and FeCl\(_4^-\). The Fe(II)—Cl bond length is 11 pm shorter than the Fe(II)—Cl bond length.\(^{20}\)

For transition metals the multiplicity of the spin state affects the way in which the anions can approach the cation; this alters the effective radius. Although this is an important factor in determining cationic radii, it is beyond the scope of the present chapter and will be deferred to Chapter 11.

For both cations and anions the crystal radius increases with the increase in coordination number. As the coordination number increases, the repulsions among the coordinating counterions become greater and cause them to "back off" a bit. Alternatively, one can view a lower coordination number as allowing the counter-ions to compress the central ion and reduce its crystal radius.

As we shall see over and over again, the simple picture of billiard-ball-like ions is easy to describe but generally unrealistic. The fluorides and oxides come closest to this picture, and so the values in Table 4.4 work best with them. Larger, softer anions in general will present more problems. Little work has been done in this area, but Shannon\(^{21}\) has presented a table, analogous to Table 4.4, for sulfides.

The sizes of polyatomic ions such as NH\(_4^+\) and SO\(_4^{2-}\) are of interest for the understanding of the properties of ionic compounds such as (NH\(_4\))\(_2\)SO\(_4\), but the experimental difficulties attending their determination exceed those of simple ions. In addition, the problem of constancy of size from one compound to the next—always a problem

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19 Shannon, R. D.; Prewitt, C. T. Acta Crystallogr. 1969, A25, 925; Shannon, R. D. ibid. 1976, A32, 751. Many inorganic books in the past, including the first edition of the present one, have given some set of "traditional" ionic radii based on indirect estimates. The Shannon and Prewitt crystal radii given in Table 4.4 are about 14 pm larger for cations and 14 pm smaller for anions than the best set of ionic radii.


The process responsible for the "ozone hole" over Antarctica is thought to be similar, though it may be heterogeneous, taking place on ice particles.\(^{34}\)

\[
\begin{align*}
2\text{Cl}^- + \text{O}_3 & \longrightarrow \text{ClO}^+ + \text{O}_2 \\
\text{ClO}^+ + \text{ClO}^- + \text{M} & \longrightarrow \text{ClO}_2^+ + \text{M} \\
(\text{ClO}_2^+ + \text{H}^+) & \longrightarrow \text{Cl}^- + \text{ClO}_2^- \\
\text{ClO}^+ + \text{M} & \longrightarrow \text{Cl}^- + \text{O}_3 + \text{M}
\end{align*}
\]

(6.23)-(6.25)

Net: \(2\text{O}_3 \longrightarrow 3\text{O}_2\)

(6.26)-(6.27)

6.1 Draw Lewis structures for the following molecules and predict the molecular geometry:

\(\text{a. } \text{BCl}_3\)  
\(\text{b. } \text{BeH}_2\)  
\(\text{c. } \text{SnBr}_4\)  
\(\text{d. } \text{TeF}_5\)  
\(\text{e. } \text{AsF}_5\)  
\(\text{f. } \text{XeO}_4\)

6.2 Draw Lewis structures for the following molecules and predict the molecular geometry including expected distortions:

\(\text{a. } \text{TiCl}_4\)  
\(\text{b. } \text{ICl}_2^+\)  
\(\text{c. } \text{ClF}_3\)  
\(\text{d. } \text{SO}_2\)  
\(\text{e. } \text{XeF}_2\)  
\(\text{f. } \text{XeF}_4\)

6.3 What is the simplest reason for believing that molecular structure is more often governed by \(\sigma^2\)-orbital contributions than by the \(\sigma^1\)-BP contributions?

6.4 Use Eq. 6.1 to derive the bond angles in \(\text{sp}^3\), \(\text{sp}^2\), and \(\text{sp}^1\) hybrid orbitals.

6.5 Assuming that the orbitals are directed along the internuclear axes (i.e., the bonds are not bent) use Eq. 6.1 to calculate the \(\pi\) character in the bonds of \(\text{NH}_3\). The bond angle in \(\text{NH}_3\) is 104.5°. What is the \(\pi\) character of the lone pair?

6.6 The bond angles in the fluoromethanes are:

<table>
<thead>
<tr>
<th>Molecule</th>
<th>(\text{H}^-\text{C}^-\text{H})</th>
<th>(\text{F}^-\text{C}^-\text{F})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CH}_2\text{F}_2)</td>
<td>111.9 ± 0.4°</td>
<td>108.3 ± 0.1°</td>
</tr>
<tr>
<td>(\text{CHF}_3)</td>
<td>—</td>
<td>108.8 ± 0.7°</td>
</tr>
</tbody>
</table>

\(\text{a. } \) Calculate the \(\pi\) character used by the carbon atom in the orbitals directed to the hydrogen and fluorine atoms.

\(\text{b. } \) Discuss the results in terms of Bent's rule.

6.7 Show in a qualitative way why the energy levels of \(\text{AH}_3\) in Fig. 6.16 increase or decrease in the way they do upon bending the molecule. Attempt to account for small and large changes.

---


---

6.8 Consider the free radicals \(\text{CH}_2^+\) and \(\text{CF}_3^+\). One is planar, the other pyramidal. Which is which? Why?

6.9 Group VIA (6) tetrafluorides act as Lewis acids and form anions:\(^{36}\)

\[
\begin{align*}
\text{Cl}^+\text{F}^- + \text{SF}_4 & \longrightarrow \text{Cl}^+\text{[SF}_4^-] \\
\text{Cl}^+\text{F}^- + \text{SeF}_4 & \longrightarrow \text{Cl}^+\text{[SeF}_4^-] \\
\text{Cl}^+\text{F}^- + \text{TeF}_4 & \longrightarrow \text{Cl}^+\text{[TeF}_4^-]
\end{align*}
\]

(6.28)-(6.30)

6.10 From Fig. 6.23, derive an equation for tungsten analogous to Eq. 6.3 for carbon.

6.11 a. Predict the carbon-carbon bond length(s) in benzene.

b. Predict the carbon-carbon bond length(s) in benzil.

6.12 Consider the molecule \(\text{CH}_3\text{C}^-\text{H}^+\). Applying Bent's rule in its classical form, predict whether the bond angles, \(\text{H}^-\text{C}^-\text{H}^+\), are greater or less than 109°. Considering the arguments on overlap on page 228, predict again. (The experimental result is given by Costain, C. C.; J. Chem. Phys. 1958, 39, 868.)

6.13 Consider the molecule \(\text{Cl}_2\text{F}_2\), with chlorine the central atom. How many isomers are possible? Which is the most stable? Assign point group designations to each of the isomers.

6.14 The structure for \(\text{Al}_3\text{Br}_4\) (Fig. 6.14) is assumed by both \(\text{Al}_3\text{Br}_4\) and \(\text{Al}_3\text{Cl}_4\) in the gas phase. In the solid, however, the structure can best be described as closest packed arrays of halogen atoms (or ions) with aluminum atoms (or ions) in tetrahedral or octahedral holes. In solid aluminum bromide the aluminum atoms are found in pairs in adjacent tetrahedral holes. In solid aluminum chloride, sodium ions are found in one-third of the octahedral holes.

a. Discuss these two structures in terms of an ionic model for the solid. What factors favor or disfavor this interpretation?

b. Discuss these two structures in terms of covalent bonding in the solid. What factors favor or disfavor this interpretation?

6.15 Obtain the covalent and van der Waals radii of phosphorus and the halogenes from Table 8.1.

a. Show that for an assumed bond angle of 109° the phosphorus trihalides there must be van der Waals contacts among the halogen atoms.

b. Show that because of the concomitant increase in both covalent and van der Waals radii, the repulsion between the halogens does not become worse as one progresses from \(\text{F}\) to \(\text{I}\).

6.16 One of the few phosphorus compounds that exhibit square pyramidal geometry is shown in Fig. 6.32. Rationalize the preferred geometry of \(\text{P}_5\) over \(\text{TBP}\) in terms of the presence of the four- and five-membered rings. (Holmes, R. R. J. Am. Chem. Soc. 1975, 97, 5379.)

6.17 Consider the cyclic compounds I and II. In I the rapid exchange of the fluorine atoms is inhibited just as it is in (\(\text{CH}_2\text{F}_2\))\(_2\). However, exchange in II is very rapid. Suggest a reason.

---

114

4

Bonding Models in Inorganic Chemistry: 1. Ionic Comp
Size Effect'

Table 4.4

Table 4.4 (Continued)

Effective ionic radii of
the elements"

1 1 5

Coordination
Ion

number4

Coordination
pm

Ac3+

6

Ag' +

2

81

4

Ag2+

ai3*

Am2*

pm

6

97

8

107

114

Br"

6

182

4 SQ

116

Br3*

4 SQ

73

5

123

Br3*

3 PY

6

129

Br7*

7

136

8

142

6
Ag3+

number4

Bk4*

4 SQ

126

Ion

Coordination

CJ*

number4

Co4*

4

Effective ionic radii of
pm

6 HS

67

6 LS

87

HS

94

45

Cr3*

6

75.5

4

39

Cr4*

4

55

6

53

6

69

3

6

4

48.5

93

4

29

6

63

108

6

30

8

71

4

40

6

58

6

181

81

6

114

6

89

7

120

53

8

126

5

62

6

67.5

Ca2*

Cr3*

Cr6*
Cs1*

the elements"

Ion

Coordination
number4

pm

Ion

3

116

In3*

4

117

54

Cr2*

4 SQ
4

Ion

8

106

5

64

6

82

6

73

Fe2*

4 HS

77

Ir4*

6

76.5

7

87

4 SQ HS

78

lrs*

6

71

N"

4

132

6 LS

75

K"

—

313'

N3*

6

30

HS

92

K'*

4

151

N5*

3

8 HS

106

6

152

4 HS

63

7

160

Na"

_

5

72

8

165

Na1*

4

113

6 LS

69

9

169

5

114

10

173

12

Fe3*

HS

78.5

116

7

126

117.2

8

132

7

124

9

138

8

130

12

153

61

9

135.6

Nb3*

6

86

5

69

10

141

Mb4*

6

82

6

76

12

150

8

93

6

107.8

4

73

4

62

7

114

6

90

6

78

8

119.3

8

106

7

83

9

124.7

6

100.1

8

111.7

9

117.2

188

8 HS

92

9

192

Fe4*

6

72.5

12

148

10

195

Fe6*

4

39

4

92

11

199

Fr'*

6

194

12

Ga3*

4

145

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101

6

111.5

6

109

Cs"

10

202
348-

8

123

7

117

Cu"

2

60

6

99

8

124

4

74

8

109

12

145

6

91

As3-

6

210“'

6

115

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71

As3*

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72

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121

4 SQ

71

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47.5

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128.3

5

79

Gc2*

6

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60

9

133.6

6

87

Ge4*

4

53

68

6

67

1

6

76

10

139

Cu3*

6 LS

6

151

12

148

Dy'*

2

4

Au3*

4 SQ

82

6

101

Dy2*

6

121

6

99

8

III

7

127

Au3*

6

71

10

121

8

133

B3*

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15

12

128

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105.2

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Cf3*

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109

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III

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CfJ*

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116.7

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149

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122.3

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152

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103

Ba2*

Bi3*

Dy3*

96.1

8

106

Cl"

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Cl3*

3 PY

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Cl7*

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114.4

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Be2*

Ce“*

Er3*

II

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Cm3*

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Cm4*

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Eu3*

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6 LS
HS

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Hr"

Hg'*
Hg2*

Ho3*

276'

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137

Alt'*

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178

132

Gd3*

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Mo6*

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Cu2*

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pm

119

140

Ce3*

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number4

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Am**

4

Ion

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135

Am3*

Coordination
pm

F7*

7

Cd2*

Coordination
number4

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Li'*

Lu3*

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Mg2*

Nb3*

Nd2*

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-4

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130.3

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103

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85

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Mn2*

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80

90

5 HS

89

8

97

6 LS

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111

HS

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133

7 HS

104

2

83

8

no

4

110

5

72

6

116

6 LS

8

128

HS

Mn3*

Ni2*

141

4

69

4 SQ

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81

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77

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Ni3*

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6 LS

70

HS

74

Ni4*

6 LS

72

No2*

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124

78.5

Np2*

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124

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53

Np3*

6

115

6

67

Np4*

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101

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112

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104.1

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115.5

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121.2

Mn3*

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Mn4*

Nd3*

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126

Mn6*

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39.5

Np3*

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6

89

l"

6

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Mn7*

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Np6*

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108.7

86

I3*

3 PY

7

115

8

120.6

9

126

2

114.5
Continued

I7*

58

6

60

Np7*

6

85

6

109

Mo3*

6

83

O2*

2

121

4

56

Mo4*

6

79

3

122

6

67

Mo3*

4

60

4

124
Continued


inversion or the less common retention, there is a contrast with the loss of stereochemistry associated with a carboxylation mechanism.

The stability of five-coordinate intermediates also makes possible the ready racemization of optically active silanes by catalytic amounts of base. The base can add readily to form a five-coordinate intermediate. The latter can undergo Berry pseudorotation with complete scrambling of substituents followed by loss of the base to yield the racemized silane.

Most of the reactions the inorganic chemist encounters in the laboratory involve ionic species such as the reactants and products in the reactions just discussed or those of coordination compounds (Chapter 13). However, in the atmosphere there are many free radical reactions initiated by sunlight. One of the most important and controversial sets of atmospheric reactions at present is that concerning stratospheric ozone.

The importance of ozone and the effect of ultraviolet (UV) radiation on life has been much discussed. Here we note briefly that only a small portion of the sun’s spectrum reaches the surface of the earth and that parts of the UV portion that are largely screened can cause various ill effects to living systems.

The earth is screened from far-UV (extremely high energy) radiation by oxygen in the atmosphere. The UV radiation cleaves the oxygen molecule to form two free radicals (oxygen atoms):

\[
O_2 + hv \text{ (below 242 nm)} \rightarrow O^+ + O^- \quad (6.11)
\]

The oxygen atoms can then attack oxygen molecules to form ozone:

\[
O^+ + O_2 + M \rightarrow O_3 + M \quad (6.12)
\]

The neutral body M carries off some of the kinetic energy of the oxygen atoms. This reduces the energy of the system and allows the bond to form to make ozone. The net reaction is therefore:

\[
3O_2 + hv \rightarrow O_3 \quad (6.13)
\]

This process protects the earth from the very energetic, short-wavelength UV radiation and at the same time produces ozone, which absorbs somewhat longer wavelength radiation (moderately high energy) by a similar process:

\[
O_2 + hv \text{ (220-320 nm)} \rightarrow O_3 + O^+ \quad (6.14)
\]

The products of this reaction can recombine as in Eq. 6.12, in which case the ozone has been regenerated and the energy of the ultraviolet radiation has been degraded to thermal energy. Alternatively, the oxygen atoms can recombine to form oxygen molecules by the reverse of Eq. 6.11, thereby reducing the concentration of ozone. An equilibrium is set up between this destruction of ozone and its generation via Eq. 6.13 and so under normal conditions the concentration of ozone remains constant.

The controversy over supersonic transports (SSTs) of the Concorde type revolves around the production of nitrogen oxides whenever air containing oxygen and nitrogen passes through the very high temperatures of a jet engine. One of these products, nitric oxide, reacts directly with ozone, thereby reducing its concentration in the atmosphere:

\[
NO + O_3 \rightarrow NO_2 + O_2 \quad (6.15)
\]

Furthermore, nitrogen dioxide formed in Eq. 6.15 or directly in the combustion process can react to scavenge oxygen free radicals and prevent their possible recombination with molecular oxygen to regenerate ozone (Eq. 6.12):

\[
NO_2 + O^+ \rightarrow NO + O_2 \quad (6.16)
\]

Note that a combination of reactions (Eq. 6.15 and 6.16) results in the net conversion of ozone to oxygen:

\[
O^+ + O_3 \rightarrow 2O_2 \quad (6.17)
\]

and that the nitrogen oxides, either NO or NO_2, continuously recycle and thus act as catalysts for the decomposition of ozone:

\[
O_3 \rightarrow NO + O_2 \quad (6.18)
\]

The current controversy revolves around the extent to which nitrogen oxides, NO_x, would be formed by SSTs and how much the ozone concentration would be affected.35

The ozone question is complicated by the fact that other chemicals are implicated in its destruction. Chlorofluorocarbons were formerly widely used as propellants in spray cans, and they continue to be used as refrigerants.56 They are extremely stable and long-lived in the environment. However, they too can undergo photolysis in the upper atmosphere:

\[
F_2CCF_2 + hv \text{ (90-220 nm)} \rightarrow F_2C^+ + Cl^- \quad (6.19)
\]

The chlorinated free radical can then interact with ozone in several different ways analogous to the NO cycle. At mid-latitudes the reaction is:

\[
Cl^+ + O_3 \rightarrow ClO^+ + O_2 \quad (6.20)
\]

\[
ClO^+ + O^- \rightarrow Cl^- + O_2 \quad (6.21)
\]

for a net reaction of:

\[
O^+ + O_3 \rightarrow 2O_2 \quad (6.22)
\]

with regeneration of the monatomic chlorine. The chlorine thus acts as a catalyst, and present evidence indicates that the ClO cycle may be more efficient in the destruction of ozone than is the NO_x cycle.57

Table 4.4 (Continued)

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continued
The Structure and Reactivity of Molecules

The pseudorotation.

Substitution of alkyl groups on the phosphorus atom provides some interesting effects. If a single methyl group replaces a fluorine atom, it occupies one of the equatorial positions as expected and rapid exchange of the two axial and the two equatorial fluorine atoms is observed, as in PF$_3$. If two methyl groups are present, (CH$_3$)$_2$PF$_3$, the molecule becomes rigid and there is no observable exchange among the three remaining fluorine atoms. This dramatic change in behavior appears to be attributable to the presence of the three remaining fluorine atoms together with an increased stability of five-coordinate intermediates. This difference is attributable to the presence of $d$ orbitals in the heavier elements (Chapter 18).

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This difference in energy can be shown dramatically in the sulfurane

\[
\text{S-Cl} \quad \text{S-Cl} \quad \text{S-Cl} \quad \text{S-Cl}
\]

This molecule has an approximately TBP electronic structure and is chiral. However, potentially it could racemize via a series of Berry pseudorotations. If it does not do so readily, and is therefore the first optically active sulfurane to be isolated, has been attributed to the fact that all racemization pathways must proceed through a TBP with an apical lone pair. As we have seen in the preceding chapter, there is a very strong tendency for the lone pair to seek an equatorial site. The reluctance of the lone pair to occupy an apical site appears to be a sufficient barrier to allow the enantiomers to be isolated.

The question might be asked: Are there similar mechanisms for changing the configuration of molecules without breaking bonds in molecules with coordination numbers other than 3 and 5? The answer is "yes." One of the most important series of inorganic compounds consists of six-coordinate chelate compounds exemplified by the tris(ethylenediamine)cobalt(III) ion. Because of the presence of the three chelate rings, the ion is chiral and racemization can take place by a mechanism that is closely related to atomic inversion or Berry pseudorotations (the mechanism for six-coordination is termed the "Bailar twist"; see Chapter 13).

The crux of organic mechanistic stereochemistry may be the Walden inversion, the inversion of stereochemistry about a four-coordinate carbon atom by nucleophilic attack of, for example, a hydroxide ion on an alkyl halide. Many reactions of inorganic molecules follow the same mechanism. In contrast, the dissociative mechanism of tertiary halides to form tertiary carbocation intermediates is essentially unknown among the nonmetallic elements silicon, germanium, phosphorus, etc. The reason for this is the generally lower stability of species with coordination numbers of less than 4, together with an increased stability of five-coordinate intermediates. This difference is attributable to the presence of $d$ orbitals in the heavier elements (Chapter 18).

The simplest reaction path for nucleophilic displacement may be illustrated by the solvolysis of a chlorodiallylphosphine oxide:

\[
\text{CH}_3\text{O}^- + \text{P(OCl)}_2 \rightarrow \text{CH}_3\text{O}^- \text{P(OCl)}_2 \rightarrow \text{CH}_3\text{O}^- \text{P(OCl)}_2 + \text{Cl}^- \tag{6.10}
\]

We would expect the reaction to proceed with inversion of configuration of the phosphorus atom. This is generally observed, especially when the entering and leaving groups are highly electronegative and are thus favorably disposed at the axial positions, and when the leaving group is one that is easily displaced. In contrast, in some cases when the leaving group is a poor one it appears as though front side attack takes place because there is a retention of configuration. In either case, the common
and Crystal Lattices

...for packing them which are more efficient than others. This

If we consider atoms and ions to be hard spheres, we find that there are certain
good geometric arrangements for packing them which are more efficient than others. This
can be confirmed readily in two dimensions with a handful of coins. For example, if
a set of coins of the same size (dimes, for example) is arranged, it will be found that
six of them fit perfectly around another (i.e., touching each other and the central
dime), giving a coordination number of 6. However, only five quarters or four silver
dollars will fit around a dime.

The reader is strongly urged to build these structures using Styrofoam spheres and to consult texts
on structural chemistry such as Wells, A. F. Structural Inorganic Chemistry, 5th ed. 1984; The 72nd
Edition of Chemistry, Clarendon: Oxford, 1956. The present discussion merely presents the more
salient features of the subject.

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material can take place via the mechanism shown in Eq. 6.9. It is of interest that the energy barrier to inversion is strongly dependent on the nature of the central atom and that of the substituents. For example, the barrier to inversion of ethyl(propyl)phenylphosphine (Fig. 6.28b) is about 120 kJ mol\(^{-1}\). This is sufficient to allow the separation of optical isomers, and their racemization may be followed by classical techniques. In contrast, the barrier to inversion in most amines is lower (about 10-20 kJ mol\(^{-1}\) in methyl(propyl)phosphinamidic, about 25 kJ mol\(^{-1}\) in ammonia). With such low barriers to inversion, optical isomers cannot be separated because racemization takes place faster than the resolution can be effected. Since traditional chemical separations cannot effect the resolution of the racemate mixture, the chemist must turn to spectroscopy to study the rate of interconversion of the enantiomers. The techniques involved are similar to those employed in the study of fluxional organometallic molecules (Chapter 13), and for now we may simply note that for inversion barriers of 20-100 kJ mol\(^{-1}\), nuclear magnetic resonance is the tool of choice.

Because the transition state in the atomic inversion process of Eq. 6.9 involves a planar, \(sp^2\) hybridized central atom, the barrier to inversion will be related to the case with which the molecule can be converted from its pyramidal ground state. We should therefore expect that highly strained rings such as that shown in Fig. 6.28 would inhibit inversion, and this is found (145 kJ mol\(^{-1}\)). Furthermore, all of the effects we have seen previously affecting the bond angles in amines and phosphines should be parallel in the inversion phenomenon. For example, the smaller bond angles in phosphines require more energy to open up to the planar transition state than those of the corresponding amines; hence the optical stability of phosphines in contrast to the usual instability of most amines. In addition, the presence of electron-withdrawing substituents tends to increase the height of the barrier, but electron-donating groups will lower it. Just as in the case of the stereochemistry of pyramidal molecules, the results can be rationally accommodated by a variety of interpretations.

We have seen previously that in PF\(_5\), the fluorine atoms are indistinguishable by means of PF\(_5\) NMR (page 236). This means that they are exchanging with each other faster than the NMR instrument can distinguish them. The mechanism for this exchange is closely related to the inversion reaction we have seen for amines and phosphines. The exchange is believed to take place through conversion of the ground state trigonal bipyramid (TBP) into a square pyramidal (SP) transition state and back to a new TBP structure (Fig. 6.29). This process results in complete scrambling of the fluorine atoms at the equatorial and axial positions in phosphorus pentafluoride, and if it occurs faster than the time scale of the NMR experiment (as it does), then all of the fluorine atoms appear to be identical. Because it was first suggested by Berry,\(^{34}\) and because, if all of the substituents are the same as in PF\(_5\), the two TBP arrangements (Fig. 6.29) are related to each other by simple rotation, the entire process is called a Berry pseudorotation. Note that the process can take place very readily because of the similarity in energy between TBP and SP structures (page 223). In fact, the series of five-coordinate structures collected by Muetterties and Guggenberger, which are intermediate between TBP and SP geometries (Table 6.3), effectively provides a reaction coordinate between the extreme structures in the Berry pseudorotation.

The exchange of fluorine atoms in PF\(_5\) is too rapid to monitor with NMR spectroscopy. The amines in some other molecules exchange more slowly, especially at lower temperatures. For example, PCIP is expected to be a trigonal bipyramid with two apicophilic fluorine atoms in the axial positions, and two chlorine atoms and the third fluorine in equatorial positions. At temperatures of \(-22^\circ\)C and above, the resonance of fluorine is observed as a single doublet (Fig. 6.36a). However, if the temperature is lowered to \(-14^\circ\)C, the two axial fluorine atoms can be distinguished from the single equatorial fluorine (Fig. 6.36d).

All three PF\(_5\) nuclei (Fig. 6.30) are split by the \(\text{\(^{31}\)P}\) nucleus (Fig. 6.30) with a coupling constant of \(J_\text{P,F} = 1048\) Hz. At \(-14^\circ\)C this produces a downfield doublet (Fig. 6.30). The single equatorial fluorine atom splits each component of the doublet of the two axial fluorine atoms into another doublet (Fig. 6.30a) with \(J_\text{P,F} = 124\) Hz. In the same way the doublet pattern of the single equatorial atom is split into singlets (eq. 6.9, n = 1) with \(J_{\text{P,F}} = 124\) Hz. The overall intensity of the axial fluorine resonance is twice that of the single equatorial fluorine. Also, the weighted average of the chemical shifts at \(-14^\circ\)C (Fig. 6.30a) is the same as that at \(-22^\circ\)C (Fig. 6.30d) indicating that the structure does not change on warming, even though the fluorine exchange accelerates. The fact that phosphorus-fluorine coupling is present on warming indicates that there is no intermolecular exchange, but that the coalescence of the spectrum at higher temperatures is the result of an intramolecular rearrangement.

![Fig. 6.28 Chiral amines and phosphines.](image)

![Fig. 6.29 Berry pseudorotation in a pentavalent phosphorus compound.](image)

The fee consists of a closest packed array of fifteen atoms. Consider this the "A layer", (b) A closest packed layer of six atoms in the "A layer" (as it would if this were placed on (a). Consider this the "B layer", (c) The final atom, a member of the "C layer," is added to complete the Fig. 4.14 Unit cells in the cubic closest packed systems, (a) A face-centered array of atoms. Note that the exposed layer is the most stable structure when the sizes of the cation and anion are comparable. This is referred to as the ccp structure. If all the packing atoms are no longer neutral (e.g., half are cations and half are anions), the closest packed structures are no longer the most stable, as can be seen from the similar two-dimensional case (see above). However, these structures may still be useful when considered as limiting cases for certain ionic crystals. Consider lithium iodide, in which the iodide anions are so much larger than the lithium cations that they may be assumed to touch or nearly touch. They can be considered to provide the framework for the crystal. The much smaller lithium ions can then fit into the small interstices between the anions. If they expand the lattice slightly to remove the anion–anion contact, the anionic repulsion will be reduced and the crystal stabilized, but the simple model based on a closest packed system of anions may still be taken as the limiting case and a useful approximation.

Where the lithium ions fit best will be determined by their size relative to the iodide ions. Note from above that there are two types of interstices in a closest packed structure. These represent tetrahedral (t) and octahedral (o) holes because the coordination of a small ion fitted into these is tetrahedral or octahedral (see Fig. 4.13). The octahedral holes are considerably larger than the tetrahedral holes and can accommodate larger cations without severe distortion of the structure. In lithium iodide the lithium ions fit into the octahedral holes in a cubic closest packed lattice of iodide ions. The resulting structure is the zinc blende or face-centered cubic structure. These represent tetrahedral (t) and octahedral (o) holes because the coordination of a small ion fitted into these is either tetrahedral or octahedral (see Chapter 11) can affect the stability of ions in particular sites. Size will usually be the determining factor when these additional factors are of small importance—for example, when considering alkali and alkaline earth ions. The concept of closest packing of anions is also very useful in considering polar covalent macromolecules such as the silicates and iso- and heteropolyanions.59

<table>
<thead>
<tr>
<th>Technique</th>
<th>Nature of the effect</th>
<th>Information</th>
<th>Interaction time</th>
<th>Sensitivity</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray diffraction</td>
<td>Scattering, mainly by electrons, followed by interference (λ = 0.01–1 nm)</td>
<td>Electron density map of crystal</td>
<td>10^{-18} s but averaged over vibrational motion</td>
<td>~10^{-3} cm³</td>
<td>Location of light atoms or distinction between atoms of similar scattering factor difficult in presence of heavy atoms</td>
</tr>
<tr>
<td>Neutron diffraction</td>
<td>Scattering, mainly by nuclei, followed by interference (λ = 0.1 nm)</td>
<td>Vector intermolecular distances</td>
<td>10^{-18} s but averaged over vibrational motion</td>
<td>~1 cm³</td>
<td>Extensively used to locate hydrogen atoms. May give additional information due to spin on neutron leading to magnetic scattering</td>
</tr>
<tr>
<td>Electron diffraction</td>
<td>Diffraction (atom or molecule) mainly by nuclei, but also by electrons (λ = 0.01–0.1 nm)</td>
<td>Scalar distances due to random orientation</td>
<td>10^{-18} s but averaged over vibrational motion</td>
<td>100 Pa (1 torr)</td>
<td>Thermal motions cause blurring of distances. Preferably only one (small) species present. Heavy atoms easy to detect</td>
</tr>
<tr>
<td>Microwave</td>
<td>Absorption of radiation due to dipole change during rotation (λ = 0.1–30 cm; 300–1 GHz in frequency)</td>
<td>Mean value of χ² terms; potential function</td>
<td>10^{-10} s</td>
<td>10^{-2} Pa (10^{-4} torr)</td>
<td>Mean value of χ² does not occur at r, even for harmonic motion. Dipole moment necessary. Only one component may be detected. Analysis difficult for large molecules of low symmetry</td>
</tr>
<tr>
<td>Vibrational infrared</td>
<td>Absorption of radiation due to dipole change during vibration (λ = 10^{-14}–10^{-15} cm)</td>
<td>Qualitative for large molecules</td>
<td>10^{-13} s</td>
<td>100 Pa (1 torr)</td>
<td>Useful for characterization. Some structural information from number of bands, position, and possibly isotope effects. All states of matter</td>
</tr>
<tr>
<td>Vibrational Raman</td>
<td>Scattering of radiation with charged frequency due to polarizability change during a vibration (λ = visible usually)</td>
<td>Qualitative for large molecules</td>
<td>10^{-14} s</td>
<td>10⁴ Pa (10⁴ torr)</td>
<td>Useful for characterization. Some structural information from number of bands, position, depolarization ratio, and possibly isotope effects. All states of matter</td>
</tr>
<tr>
<td>Electronic</td>
<td>Absorption of radiation due to dipole change during an electronic transition (λ = 10^{-10} cm)</td>
<td>Qualitative for large molecules</td>
<td>10^{-12} s</td>
<td>1 Pa (10^{-2} torr)</td>
<td>Useful for characterization. Some structural information from number of bands and position. All states of matter</td>
</tr>
<tr>
<td>Nuclear magnetic resonance</td>
<td>Interaction of radiation with a nuclear transition in a magnetic field (λ = 10^{-10}–10⁷ cm; 3 kHz to 300 MHz)</td>
<td>Number of magnetically equivalent nuclei in each environment</td>
<td>10^{-1}–10^{-9} s</td>
<td>10⁴ Pa (10⁴ torr 1⁴H)</td>
<td>Useful for characterization. Structural information from number and multiplicity of signals</td>
</tr>
<tr>
<td>Mass spectrometry</td>
<td>Detection of fragments by charge/mass</td>
<td>Mass number, plus fragmentation patterns</td>
<td>—</td>
<td>10⁷ Pa (10⁷ torr)</td>
<td>Useful for characterization of species in a vapor, complicated by reactions in spectrometer. Does not differentiate isomers directly. Important for detecting hydrogen in a molecule</td>
</tr>
<tr>
<td>Extended X-ray absorption</td>
<td>Backscattering of photoelectrons off ligands</td>
<td>Radial distances, number, and types of bonded atoms</td>
<td>10^{-18} s but averaged over vibrational motion</td>
<td>Any state</td>
<td>Especially useful for metallobiomolecules and heterogeneously supported catalysts</td>
</tr>
</tbody>
</table>

It is not difficult to calculate the size of the octahedral hole in a lattice of closest packed anions. Figure 4.16 illustrates the geometric arrangement resulting from six anions in contact with each other and with a cation in the octahedral hole. Simple geometry allows us to (ix the diagonal of the square as $2r_0 + 2r_+$. The angle formed by the diagonal in the corner must be $45^\circ$, so we can say:

$$\frac{2r_0}{2r_0 + 2r_+} = \cos 45^\circ = 0.707 \tag{4.21}$$

$$r_0 = 0.707r_+ + 0.707r_+ \tag{4.22}$$

This will be the limiting ratio since a cation will be stable in an octahedral hole only if it is at least large enough to keep the anions from touching, that is, $r_+/r_0 > 0.414$. Smaller cations will preferentially fit into tetrahedral holes in the lattice. By a similar geometric calculation it is possible to determine that the lower limit for tetrahedral coordination is $r_+/r_0 = 0.225$. For radius ratios ranging from 0.225 to 0.414, tetrahedral sites will be preferred. Above 0.414, octahedral coordination is favored. By similar calculations it is possible to find the ratio when one cation can accommodate eight anions (0.732) or twelve anions (1.000). A partial list of limiting radius ratio values is given in Table 4.6.

The use of radius ratios to rationalize structures and to predict coordination numbers may be illustrated as follows:

Consider beryllium sulfide, in which $r_{\text{Be}}/r_{\text{S}} = 59 \text{ pm}/170 \text{ pm} = 0.35$. We should thus expect a coordination number of 4 as the $\text{Be}^{2+}$ ion fits most readily into the tetrahedral holes of the closest packed lattice, and indeed this is found experimentally: $\text{BeS}$ adopts a wurtzite structure.

In the same way we can predict that sodium ions will prefer octahedral holes in a closest packed lattice of chloride ions ($r_{\text{Na}}/r_{\text{Cl}} = 116 \text{ pm}/167 \text{ pm} = 0.69$), forming the well-known sodium chloride lattice with a coordination number of 6 (Fig. 4.1a).

With larger cations, such as cesium, the radius ratio $r_{\text{Cs}}/r_{\text{Cl}} = 181 \text{ pm}/167 \text{ pm} = 1.08$ increases beyond the acceptable limit for a coordination number of 6; the coordination number of the cations (and anions) increases to 8, and the cesium chloride lattice (Fig. 4.1b) results. As we have seen, although this is an efficient structure for cations and anions of about the same size, it cannot be directly related to a closest packed structure of anions.

Table 4.6 indicates that a coordination number of 12 should be possible when the radius ratio is 1.00. Geometrically it is possible to fit 12 atoms about a central...
The Structure and Reactivity of Molecules

Br

Br,

Cl

consists of a single doublet, indicating that all fluorine atoms are equivalent. This structure. For now, one general method may be illustrated by the Mössbauer elucidation of the structure of \( \text{I}_2\text{Cl}_4 \). By analogy with \( \text{LiCIF} \) (Fig. 6.26a), we might expect a bridged structure with either chloro or bromo bridges (Fig. 6.26b–d). The experimental result\(^{48} \) that the two iodine atoms are in different environments (Fig. 6.27) rules out the symmetrical structures shown in Fig. 6.26b, c and strongly suggests that the correct structure is Fig. 6.26d.

This has been a brief survey of some of the methods available to the inorganic chemist for the determination of structure. Further examples will be encountered later in the text illustrating methods. A useful summary of some of the methods of structure determination has been provided by Beattie,\(^{49} \) listing some of the characteristics that have been discussed above as well as some other features of their use (Table 6.5).

Some Simple Reactions of Covalently Bonded Molecules

One of the major differences between organic and inorganic chemistry is the relative emphasis placed on structure and reactivity. Structural organic chemistry is relatively simple, as it is based on dipolar, trigonal, or tetrahedral carbon. Thus organic chemistry has turned to the various mechanisms of reaction as one of the more exciting aspects of the subject. In contrast, inorganic chemistry has a wide variety of structural types to consider, and even for a given element there are many factors to consider. Inorganic chemistry has been, and to a large extent still is, more concerned with the "static" structures of reactants or products than with the way in which they interconvert. This has also been largely a result of the paucity of unambiguous data on reaction mechanisms. However, this situation is changing. Interest is increasingly centering on how inorganic molecules change and react. Most of this work has been done on coordination chemistry, and much of it will be considered in Chapter 13, but a few simple reactions of covalent molecules will be discussed here.

Atomic Inversion

The simplest reaction a molecule such as ammonia can undergo is the inversion of the hydrogen atoms about the nitrogen atom, analogous to the inversion of an umbrella in a high wind:

\[
\begin{align*}
\text{H} & \quad \text{N} \\
\text{H} & \quad \text{N}
\end{align*}
\]

(6.9)

One might argue that Eq. 6.9 does not represent a reaction because the "product" is identical to the "reactant" and no bonds were formed or broken in the process.\(^{50} \) Semantics aside, the process illustrated in Eq. 6.9 is of chemical interest and worthy of chemical study. For example, consider the trisubstituted amines and phosphines shown in Fig. 6.28. Because these molecules are nonsuperimposable upon their mirror images (i.e., they are chiral), they are potentially optically active, and separation of the enantiomers is at least theoretically possible. Racemization of the optically active

---


\(^{50}\) Obviously, the same result can be obtained by dissociating a hydrogen atom from the nitrogen atom and allowing it to recombine to form the opposite configuration. For a discussion of the various competing mechanisms that must be distinguished in studying Eq. 6.9, as well as values for barrier energies and methods for obtaining them, see Lambert, J. B. Topics Stereochem. 1971, 6, 19-105.
atom (see the discussion of closest packing in metals, page 119), but it is impossible to obtain mutual twelve-coordination of cations and anions because of the limitations of geometry. Twelve-coordination does occur in complex crystal structures of mixed metal oxides in which one metal acts as one of the closest packing atoms and others fit into octahedral holes, but a complete discussion of such structures is more appropriate in a book devoted to the structures of solids. The change in coordination number as a result of the ratio of ionic radii is shown graphically in Fig. 4.17. In general, as the cation decreases in size the lattice is stabilized (lattice energy becomes more negative) until anion-anion contact occurs. Further shrinkage of the lattice is impossible without a reduction in coordination number; therefore, zinc sulfate adopts the wurtzite or the zinc blende structure, gaining additional energy over what would be possible in a structure with a higher coordination number. Note that although there is a significant difference in energy between structures having coordination numbers 4 and 6, there is little difference between 6 and 8 (the two lines almost coincide in Fig. 4.17 on the left). The difference in energy between six- and eight-coordinate structures is less than 1% based on electrostatics.

In a 1:1 or 2:2 salt, the appropriate radius ratio is obviously the ratio of the smaller ion (usually the cation) to the larger to determine how many of the latter will fit around the smaller ion. In compounds containing different numbers of cations and anions (e.g., SrF₂, TiO₂, Li₂O, Rb₂S) it may not be immediately obvious how to apply the ratio. In such cases it is usually best to perform two calculations. For example, consider SrF₂:

\[
\frac{r_{Sr^+}}{r_{F^-}} = \frac{122}{119} = 1.044 \\
\frac{r_{F^-}}{r_{Sr^+}} = \frac{119}{122} = 0.981
\]

Now there must be twice as many fluoride ions as strontium ions, so the coordination number of the strontium ion must be twice as large as that of fluoride. Coordination numbers of 8 (Sr²⁺) and 4 (F⁻) are compatible with the maximum allowable coordination numbers and with the stoichiometry of the crystal. Strontium fluoride crystallizes in the fluorite lattice (Fig. 4.3). A second example is SnO₂:

\[
\frac{r_{Sn^{4+}}}{r_{O^{2-}}} = \frac{83}{126} = 0.66 \\
\frac{r_{O^{2-}}}{r_{Sn^{4+}}} = \frac{126}{83} = 1.52
\]

Considering the stoichiometry of the salt, the only feasible arrangement is with C.N.Sn⁺ = 3, C.N.O⁻ = 6; tin dioxide assumes the TiO₂ or rutile structure of Fig. 4.4. Note that the radius ratio would allow three more tin(IV) ions in the coordination sphere of the oxide ion, but the stoichiometry forbids it.

One final example is K₂O:

\[
\frac{r_{K^+}}{r_{O^{2-}}} = \frac{152}{126} = 1.21 \\
\frac{r_{O^{2-}}}{r_{K^+}} = \frac{126}{152} = 0.83
\]

Considering the stoichiometry of the salt, the structure must be antifluorite (Fig. 4.3, reversed) with C.N.K⁺ = 8, C.N.O⁻ = 4.

The radius ratio quite often predicts the correct coordination numbers of ions in crystal lattices. It must be used with caution, however, when covalent bonding becomes important. The reader may have been puzzled as to why beryllium sulfide was chosen to illustrate the radius ratio rule for coordination number 4 (page 123) instead of zinc sulfide, which was used repeatedly earlier in this chapter to illustrate four-coordinate structures such as wurtzite and zinc blende. The reason is simple. If ZnS had been used, it would have caused more confusion than enlightenment. It violates the radius ratio rule! Proceeding as above, we have r⁺/r⁻ = 88 pm/170 pm = 0.52, indicating a coordination number of 6, yet both forms of ZnS, wurtzite and zinc blende, have a C.N. of 4, for both cations and anions. If one argues that 0.52 does not differ greatly from 0.41, the point is well taken, but there exist more vexing cases. The radius ratio for mercury(II) sulfide, HgS, is 0.68, yet it crystallizes in the zinc blende structure. In both of these examples the sp³ hybridized covalent bonding seems to be the dominant factor. Both ZnS and especially HgS are better regarded as infinite covalent lattices (see Chapter 7) than as ionic lattices.
In order to solve a structure by X-ray diffraction, one generally needs a single crystal. Although powder data can provide “fingerprint” information and, in simple cases, considerable data, it is generally necessary to be able to grow crystals for more extensive analysis. X-rays are diffracted by electrons; therefore what are located are the centers of electron clouds, mainly the core electrons. This has two important consequences: First, if there is a great disparity in atomic number between the heavy and light atoms in a molecule, it may not be possible to locate the light atom (especially if it is hydrogen), or to locate it as accurately as the heavier atom. Second, there is a small but systematic tendency for the hydrogen atom to appear to be shifted 10–20 pm toward the atom to which it is bonded.43 This is because hydrogen is unique in not having a core centered on the nucleus (which is what we are seeking) and the bonding electrons are concentrated toward the binding atom.

Because the location of an atom in a molecule as obtained by X-rays is in the time average of all positions it occupied while the structure was being determined, the resultant structure is often presented in terms of thermal ellipsoids, which are probability indicators of where the atoms are most likely to be found (see Fig. 6.25). Occasionally, from the size and orientation of an ellipsoid, something may be ventured about the bond axis. If the ellipsoid is prolate (ovoid, American football shaped), the motion of the atom is mostly back and forth along the bond axis; and if oblate (curling-stone shaped), the motion is mostly wobbling about the bond axis. Obviously, the less the atom moves in the molecule, the smaller its thermal ellipsoid. In the molecule shown in Fig. 6.25, the carbon atoms in trimethylphosphine and in the phenyl rings “waggle” a good deal; the atoms “locked” in the central five-membered ring move relatively little. This is especially true of the platinum atoms; they are heavy and so they have less thermal motion. For someone used to “ball-and-stick” models, ORTEP is an acronym for “Oak Ridge Thermal Ellipsoid Program,” a computer program frequently used in structural analysis. The acronym is often used as a short label to indicate a drawing in which ellipsoids indicate the extent of thermal motions of the atoms.

Methods Based on Molecular Symmetry

There are many methods that give spectroscopic shifts, sometimes called chemical shifts, depending on the electronic environment of the atoms involved. For many of these methods, it is necessary to use symmetry considerations to decide whether atoms are chemically equivalent (symmetry equivalent) in interpreting the spectroscopic results. Two atoms will be symmetry equivalent if there is at least one symmetry operation that will exchange them. For example, the chloro groups of PCl52− (D3h) are all equivalent since any one chloro group can be moved into the position occupied by another one by a C2 rotation or by a reflection (αv). On the other hand, in Al3B4 (D2h, Fig. 6.10) the bridging bromo groups are not equivalent to the terminal bromo groups since no symmetry operation within D2h allows them to interchange positions. Operations do exist, however, that interchange the two bridging bromo groups with each other and they therefore are equivalent. Likewise, the four terminal groups are equivalent because they can be interchanged by a symmetry operation.

Fig. 6.25 ORTEP diagram of complex containing trimethylphosphine and nitrosobenzene ligands, and two platinum atoms. Note the differences in the sizes of the thermal ellipsoids for C, N, and Pt. For a discussion of the types of bonding in this complex, see Chapter 12. [From Packett, D. L.; Troger, W. C.; Rheingold, A. L. Inorg. Chem. 1987, 26, 4309. Reproduced with permission.]

40 ORTEP is an acronym for “Oak Ridge Thermal Ellipsoid Program,” a computer program frequently used in structural analysis. The acronym is often used as a short label to indicate a drawing in which ellipsoids indicate the extent of thermal motions of the atoms.

41 For further examples of the use of dipole moments in structure analysis, see Moody, G. J.; Thomas, J. D. R. Dipole Moments in Inorganic Chemistry; Edward Arnold: London, 1971.
It should be kept clearly in mind that the radius ratio rules apply strictly only to the packing of hard spheres of known size. As this is seldom the case, it is surprising that the rules work as well as they do. Anions are not “hard” like billiard balls, but polarizable under the influence of cations. To whatever extent such polarization or covalency occurs, errors are apt to result from application of the radius ratio rules. Covalent bonds are directed in space unlike electrostatic attractions, and so certain orientations are preferred.

There are, however, other exceptions that are difficult to attribute to directional covalent bonds. The heavier lithium halides only marginally obey the rule, and perhaps a case could be made for C.N. = 4 (LiF) (Fig. 4.18). Much more serious, however, is the problem of coordination number 6 versus 8. The relative lack of eight-coordinate structures—CsCl, CsBr, and CsI being the only known alkali metal examples—is commonly found, if hard to explain. There are no eight-coordinate examples is commonly found, if hard to explain. There are no eight-coordinate examples.

An analysis of 227 compounds indicated that the radius ratio rule worked about two-thirds of the time. Particularly troublesome were Group IB (11) and IIB (12) chalcogenides like HgS. Nathan, L. C. J. Chem. Educ. 1985, 62, 215-218.

Fig. 4.18 Actual crystal structures of the alkali halides (as shown by the symbols) contrasted with the predictions of the radius ratio rule. The figure is divided into three regions by the lines r1/r2 = 0.414 and r1/r3 = 0.732, predicting coordination number 4 (wurtzite or zinc blende, upper left), coordination number 6 (rock salt, NaCl, middle), and coordination number 8 (CsCl, lower right). The crystal radius of lithium, and to a lesser extent that of sodium, changes with coordination number, so both the radii with C.N. = 4 (left) and C.N. = 6 (right) have been plotted.

The Predictive Power of Thermochemical Calculations on Ionic Compounds

The following example will illustrate the way in which the previously discussed parameters, such as ionic radii and ionization energies, can be used advantageously to explore the possible existence of an unknown compound. Suppose one was interested in dioxygenyl tetrafluoroborate, \( \text{O}_2^+\text{BF}_4^- \). At first thought it might seem an unlikely candidate for existence since oxygen tends to gain electrons rather than lose them. However, the ionization energy of molecular oxygen is not excessively high (1165 kJ mol\(^{-1}\); cf. Hg, 1009 kJ mol\(^{-1}\)), so some trial calculations might be made as follows.

The first values necessary are some estimates of the ionic radii of \( \text{O}^2^- \) and \( \text{BF}_4^- \). For the latter we may use the value obtained thermochemically by Yatsimirskii, 218 pm. An educated guess has to be made for \( \text{O}^2^- \); since if we are attempting to make it for the first time (as was assumed above), we will not have any experimental data available for this species. However, we note that the C.N. = 8, a diatomic ion which should be similar in size, has a thermochemical radius of 177 pm. Furthermore, an estimate based on covalent and van der Waals radii (see Chapter 8) gives a similar value. Because \( \text{O}^2^- \) has lost one electron and is positively charged, it will probably be somewhat smaller than this. We can thus take 177 pm as a conservative estimate; if the cation is smaller than this, the compound will be more stable than our prediction and even more likely to exist. Adding the radii we obtain an estimate of 395 pm for the ionic distance.

Next the lattice energy can be calculated. One method would be to assume that we know nothing about the probable structure and use the Kapustinskii equation (Eq. 4.40) and \( r_\lambda = 395 \text{ pm} \). The resulting lattice energy is calculated to be \(-553 \text{ kJ mol}^{-1}\).

Alternatively, we might examine the radius ratio of \( \text{O}^2^-/\text{BF}_4^- \) and get a crude estimate of \( \Delta_{\text{th}} = 0.8 \). The accuracy of our values does not prevent us to choose between coordination number 6 and 8, but since the value of the Madelung constant does not differ appreciably between the sodium chloride and cesium chloride structures, a value of 1.22 may be taken which will suffice for our present rough calculations. We may then use the Born–Landé equation (Eq. 4.13), which provides an estimate of \(-616 \text{ kJ mol}^{-1}\) for the attractive energy, which will be decreased by about 10% if...
Bond lengths and multiple bonding were discussed in Chapter 5, and a comparison of various types of atomic radii will be discussed in Chapter 8, but a short discussion of factors that affect the distance between two bonded atoms will be given here to complement the previous discussion of steric factors.

**Bond Multiplicity**

One of the most obvious factors affecting the distance between two atoms is the bond multiplicity. Single bonds are longer than double bonds, which are longer than triple bonds: C–C = 154 pm, C≡C = 134 pm, C=N = 120 pm, N–N = 145 pm, N≡N = 123 pm, N=N = 110 pm, O–O = 148 pm, O=O = 121 pm, etc. For carbon, Pauling has derived the following empirical relationship between bond length (\(D\) in pm) and bond order (\(n\)):

\[
D_{nm} = D_1 - 71 \log n
\]

(6.8)

This relationship holds not only for integral bond orders but also for fractional ones (in molecules with resonance, etc.). One can thus assign variable bond orders depending upon the length of the bond. In view of the many factors affecting bond lengths, to be discussed below, it does not seem wise to attempt to quantify the bond order–bond length relationship accurately. Nevertheless, bonds formed by elements other than carbon show similar trends (Fig. 6.23), and the general concept certainly is a valid one.

We have seen in Chapter 5 that the strength of a bond depends to a certain extent upon the hybridizations of the atoms forming the bond. We should therefore expect bond length to vary with hybridization. Bent has shown that this variation is quite regular: C–C bond lengths are proportional to \(p^2\) character (Fig. 6.24) or, to say it another way, increasing \(s\) character increases overlap and bond strength and thus shortens bonds.

Another factor that affects bond length is electronegativity. Bonds tend to be shortened, relative to the expectations for nonpolar bonds, in proportion to the electronegativity difference of the component atoms. Thus the experimental bond length in HF is 91.8 pm versus an expected value of 108 pm. The quantitative shortening of bonds because of electronegativity differences and multiple bonding in elements other than carbon will be discussed in Chapter 8.

---

**Experimental Determination of Molecular Structure**

It is impossible to present the theory and practice of the various methods of determining molecular structure completely. No attempt will be made here to go into these methods in depth, but a general feeling of the importance of the different techniques can be gathered together with their strengths and shortcomings. For more material on these subjects, the reader is referred to texts on the application of physical methods to inorganic chemistry.

X-ray diffraction (Chapter 3) has provided more structural information for the inorganic chemist than any other technique. It allows the precise measurement of bond angles and bond lengths. Unfortunately, in the past it was a time-consuming and difficult process, and molecular structures were solved only when there was reason to believe they would be worth the considerable effort involved. The advent of more efficient methods of gathering data and doing the computations has made it relatively easy to solve most structures.
It is possible to evaluate each term in a Born-Haber cycle based on Eq. 4.25. Because the oxidation of oxygen is expected to be difficult to accomplish we might choose vigorous oxidizing conditions, such as the use of elemental fluorine:

$$\text{O}_2 + \text{F}_2 \rightarrow \text{O}_2^+ + e^-$$

It is a quite stable lattice and might be sufficient to stabilize the compound. The two calculations thus agree that the lattice energy will be in the range $-480$ to $-560 \text{ kJ mol}^{-1}$ ($-115$ to $-134 \text{ kcal mol}^{-1}$). This is a quite stable lattice and might be sufficient to stabilize the compound.

It is probable that every heteronuclear bond the chemist has to deal with contains a mixture of covalent and ionic character. Ordinarily we speak glibly of an ionic compound or a covalent compound as long as the compound in question is predominantly one or the other. In many cases, however, it is convenient to be able to say something about intermediate situations. In general, there are two ways of treating ionic-covalent bonding. The method that has proved most successful is to consider the bond to be covalent and then consider the effect of increasing charge displacement from one atom toward another. This method will be discussed in the next chapter. Another method is to consider the bond to be ionic and then allow for a certain amount of covalency to occur. The second method was championed by Kajin Fajans and is known as his quanticule theory. The latter theory has found no place in the repertoire of the theoretical chemist largely because it has not proved amiable to the quantitative calculations which other theories have developed. Nevertheless, the qualitative ideas embodied in "Fajans' rules" offer simple if inexact approaches to the problem of partial covalent character in ionic compounds.

Fajans considered the effect which a small, highly charged cation would have on an anion. If the anion were large and "soft" enough, the cation should be capable of polarizing it, and the extent of this polarization would be the cation actually penetrating the anionic electron cloud giving a covalent (shared electron) bond (Fig. 4.19).

References:

The substitution of fluorine causes the bond angles to decrease (108.6°, 108.3°), but the corresponding chlorine compounds show larger bond angles (111.3°, 111.8°).

An interesting example of this effect is isobutylene, CH$_2$=C(CH$_3$)$_2$. Naively we might assume substituents on an ethylene to be bonded at 120°. We have seen that VSEPR predicts that the double bond will tend to close down the CH$_3$—C—CH$_3$ angle, but how much? Bartell has pointed out that if you assume that the two methyl groups and the methylene group can be portrayed by spheres representing the van der Waals radius of the carbon plus hydrogen substituents, then the short C=C double bond naturally causes repulsions at 120° that can be relaxed if the CH$_3$—C—CH$_3$ angle closes. Furthermore, it should close exactly enough to make all repulsions equal; thus the three substituent carbon atoms should lie very nearly on the corners of an equilateral triangle, which they do (Fig. 6.20). Furthermore, it is possible to quantify these qualitative arguments and reproduce the bond angles in some representative hydrocarbons quite well (Fig. 6.21).

The overlap of two atomic orbitals is maximized if they bond "head on," that is, with the maximum electron density directly between the nuclei. However, small rings exhibit "ring strain" in the form of poorer overlap. Although rehybridization occurs as ring size decreases, which places more $p$ character within the ring and more $s$ character in exocyclic bonds, the minimum interorbital angle possible with only $s$ and $p$ orbitals is $90^\circ$ (pure $p$). In three-membered rings the orbitals cannot follow the internuclear axis; therefore the so-called $p_r$ bonds are not symmetrical about that axis, but are distinctively bent. The bending of these bonds can actually be observed experimentally with a buildup of electron density outside the ring (Fig. 6.22). For example, in 3-(p-nitrophenoxy)methyl-3-chlorodiazirine

\[ \text{NO}_2\text{CH}_2\text{Cl} \]

the increase in electron density is clearly seen both in the cyclic bonds (outside the C—N—N triangle) and in the N=N double bond.©

Fig. 6.20 Relaxation of nonbonded repulsions in a perfectly trigonal ethylene molecule to form 114° bond angle observed experimentally. [From Bartell, L. S., J. Chem. Educ. 1968, 45, 754. Used with permission.]

Fig. 6.22 The three-membered C—N—N ring in a diazirine molecule: (a) Electron density through the plane of the diazirine ring. Contours are at $3 \times 10^{-7}$ eÅ$^{-3}$. (b) Differential electron density map through the plane of the diazirine ring showing increases (solid lines) and decreases (broken lines) of electron density upon bond formation. Contours are at $4 \times 10^{-4}$ eÅ$^{-3}$. Note the build-up of electron density outside the C—N—N triangle. The effects can best be seen by superimposing a transparency (as made for overhead projectors, for example) of part (b) over part (a). (c) Interpretation of (a) and (b) in terms of hybrid orbitals. [From Cameron, T. S.; Bakshi, P. K.; Borceka, B.; Liu, M. T. H. J. Am. Chem. Soc. 1992, 114, 1889-1890. Reproduced with permission.]

Fajans suggested the following rules to estimate the extent to which a cation could polarize an anion and thus induce covalent character. Polarization will be increased by:

1. High charge and small size of the cation. Small, highly charged cations will exert a greater effect in polarizing anions than large and/or singly charged cations. This is often expressed by the ionic potential \( \delta \) of the cation: \( \delta = \frac{Z}{r} \).

For some simple ions, ionic potentials are as follows (\( r \) in pm):

- Li\(^+\): 14
- Be\(^{2+}\): 48
- Na\(^+\): 9
- Mg\(^{2+}\): 28
- Al\(^{3+}\): 56
- K\(^+\): 18
- Ca\(^{2+}\): 56

Obviously there is no compelling reason for choosing \( Z/r \) instead of \( Z/r^2 \) or several other functions that could be suggested, and the values above are meant merely to be suggestive. Nevertheless, polarization does follow some charge-to-size relationship, and those cations with large ionic potentials are those which have a tendency to combine with polarizable anions to yield partially covalent compounds. The ionic potentials listed also rationalize an interesting empirical observation indicated by the dashed arrows: The first element in any given family of the periodic chart tends to resemble the second element in the family to the right. Thus lithium and magnesium have much in common (the best known examples are the organometallic compounds of these elements) and the chemistry of beryllium and aluminium is surprisingly similar despite the difference in preferred oxidation state. This relationship extends across the periodic chart; for example, phosphorus and carbon resemble each other in their electronegativities (see Chapter 18).

A word should be said here concerning unusually high ionic charges often found in chains of ionic radii. Ionic radii are often listed for \( \text{Si}^{4+} \), \( \text{P}^{5+} \), and even \( \text{Cl}^{2-} \). Although at one time it was popular, especially among geochemists, to discuss silicates, phosphates, and chlorates as though they contained these highly charged ions, no one today believes that such highly charged ions have any physical reality. The only possible meaning a radii can have is to indicate that if a ion such as \( \text{P}^{5+} \) or \( \text{Cl}^{2-} \) existed, its high charge combined with small size would cause it immediately to polarize some adjacent anion and form a covalent bond.

2. High charge and large size of the anion. The polarizability of the anion will be related to its "softness," that is, to the deformability of its electron cloud. Both increasing charge and increasing size will cause this cloud to be less under the influence of the nuclear charge of the anion and more easily influenced by the charge on the cation. Thus large anions such as \( \text{I}^- \), \( \text{Se}^{2-} \), and \( \text{Te}^{2-} \) and highly charged cations such as \( \text{As}^{5+} \) and \( \text{Sb}^{5+} \) are especially prone to polarization and covalent character.

A question naturally occurs: What about the polarization of a large cation by a small anion? Although this occurs, the results are not apt to be so spectacular as in the reverse situation. Even though large, a cation is not likely to be particularly "soft" because the ionic charge will hold on to the electrons. Likewise, a small anion can tend to polarize a cation, that is, repel the outside electrons and thus make it possible to "see" the nuclear charge better, but this is not going to lead to covalent bond formation. No convincing examples of reverse polarization have been suggested.

3. Absence of the cation of the cation. The simple form of the ionic potential considers only the net ionic charge of the ion with respect to its size. Actually an anion or polarizable molecule will feel a potential resulting from the total positive charge minus whatever shielding the electrons provide. To use the ionic charge is to assume implicitly that the shielding of the remaining electrons is perfect, that is, 100% effective. The most serious problems with this assumption occur with the transition metal ions since they have one or more d electrons which shield the nucleus poorly. Thus for two ions of the same size and charge, one with an \( (n-1)d^{10} \) electronic configuration (typical of the transition elements) will be more polarizing than a cation with a noble gas configuration \((n-1)d^{10}(n-2)p^{6}\) (alkali and alkaline earth metals, for example). As an example, \( \text{Hg}^{2+} \) has an ionic radius (C.N. = 6) of 115 pm, yet it is considerably more polarizing and its compounds are considerably more covalent than those of \( \text{Ca}^{2+} \) with almost identical size (114 pm) and the same charge.

One of the most common examples of covalency resulting from polarization can be seen in the melting and boiling points of compounds of various metals. Comparing the melting points of compounds having the same anion, but cations of different size, we have \( \text{BeCl}_2 = 405 ^\circ \text{C} \), \( \text{CaCl}_2 = 782 ^\circ \text{C} \); for cations of different charge, we have \( \text{NaBr} = 747 ^\circ \text{C} \), \( \text{MgBr}_2 = 700 ^\circ \text{C} \), \( \text{AlBr}_3 = 97.5 ^\circ \text{C} \); and for anions of different charges, we have \( \text{LiF} = 845 ^\circ \text{C} \), \( \text{LiCl} = 605 ^\circ \text{C} \), \( \text{LiBr} = 550 ^\circ \text{C} \), \( \text{LiI} = 439 ^\circ \text{C} \), and for ions having the same size and charge, the effect of electron configuration can be seen from \( \text{CaCl}_2 = 782 ^\circ \text{C} \), \( \text{HgCl}_2 = 278 ^\circ \text{C} \). Care must be taken not to interpret melting points and boiling points too literally as indicators of the degree of covalency bonding, there are many effects operative in addition to covalency and these will be discussed at some length in Chapter 8.

A second area in which polarization effects show up is the solubility of salts in polar solvents such as water. For example, consider the silver halides, in which we have silver fluoride, which is quite ionic, is soluble in water, but the less ionic silver chloride is soluble only with the inducement of complexing ammonia. Silver bromide is only slightly soluble and silver iodide is insoluble even with the addition of ammonia. Increasing covalency from fluoride to iodide is expected and decreasing solubility in water is observed.
prepared by Martin and coworkers. These, as well as related phosphoranes, provide interesting insight into certain molecular rearrangements (see page 240).

Bent's rule is also consistent with, and may provide alternative rationalization for, Gillespie's VSEPR model. Thus the Bent's rule predication that highly electronegative substituents will "attract" $p$ character and reduce bond angles is compatible with the reduction in angular volume of the bonding pair when held tightly by an electronegative substituent. Strong, $p$-rich covalent bonds require a larger volume in which to bond. Thus, doubly bonded oxygen, despite the high electronegativity of oxygen, seeks $p$-rich orbitals because of the shortness and better overlap of the double bond. Again, the explanation, whether in purely $p$-character terms (Bent's rule) or in larger angular volume for a double bond (VSEPR), predicts the correct structure.

It is sometimes philosophically unsettling to have multiple "explanations" when we are trying to understand what molecules behave as they do. It is only human "to want to know for sure" why things happen. On the other hand, alternative, nonconflicting hypotheses give us additional ways of remembering and predicting facts, and if we seem to find them in conflict, we have made either: (1) a mistake (which is good to catch) or (2) a discovery!

The mechanism operating behind Bent's rule is not completely clear. One factor favoring increased $p$ character in electronegative substituents is the decreased bond angles of $p$ orbitals and the decreased steric requirements of electronegative substituents. There may also be an optimum "strategy" of bonding for a molecule in which $p$ character (and hence improved overlap) is concentrated in those bonds in which the electronegativity difference is small and covalent bonding is important. The $p$ character, if any, is then directed toward bonds to electronegative groups. The latter will result in greater ionic bonding in a situation in which covalent bonding would be less anyway (because of electronegativity differences). Some light may be shed on the workings of Bent's rule by observations of apparent exceptions to it. The rare exceptions to broadly useful rules are unfortunate with respect to the universal application of those rules. They also have the annoying tendency to be confusing to someone who is encountering the rule for the first time. On the other hand, any such exception or apparent exception is a boon to the research scientist since it almost always provides insight into the mechanism operating behind the rule. Consider the cyclic bromophosphate ester:

![Cyclic Bromophosphate Ester](image)

The phosphorus atom is in an approximately tetrahedral environment using four $s$ bonds of approximately $sp^3$ character. We should expect the more electronegative oxygen atoms to bond to $s$-poor orbitals on the phosphorus and the two oxygen atoms in the ring do attract hybridizations of about $20\%$. The most electronegative substituents on the phosphorus is the bromine atom and Bent's rule would predict an $s$-rich orbital, but instead it draws another $s$-poor orbital, slightly less than $20\%$. The only $s$-rich orbital on the phosphorus atom is that involved in the $s$ bond to the exocyclic oxygen atom. This orbit is nearly $45\%$ $p$ character! This oxygen ought to be about as electronegative as the other two, so why the difference? The answer probably lies in the overlap aspect: (1) The large bromine atom has diffuse orbitals that overlap poorly with the relatively small phosphorus atom; thus, even though the bromine is less electronegative than the oxygen, it probably does not form as strong a covalent bond. (2) The presence of a $s$ bond shortens the exocyclic double bond and increases the overlap of the $s$ orbitals. If molecules respond to increases in overlap by rehybridization in order to profit from it, the increased $s$ character then becomes reasonable. From this point of view, Bent's rule, might be reworded: The $p$ character tends to concentrate in orbitals for a double bond (VSEPR), predicts the correct structure.

For anyone who has encountered steric hindrance in organic chemistry, the emphasis thus far placed on electronic effects as almost the only determinant must seem puzzling. However, the predominance of electronic over steric effects can be rationalized in terms of the following points: (1) Even the largest "inorganic atomic substituent," the iodine atom, is no larger than a methyl group (see Table 8.1 for van der Waals radii), to say nothing of $s$-butyl or $s$-diorthosubstituted phenyl groups. (2) The wider range of hybridizations, the larger variety of varying electronegativities, and the greater importance of small molecules all combine to enhance electronic effects, so much so, in fact, that it is easy to forget nonbonded interactions in the discussion of electron-pair repulsions, overlap, etc., in the preceding sections. Bartell has called attention to the importance of nonbonded repulsions and to the situations in which they may be expected to be important. In general, the latter are apt to be molecules in which a small central atom is surrounded by large substituent atoms. Consider the water molecule, for example, with a bond angle of $104.5^\circ$. Replacing the hydrogen atoms with more electronegative halogen atoms should reduce the bond angle in terms of either Bent's rule or VSEPR-electron geometry models (rule 4, page 217). Indeed, $OF_2$ has a slightly smaller bond angle, $103.2^\circ$. On the other hand, the bond angle in $Cl_2O$ is larger than tetrahedral; it is $110.8^\circ$. Similarly, in the halofluorines

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37 For a review, see Martin, J. C. Science 1983, 221, 509-514.
38 For a further discussion of ionic versus covalent bonding and the total bond energy resulting from the sum of the two, see Chapter 5, "Electronegativity and Modern Bonding."
39 In addition to the example given here, see Problem 6.12.

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42 Bartell, L. S., J. Chem. Educ. 1968, 45, 754-767. This is another example of the principle that if overlap is included, nonbonding orbitals are more destabilizing than the corresponding bonding orbitals are stabilizing. Nonbonded repulsions are merely another name for describing the forced overlap of two orbitals already filled with electrons and the destabilization that occurs as the nonbonding orbital rises in energy faster than the bonding one lowers.
In this case the reason for the correlation is fairly obvious. The parameter \( r_{\text{eff}} \) is equal to the ionic radius plus a constant, 85 pm, the radius of the oxygen atom in water. Therefore, \( r_{\text{eff}} \) is effectively the interionic distance in the hydrate, and the Born-Lande equation (Eq. 4.13) can be applied.

A third, and perhaps the most fundamental, aspect of polarization can be seen in the bond lengths of silver halides. If we predict these distances using the ionic radii of Table 4.4, our accuracy decreases markedly in the direction AgF > AgCl > AgBr > AgI:

<table>
<thead>
<tr>
<th>Compound</th>
<th>( r^+ + r^- )</th>
<th>( r_{\text{exp}} )</th>
<th>( \Delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgF</td>
<td>248</td>
<td>246</td>
<td>-2</td>
</tr>
<tr>
<td>AgCl</td>
<td>296</td>
<td>277</td>
<td>-19</td>
</tr>
<tr>
<td>AgBr</td>
<td>311</td>
<td>289</td>
<td>-22</td>
</tr>
<tr>
<td>AgI</td>
<td>320</td>
<td>281</td>
<td>-39</td>
</tr>
</tbody>
</table>

The Shannon-Prewitt ionic radii \( (r^+ + r^-) \) are based on the most ionic compounds, the fluorides and oxides for the radii of the metal cations, and the alkali halides for the radii of the anions of the remaining halides. The shortening of silver halide bond lengths is attributable to polarization and covalency.

The basis for other correlations between size, charge, and chemical properties is not so clearcut. Chemical reactions can often be rationalized in terms of the polarizing power of a particular cation. In the alkaline earth carbonates, for example, there is a tendency toward decomposition with the evolution of carbon dioxide:

\[
\text{MCO}_3 \rightarrow \text{MO} + \text{CO}_2
\]

The ease with which this reaction proceeds (as indicated by the temperature necessary to induce it) decreases with increasing cation size: BeCO\(_3\), unstable; MgCO\(_3\), 350 °C; CaCO\(_3\), 900 °C; SrCO\(_3\), 1290 °C; BaCO\(_3\), 1360 °C. The effect of d electrons is also clear: Both CoCO\(_3\) and PbCO\(_3\) decompose at approximately 350 °C despite the fact that Co\(^{2+}\) and Pb\(^{2+}\) are approximately the same size as Ce\(^{2+}\). The decomposition of these carbonates occurs as the cation polarizes the carbonate ion, splitting it into an \( \text{O}^{2-} \) ion and \( \text{CO}_2 \).

Stern\(^{37}\) has extended the qualitative argument on decomposition by showing that the enthalpies of decomposition of carbonates, sulfates, nitrates, and phosphates are linearly related to a charge/size function, in this case \( r^+ Z^+ \) (see Fig. 4.21). Although the exact theoretical basis of this correlation is not clear, it provides another interesting example of the general principle that size and charge are the important factors that govern the polarizing power of ions and, consequently, many of their chemical properties.

From the preceding, it might be supposed that covalent character in predominantly ionic compounds always destabilizes the compound. This is not so. Instability results from polarization of the anion causing it to split into a more stable compound (in the above cases the oxides) with the release of gaseous acidic anhydrides. As will be seen in Chapter 16, many very stable, very hard minerals have covalent-ionic bonding.

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In the phosphorus atom there is little initial promotion energy: the ground state is trivalent, as is the valence state. Note that any hybridization will cost energy as a filled 3s orbital is raised in energy and half-filled 3p orbitals are lowered in energy:

\[ \text{Energy increases} \quad 3p \rightarrow \text{Charge in energy} \quad \(entry) \quad 3p \]

This energy of hybridization is of the order of magnitude of bond energies and can thus be important in determining the structure of molecules. It is responsible for the tendency of some lone pairs to occupy spherical, nontetrahedrally active p orbitals rather than sterically active hybrid orbitals (see page 215). For example, the hydrides of the Group VA (15) and VIA (16) elements are found to have bond angles considerably reduced as one progresses from the first element in each group to those that follow (Table 6.4). An energy factor that favors reduction in bond angle in these compounds is the hybridization discussed above. It costs about 600 \( \text{kJ mol}^{-1} \) to hybridize the central phosphorus atom. From the standpoint of this energy factor alone, the most stable arrangement would be utilizing pure p orbitals in bonding and letting the lone pair "sink" into a pure s orbital. Opposing this tendency is the repulsion of electrons, both bonding and nonbonding (VSEPR). This favors an approximately tetrahedral arrangement. In the case of the elements N and O the steric effects are most pronounced because of the small size of atoms of these elements. In the larger atoms, such as those of P, As, Sb, Se, and Te, these effects are somewhat relaxed, allowing the reduced hybridization energy of more p character in the bonding orbitals to come into play.

Another factor which affects the most stable arrangement of the atom in a molecule is the variation of bond energy with hybridization. The directed lobes of \( s-p \) hybrid orbitals overlap more effectively than the undirected \( s \) orbitals, the two lobed \( p \) orbitals, or the diffuse \( d \) orbitals. The increased overlap results in stronger bonds.

**Table 6.4**

| Bond angles in the hydrides of Groups VA (15) and VIA (16) |
|-------------------|-------------------|-------------------|-------------------|-------------------|
| \( \text{NH}_3 \)  | 101.2°            | \( \text{PH}_3 \)  | 91.8°            | \( \text{AsH}_3 \) | 91.8°            | \( \text{SbH}_3 \) | 91.3°            |
| \( \text{CH}_2 \)  | 104.5°            | \( \text{SH}_2 \)  | 92°              | \( \text{SeH}_2 \) | 91°              | \( \text{TeH}_2 \) | 89.5°            |

Problems

4.1 Both CsCl and CaF₂ exhibit a coordination number of 8 for the cations. What is the structural relationship between these two lattices?

4.2 The contents of the unit cell of any compound must contain an integral number of formula units. (Why?) Notice that unit cell boundaries "slice" atoms into fragments. An atom on a face will be split into quarters among four cells, etc. Identify the number of Na⁺ and Cl⁻ ions in the unit cell of sodium chloride illustrated in Fig. 4.1a and state how many formula units of NaCl the unit cell contains. Give a complete analysis.

4.3 The measured density of sodium chloride is 2.167 g cm⁻³. From your answer to Problem 4.2 and your knowledge of the relationships among density, volume, Avogadro’s number, and formula weight, calculate the volume of the unit cell and thence the length of the edge of the cell. Calculate the length r₁ + r₂ for Na⁺ and Cl⁻. Check your answer, r₁ + r₂, against values from Table 4.4.

4.4 Study Figs. 4.1–4.3 and convince yourself of the structural relationship of all of the cubic structures and of all of the hexagonal structures.

4.5 The structure of diamond, a covalent crystal, is shown in Fig. 7.1. How is it related to some of the structures of ionic compounds discussed in this chapter?

4.6 What simple mathematical relationship exists between the empirical formula, numbers of cations and anions in the unit cell, and the coordination numbers of the cations and anions in a binary metal halide, MX₂?

4.7 If you did not do Problem 2.21 when you read Chapter 2, do so now.

4.8 One generalization of the descriptive chemistry of the transition metals is that the heavier congeners (e.g., Mo, W) more readily show the highest oxidation state than does the lightest congener (e.g., Cr). Discuss this in terms of transition energies.

4.9 Show your understanding of the Born-Haber cycle by calculating the heat of formation of potassium fluoride analogous to the one in the text for sodium chloride.

4.10 Using any necessary data from appropriate sources, predict the enthalpy of formation of CsCl by means of a Born-Haber cycle. You can check your lattice energy against Table 4.1.

4.11 Using any necessary data from appropriate sources, predict the enthalpy of formation of CaS by means of a Born-Haber cycle.

4.12 Show your understanding of the meaning of the Madelung constant by calculating k for the isolated F⁻Be⁺F⁻ fragment considered as a purely ionic species.

4.13 The ionic bond is often described as "the metal wants to lose an electron and the non-metal wants to accept an electron, so the two react with each other." Criticize this statement quantitatively using appropriate thermodynamic quantities.

4.14 Why is the thermite reaction:

\[ 2\text{Al} + 3\text{MgO} = 2\text{Mg} + \text{Al}_2\text{O}_3 \quad (M = \text{Fe}, \text{Cr}, \text{etc.}) \]  

so violently exothermic? (The ingredients start at room temperature and the metallic product, iron, e.g., is molten at the end of the reaction.)

4.15 We have seen, in Chapter 2, that platinum hexafluoride has an electron affinity more than twice as great as fluorine. Yet when lithium metal reacts with platinum hexafluoride, the crystalline product is LiF·F²⁻, not Li²⁺·F₆⁻. Explain.

4.16 To change Mg to Mg⁺⁺ costs two times as much energy as to form Mg²⁺. The formation of Mg⁺⁺ is endothermic rather than exothermic as for O²⁻. Nevertheless, magnesium oxide is always formulated as MgO·O²⁻ rather than as Mg²⁺·O²⁻. Explain:

a. What theoretical reason can be given for the MgO·O²⁻ formulation?

b. What simple experiment could be performed to prove that magnesium oxide was not Mg²⁺·O²⁻?

4.17 Some experimental values of the Born exponent are: LiF, 6.9; LiCl, 8.0; LiBr, 8.5; NaCl, 9.1; NaBr, 9.5. What is the percent error incurred in the calculation of lattice energies by Eq. 4.13 when Pauling’s generalization (He = 5, Ne = 7, etc.) is used instead of the experimental value of α?

4.18 Using Fig. 4.7 generate the first five terms of the series for the Madelung constant for NaCl. How close is the summation of these terms to the limiting value given in Table 4.1?

4.19 The enthalpy of formation of sodium fluoride is -771 kJ mol⁻¹. Estimate the electron affinity of fluorine. Compare your value with that given in Table 2.3.

Conclusion

Ionic crystals may be viewed quite simply in terms of an electrostatic model of lattices of hard-sphere ions of opposing charges. Although conceptually simple, this model is not completely adequate, and we have seen that modifications must be made in it. First, the bonding is not completely ionic with compounds ranging from the alkali halides, for which complete ionicity is a very good approximation, to compounds for which the assumption of the presence of ions is rather poor. Secondly, the assumption halides, for which complete ionicity is a very good approximation, to compounds for which the assumption of the presence of ions is rather poor. Secondly, the assumption of hard-sphere ions of opposing charges. Although conceptually simple, this model is not completely adequate, and we have seen that modifications must be made in it.

Problems

4.1 Both CsCl and CaF₂ exhibit a coordination number of 8 for the cations. What is the structural relationship between these two lattices?

4.2 The contents of the unit cell of any compound must contain an integral number of formula units. (Why?) Notice that unit cell boundaries "slice" atoms into fragments. An atom on a face will be split into quarters among four cells, etc. Identify the number of Na⁺ and Cl⁻ ions in the unit cell of sodium chloride illustrated in Fig. 4.1a and state how many formula units of NaCl the unit cell contains. Give a complete analysis.

4.3 The measured density of sodium chloride is 2.167 g cm⁻³. From your answer to Problem 4.2 and your knowledge of the relationships among density, volume, Avogadro’s number, and formula weight, calculate the volume of the unit cell and thence the length of the edge of the cell. Calculate the length r₁ + r₂ for Na⁺ and Cl⁻. Check your answer, r₁ + r₂, against values from Table 4.4.

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### Table 6.3

<table>
<thead>
<tr>
<th>Compound</th>
<th>Dihedral angles in the ML complex</th>
<th>Dihedral angle of the ideal structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal trigonal bipyramid</td>
<td>63.1, 53.1, 53.1</td>
<td>53.1</td>
</tr>
<tr>
<td>CdCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>63.8, 53.8, 53.8</td>
<td>53.1</td>
</tr>
<tr>
<td>Ni(CN)&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>64.2, 64.2, 64.2</td>
<td>64.2</td>
</tr>
<tr>
<td>Ni(CN)&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>65.4, 67.0</td>
<td>70.2</td>
</tr>
<tr>
<td>Ni(CN)&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>68.5, 69.2, 68.5</td>
<td>68.5</td>
</tr>
<tr>
<td>Co(CH&lt;sub&gt;3&lt;/sub&gt;NO)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>70.2, 70.2, 70.2</td>
<td>70.2</td>
</tr>
<tr>
<td>Ni(CN)&lt;sub&gt;2&lt;/sub&gt;Ni&lt;sub&gt;2&lt;/sub&gt;</td>
<td>75.0, 79.4, 75.0</td>
<td>75.0</td>
</tr>
</tbody>
</table>

*These two structures occur in the unit cell of the Cr(CN)<sub>5</sub> salt.

---

**Fig. 6.18** Real five-coordinate molecular structures illustrating intermediates between TBP (CN)<sub>5</sub> and the ideal trigonal bipyramid (TBP) (CN)<sub>5</sub>. The Cr(CN)<sub>5</sub> salt is shown in the context of Table 6.3. The dihedral angles are given in the TBP complex. The ideal trigonal bipyramid structure is also shown. (From Munterties, E. E., Guggenberger, L. J., 1974, J. Am. Chem. Soc. 96, 1748-1756. Used with permission.)

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**Fig. 6.19** Directional properties of hybrid orbitals from s, p, and d atomic orbitals. (From Kasha, M.; adapted from Kimball, G. Ann. Rev. Phys. Chem. 1981, 2, 177. Reproduced with permission.)

---

In the case of d orbitals, the relation between hybridization and bond angles is given in Fig. 6.19, although the accuracy is somewhat less than can be obtained from computation. For completely nonequivalent hybrid orbitals, simultaneous equations involving all of the bond angles and hybridizations may be solved.7

When a set of hybrid orbitals is constructed by a linear combination of atomic orbitals, the energy of the resulting hybrids is a weighted average of the energies of the participating atomic orbitals. For example, when carbon forms four covalent bonds, although there is a promotion energy from 1s<sup>2</sup>2p<sup>2</sup>, this is independent of the hybridization to the valence state.22

---

22 The levels shown are one-electron levels and do not show correlation effects. See discussion of the energetics of the valence state. Chapter 5.
4.20 Calculate the proton affinities of the halide ions. The enthalpies in question are those of
the type:
\[
X^- + \text{H}^+ \rightarrow \text{HX}
\]
Compare your values with those given in Table 9.5.

4.21 Perform radius ratio calculations to show which alkali halides violate the radius ratio
rule.

4.22 Even if there are exceptions to the radius ratio rule, or if exact data are hard to come by,
it is still a valid guiding principle. Give three independent examples of pairs of compounds
illustrating structural differences resulting from differences in ionic radii.

4.23 Berkelium is currently available in microgram quantities—sufficient to determine struc-
tural parameters but not enough for thermochemical measurements.

4.24 The crystal structure of LaF₃ is different from those discussed. Assume it is unknown.

4.25 Copper(I) halides crystallize in a zinc blende structure. Copper(II) fluoride crystallizes in ;
the type:

4.26 Thallium has two stable oxidation states, +1 and +3. Use the Kapustinskii equation to
to predict the lattice energies of TiF and TiF₃. Predict the enthalpies of formation of
these compounds. Discuss.

4.27 Plot the radii of the lanthanide(III) (La³⁺) ions from Table 4.4 versus atomic number.
Discuss.

4.28 All of the alkaline earth oxides, MO, except one crystallize in the rock salt (NaCl) struc-
ture. What is the exception and what is the likely structure for it? (Wells, A. F. Structural

4.29 It is not difficult to show mathematically that with the hard sphere model, solution-the-
nonion contact occurs at \( r/\sigma = 0.414 \) for C.N. = 6. Yet Wells (Structural Inorganic Chemistry,
5th ed.; Oxford University: Oxford, 1984) states that even with the hard sphere model, we
should not expect the change to take place until \( r/\sigma = 0.55 \). Rationalize this apparent
contradiction. (Hein, G. C.: Fig. 4.17.)

4.30 There exists the possibility that a certain circularity may develop in the radius ratio
spectrum. What is the exception and what is the likely structure for it? (Wells, A. F.

4.31 Perform a calculation similar to that on page 127 for the formation of dioxygenyl

dioxide, \( \text{O}_2 \text{O}^+ \text{O}^- \). Carefully list any assumptions.

4.32 Repeat the calculation in Problem 4.31, but for the reaction:

\[
\text{Xe} + \text{PrF} \rightarrow \text{Xe}^+ \text{PrF}^- \]

Should xenon react with platinum hexafluoride?

4.33 Suppose that someone argues with you that you answer to Problem 4.32 is invalid, and
that any prediction that Neil Bartlett might have made based on the same reasoning
(see Chapter 17) is equally invalid—he was just lucky—the reaction product of Eq. 4.31
is not a simple ionic compound, XeF₂PrF, but a mixture of compounds, and apparently
the xenon is covalently bound. What is your reply?

4.34 Calculate the enthalpy of the reaction \( \text{CuF} \rightarrow \text{CuF}_2 + \text{F}^- \). Carefully list any assumptions.

4.35 Which of the following will exhibit the greater polarizing power?

a. \( \text{K}^+ \) or \( \text{Ag}^+ \)

b. \( \text{X}^+ \) or \( \text{Li}^+ \)

c. \( \text{Li}^+ \) or \( \text{Be}^2+ \)

d. \( \text{Cu}^+ \) or \( \text{Ca}^2+ \)

e. \( \text{Ti}^3+ \) or \( \text{Ti}^4+ \)

4.36 As one progresses across a transition series (e.g., Se to Zn) the polarizing power of M⁺
ions increases perceptibly. In contrast, in the lanthanides, the change in polarizing power of M⁺
changes much more slowly. Suggest two reasons for this difference.

4.37 Some general chemistry textbooks say that if a fluorine atom, Z = 9, gains an electron, it
will become a fluoride ion with ten electrons that cannot be bound as tightly (because of
electron-electron repulsion) as the nine of the neutral atom, so the radius of the fluoride
will become a fluoride ion with ten electrons that cannot be bound as tightly (because of
electron-electron repulsion) as the nine of the neutral atom, so the radius of the fluoride
ion (119 pm) is much greater than the radius of the neutral fluorine atom (71 pm). Discuss
and criticize.

4.38 If the addition of an electron \( F^- \rightarrow F^- \) causes a great increase in size, why does not the
addition of two electrons to form the oxide \( \text{O}_2 \text{O}^- \) cause it to be much
larger than the fluoride ion \( \text{F}^- \) (r = 119 pm)?

4.39 A single crystal of sodium chloride for an X-ray structure determination is a cube 0.3 mm
on a side. Use data from Table 4.4, calculate how many unit cells are contained in this crystal.

4.40 There has been a recent flurry of interest in the possibility of "cold fusion of hydrogen
atoms (the deuterium isotope) in metallic palladium. The original idea came from the
enormous solubility of hydrogen gas in palladium. Palladium metal has an fcc lattice.
Hydrogen atoms occupy the octahedral holes. If 70% of the octahedral holes are filled
by hydrogen atoms and the lattice does not expand upon hydrogenation, how many
grams of hydrogen will be contained in one cubic centimeter of the palladium hydride?
Compare this to the density of liquid hydrogen in g cm⁻³. Comment. (Rieck, D. P. J. F.

4.41 Mingos and Rolfs have discussed the packing of molecular ions in terms of their shape
as well as size. Three indices, each ranging in value from 0.00 to 1.00, are used to describe
these compounds. Discuss.

- a. \( \text{Ni}^+ \), \( \text{Na}^+ \), \( \text{BF}_3 \), \( \text{ClO}_4^- \); \( \text{Td} \), \( \text{Pm} \), \( \text{Cs} \) all have values \( F_1 = 1.00, F_2 = 0.00, F_3 = 0.00 \).

- b. \( \text{As}^\text{III} \), \( \text{I}^\text{I} \), \( \text{P} \) each have values \( F_1 = 0.50, F_2 = 0.50, F_3 = 0.50 \).

- c. \( \text{AuCl}_3^- \), \( \text{PtCl}_2^- \) \( \text{D}_{19} \) both have values \( F_1 = 0.00, F_2 = 0.50, F_3 = 0.50, F_4 = 0.50 \).

- d. \( \text{Ni}^\text{II} \), \( \text{Ni}^\text{III} \), \( \text{Ni}^\text{IV} \) each have values \( F_1 = 0.50, F_2 = 0.50, F_3 = 0.50 \),

Thus the values are \( F_1 = 0.50, F_2 = 0.50, F_3 = 0.50 \).

- e. \( \text{AuBr}_3^- \), \( \text{PtCl}_2^- \) \( \text{D}_{19} \) both have values \( F_1 = 0.00, F_2 = 0.50, F_3 = 0.50, F_4 = 0.50 \).

- f. \( \text{Ni}^\text{II} \), \( \text{Ni}^\text{III} \), \( \text{Ni}^\text{IV} \) each have values \( F_1 = 0.50, F_2 = 0.50, F_3 = 0.50 \),


3419-3425.
orbits are not equivalent. We shall see that the trigonal bipyramidal hybridization results in three strong equatorial bonds (sp$^3$ trigonal orbitals) and two weaker axial bonds (dp linear orbitals). The square pyramidal hybridization is approximately a square planar dp set plus the p$_z$ orbital. As in the trigonal bipyramidal hybridization, the bond lengths and strengths are different.

The relation between hybridization and bond angle is simple for s-p hybrids. For two or more equivalent orbitals, the percent s character ($S$) is given by the relationship:[27]

$$\cos \theta = \frac{S}{1 + P}$$

where $\theta$ is the angle between the equivalent orbitals (°) and the $s$ and $p$ characters are expressed as decimal fractions. In methane, for example,

$$\cos \theta = \frac{0.25}{1 + 0.80} = 0.333; \quad \theta = 109.5^\circ$$

In hybridizations involving nonequivalent hybrid orbitals, such as sp$^3$d, it is usually possible to resolve the set of hybrid orbitals into subsets of orbitals that are equivalent within the subset, as the sp$^3$ subset and the dp subset. We have seen (Chapter 5) that the nonequivalent hybrids may contain fractional s and p character, e.g., the water molecule which uses bonding orbitals midway between pure p and sp$^3$ hybrid orbitals.

For molecules such as this, we can divide the four orbitals into the bonding subset (the bond angle is 104°) and the nonbonding subset (angle unknown). We can then apply Eq. 6.1 to each subset of equivalent orbitals. In water, for example, the bond angle is 104°, so

$$\cos \theta = \frac{0.250}{1 + 0.80} = \frac{0.25}{0.80} = 0.3125; \quad \theta = 104.7^\circ$$

Now of course the total p character summed over all four orbitals on oxygen must be 1.00 ($p_s + p_p = p$) and the total s character must be 1.00. If the bonding orbitals contain proportionately more p character, then the nonbonding orbitals (the two lone pairs) must contain proportionately less p character, 70%: 0.80 + 0.80 + 0.70 + 0.70 = 3.00 (p); 0.20 + 0.20 + 0.30 + 0.30 = 1.00 (s)). The opening of some bond angles and closing of others in nominally "tetrahedral" molecules is a common phenomenon. Usually the distortion is only a few degrees, but it should remind us that the terms "trigonal," "tetrahedral," etc. are only approximations. Exactly trigonal and tetrahedral hybridizations are probably restricted to molecules such as BCl$_3$ and CH$_4$, in which all the substituents on the central atom are identical. We see

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27 Equation 6.1 is restricted to molecules such as water in which the angle is known between two equivalent orbitals (e.g., the two orbitals bonding the hydrogen atoms). Equivalent and nonequivalent hybrids are discussed further on page 227. See Benesi, W. A.; Lauter, W., Angew. Chem. 1961, 25, 909-911; Belser, M. B., Jr.; Gibb, G. V., Phys. Chem. Minerals 1967, 14, 372-375; Grim, S. G., Platts, H. J.; Hubeny, C. L.; Hubeny, J. E., Phys. Minerals 1971, 1, 61-66. See also McWeeny, R. Coulson's Valence; Oxford University: Oxford, 1979, pp 95-198. The validity of this method has been questioned: Magnussen, E. J., Am. Chem. Soc. 1984, 106, 1187-1188. The lack of agreement revolves around the question of the orthogonality of hybrid orbitals.

28 The apparent exception of two stable structures, of TBP and D$_a$ symmetry, for coordination number 4 can be misleading. The square planar structure is known only where there are special stabilizing energies resulting from the 3d electron configuration in transition metal compounds.


Chapter 5

Bonding Models in Inorganic Chemistry:

2. The Covalent Bond

This chapter and the one following will be devoted to a preliminary analysis of covalent bonding. Most of the ideas presented here may be found elsewhere and with greater rigor, and many will have been encountered in previous courses. However, since they form the basis for subsequent chapters, a brief presentation is in order here. Covalent bonding will also be discussed in Chapters 6 and 11.

The Lewis Structure

This method of thinking about bonding, learned in high school and too often forgotten in graduate school or before, is a most useful first step in thinking about molecules. Before delving into quantum mechanical ideas or even deciding whether molecular orbital or valence bond theory is likely to be more helpful, a Lewis structure should be sketched. The following is a brief review of the rules for Lewis structures:

1. Normally two electrons pair up to form each bond. This is a consequence of the Pauli exclusion principle—two electrons must have paired spins if they are both to occupy the same region of space between the nuclei and thereby attract both nuclei. The definition of a bond as a shared pair of electrons, however, is overly restrictive, and we shall see that the early emphasis on electron pairing in bond formation is unnecessary and even misleading.

2. For most atoms there will be a maximum of eight electrons in the valence shell (= Lewis octet structure). This is absolutely necessary for atoms of the elements lithium through fluorine since they have only four orbitals (an s and three p orbitals) in the valence shell. It is quite common, as well, for atoms of other elements to utilize only their s and p orbitals. Under these conditions the sum of shared pairs (bonds) and unshared pairs (lone pairs) must equal the number of orbitals—four. This is the maximum, and for elements having fewer than four valence electrons, the octet will usually not be filled. The following compounds illustrate these possibilities:

3. For elements with available d orbitals, the valence shell can be expanded beyond an octet. Because orbitals first appear in the third energy level, they are too low in energy to be available for bonding in elements of Period 2 and beyond. These elements are nonmetals in the higher valence compounds and transition metals in complexes. In the nonmetals, where the number of valence electrons is usually the limiting factor, we have maximum covalencies of 5, 6, 7, and 8 in Groups VA (15), VIA (16), VIIA (17), and VIIIA (18), respectively. Note that covalency (the number of covalent bonds to an atom) and coordination number (the number of atoms bound to another atom) are not always the same. Factors determining covalencies and coordination numbers in complexes are of several kinds, and discussion of them will be deferred. Examples of molecules and ions containing more than eight electrons in the valence shell of the central atom are:

4. It has been assumed implicitly in all of these rules that the molecule will seek the lowest overall energy. This means that, in general, the maximum number of bonds will form, that the strongest possible bonds will form, and that the arrangement of the atoms in the molecule will be such as to minimize adverse repulsion energies.

Valence Bond Theory

In modern times there have been two "contenders for the throne" of bonding theory: valence bond theory (VBT) and molecular orbital theory (MOT). The allusion is apt since it seems that much of the history of these two theories consisted of contention between their respective proponents as to which was best. Sometimes overzealous supporters of one theory have given the impression that the other is "wrong." Granted that any theory can be used unwisely, it remains nonetheless a fact that neither theory should be regarded as true of the other. Given a specific question one theory may prove distinctly superior in insight, ease of calculation, or simplicity and clarity of results, but a different question may reverse the picture completely. Surely the inorganic chemist who does not become thoroughly familiar with both theories is like the carpenter who refuses to carry a saw because he already has a hammer! Both are severely limiting their skills by limiting their tools.

Valence Bond Theory grew directly out of the ideas of electron pairing by Lewis and others. In 1927 W. Heitler and F. London proposed a quantum-mechanical treatment of the hydrogen molecule. Their method has come to be known as the valence bond approach and was developed extensively by many such as Linus Pauling.
MO configuration will be $2\alpha_{1g}^2, 1\sigma_{u}^2, 1\pi_{e}^2, 1\pi_{o}^2$ for $2\alpha_1^2\beta_2^2\beta_3^2\beta_4^2$. Because the formerly nonbonding $1\pi_{o}$ orbital is greatly stabilized ($3\alpha$), on bending, the water molecule is bent rather than linear.

The Walsh diagram shown in Fig. 6.16 is accurate only for molecules in which there is a large separation between the $ns$ and $np$ energy levels of the central atom. If the $ns$-$np$ separation is small (as in $\text{SrF}_2$ and $\text{BaF}_2$), the $1\beta_2$ level (of Fig. 6.16) does not rise as rapidly as $3\alpha$, falls, and the molecule may be stabilized on bending. Note that in $\text{MF}_2$ molecules of this type, the $3\alpha$ and $1\beta_1$ levels are unoccupied.

This brief discussion cannot do justice to the MO approach to stereochemistry, but it does illustrate the reduced importance of electron-electron repulsions (usually omitted in simple approximations) and the increased importance of overlap in this approach. Although the VSEPR approach and the LCAO-MO approach to stereochemistry appear on the surface to be very different, all valid theories of bonding, when carried sufficiently far, are in agreement that the most stable molecule will have the best compromise of (1) maximizing electron-nucleus attractions and (2) minimizing electron-electron repulsions.

As we have seen in Chapter 5, it is not correct to say that a particular structure is "caused" by a particular hybridization, though such factors as overlap and energy are related to hybridization. We have also seen the usefulness of viewing structures in terms of VSEPR. We shall encounter yet further factors later in this chapter. Nevertheless it is appropriate and useful to note here that certain structures and hybridizations are associated with each other. Some of the most common geometries and their corresponding hybridizations are shown in Fig. 6.17. In addition, there are many hybridizations possible for higher coordination numbers, but they are less frequently encountered and will be introduced as needed in later discussions.

The possible structures may be classified in terms of the coordination number of the central atom and the symmetry of the resulting molecule (Fig. 6.17). Two groups about a central atom will form angular (2p orbitals, $C_2v$ symmetry) or linear (sp hybrid, $D_{\infty h}$ symmetry) molecules; three will form pyramidal ($3p_2$, $C_3v$ symmetry) or trigonal planar ($3p_3$, $D_3h$) molecules; four will usually form tetrahedral ($4p$, $T_d$) or square planar ($4d$, $D_{4h}$) molecules; five usually form a trigonal bipyramidal ($5p$, $D_{5h}$), more rarely a square pyramidal ($5p$, $C_{5v}$) molecule (both $5d$ hybrids, but using different orbitals, see Table 6.2); and six groups will usually form an octahedral molecule ($6p$, $O_h$).

If in addition to the bonding pairs there are stereochemically active lone pairs, the symmetry will be lowered ($\text{BF}_3$ is $D_{3h}$, $\text{NF}_3$ is $C_3v$). Furthermore, the hybridization of the lone pair(s) will be different from that of the bonding pairs (see below).

Most hybridizations result in equivalent hybrid orbitals, i.e., all the hybrid orbitals are identical in composition ($\frac{1}{2} s$ and $\frac{1}{2} p$ character) and in spatial orientation with respect to each other. They have very high symmetries, culminating in tetrahedral and octahedral symmetry. In the case of $4p$ hybrids, the resulting

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**Table 6.2**

<table>
<thead>
<tr>
<th>Hybridization</th>
<th>Atomic orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td>$sp$, $sp^2$, $sp^3$</td>
<td>$s$ + arbitrary $p^*$</td>
</tr>
<tr>
<td>$3p^2$</td>
<td>$d_{x^2-y^2}$ + $s$ + $p_x$ + $p_y$</td>
</tr>
<tr>
<td>$4p^2$ (TBP)</td>
<td>$d_{x^2-y^2}$ + $s$ + $p_x$ + $p_y$ + $p_z$</td>
</tr>
<tr>
<td>$4p^2$ (ISP)</td>
<td>$d_{x^2-y^2}$ + $s$ + $p_x$ + $p_y$ + $p_z$</td>
</tr>
<tr>
<td>$5p^2$</td>
<td>$d_{x^2-y^2}$ + $s$ + $p_x$ + $p_y$ + $p_z$ + $p_w$</td>
</tr>
</tbody>
</table>

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and J. C. Slater. The following discussion is adapted from the works of Pauling and Coulson.1

Suppose we have two isolated hydrogen atoms. We may describe them by the wave functions \( \psi_A \) and \( \psi_B \), each having the form given in Chapter 2 for a 1s orbital. If the atoms are sufficiently isolated so that they do not interact, the wave function for the system of two atoms is

\[
\psi = \psi_A \psi_B
\]

(5.1)

where \( A \) and \( B \) designate the atoms and the numbers 1 and 2 designate electrons number 1 and 2. Now, we know that when the two atoms are brought together to form a molecule they will affect each other and that the individual wave functions \( \psi_A \) and \( \psi_B \) will change, but we may assume that Eq. 5.1 is a good starting place as a trial function for the hydrogen molecule and then try to improve it. When we solve for energy as a function of distance, we find that the energy curve for Eq. 5.1 does indeed have a minimum (curve a, Fig. 5.1) of about \(-24 \text{ kJ mol}^{-1}\) at a distance of about 90 pm. The actual observed bond distance is 74 pm, which is not too different from our first approximation, but the experimental bond energy of \( \text{H}_2 \) is \(-438 \text{ kJ mol}^{-1}\), almost 20 times greater than our first approximation.

If we examine Eq. 5.1, we must decide that we have been overly restrictive in using it to describe a hydrogen molecule. First, we are not justified in labeling electrons since all electrons are indistinguishable from each other. Moreover, even if we could, we would not be sure that electron 1 will always be on atom A and electron 2 on atom B. We must alter Eq. 5.1 in such a way that the artificial restrictions are removed. We can do this by adding a second term in which the electrons have changed positions:

\[
\psi = \psi_A \psi_B + \psi_B \psi_A
\]

(5.2)

This improvement was suggested by Heitler and London. If we solve for the energy associated with Eq. 5.2, we obtain curve b in Fig. 5.1. The energy has improved greatly \((-303 \text{ kJ mol}^{-1}\)) and also the distance has improved slightly. Since the improvement is a result of our "allowing" the electrons to exchange places, the increase in bonding energy is often termed the exchange energy. One should not be too literal in describing this large part of the bonding energy to "exchange," however, since the lack of exchange in Eq. 5.1 was merely a result of our inaccuracies in approximating a correct molecular wave function. If a physical picture is desired to account for the exchange energy, it is probably best to ascribe the lowering of energy of the molecule to the fact that the electrons now have a larger volume in which to move. Recall that the energy of a particle in a box is inversely related to the size of the box; that is, as the box increases in size, the energy of the particle is lowered. By providing two nuclei at a short distance from each other, we have "enlarged the box" in which the electrons are confined.

A further improvement can be made if we recall that electrons shield each other (Chapter 2) and that the effective atomic number \( Z^* \) will be somewhat less than \( Z \). If we adjust our wave functions, \( \psi_A \) and \( \psi_B \), to account for the shielding from the second electron, we obtain energy curve c—a further improvement.

Lastly, we must again correct our molecular wave function for an overrestriction which we have placed upon it. Although we have allowed the electrons to exchange in Eq. 5.2, we have demanded that they must exchange simultaneously, that is, that only one electron can be associated with a given nucleus at a given time. Obviously this is too restrictive. Although we might suppose that the electrons would tend to avoid one another or else to stay on each atom, we cannot go so far as to say that they will always be in such an arrangement. It is common to call the arrangement given by Eq. 5.2 the "covalent structure" and to consider the influence of "ionic structures" on the overall wave function:

\[
\text{H}^+ + \text{H}^- \rightarrow \text{H}^+\text{H}^- \rightarrow \text{H}_2^+ \rightarrow \text{H}^++\text{H}^-
\]


When we investigate the energetics of the wave function in Eq. 5.3, we find further improvement in energy and distance (curve d, Fig. 5.1).

This is the first example we have had of the phenomenon of resonance, which we shall discuss at some length in the next section. It should be pointed out now, however, that the hydrogen molecule has one structure which is described by one wave function, \( \psi \); however, it may be necessary because of our approximations, to write \( \psi \) as a combination of two or more wave functions, each of which only partially describes the hydrogen molecule. Table 5.1 lists values for the energy and equilibrium distance for the various stages of our approximation, together with the experimental values.

Now, if one wishes, additional "corrections" can be included in our wave function, to make it more nearly descriptive of the actual situation obtained in the
To the above Drago suggested the following empirical rule which rationalizes the very small angles (~90°) in phosphine, arsine, hydrogen sulfide, etc., and which is compatible with the energetics of hybridization (page 225):

5. If the central atom is in the third row or below in the periodic table, the lone pair will occupy a stereochemically inactive s orbital and the bonding will be through p orbitals and near 90° bond angles if the substituent electronegativity is < 2.5.

Because of its intuitive appeal and its high degree of accuracy, the VSEPR model has been well received by inorganic chemists, but the theoretical basis has been a matter of some dispute. More recently, there have been strong theoretical arguments for localized, stereochemically active orbitals. Because VB methods deal with easily visualized, localized orbitals, stereochemical arguments (such as the VSEPR model) have tended to be couched in VB terminology. Several workers have attempted to modify simple LCAO-MO methods to improve their predictive power with respect to geometry. The basis for these methods consists of 

Molecular Orbitals and Molecular Structure

Fig. 6.16 Molecular orbital pictures and qualitative energies of linear and bent $\text{AB}_2$ molecules. Open and shaded areas represent differences in sign (+ or -) of the wave functions. Changes in shape which increase in-phase overlap lower the molecular orbital energy. [From Gimarc, B. M. J. Am. Chem. Soc. 1971, 93, 5933. Reproduced with permission.]

$\text{BeH}_2$ has a molecular orbital electron configuration $2\sigma^2\pi^2\pi^2$ of $\sigma$, or $\sigma$, and since $\sigma$ loses more energy than $\pi$, gains, $\text{BeH}_2$ is linear, not bent.

Similar arguments can be applied to the nonbonding and antibonding orbitals (Fig. 6.16; see Problem 6.7). In the water molecule, $\text{H}_2\text{O}$, with eight valence electrons, the

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21 Drago, R. S. J. Chem. Educ. 1972, 59, 244-245.
Resonance

When using valence bond theory it is often found that more than one acceptable structure can be drawn for a molecule or, more precisely, more than one wave function can be written. We have already seen in the case of the hydrogen molecule that we could formulate it either as H—H or as $\text{H}^+\text{H}^-$. Both are acceptable structures, but the second or ionic form would be considerably higher in energy than the "covalent" structure (because of the high ionization energy and low electron affinity of hydrogen). However, we may write the wave function for the hydrogen molecule as a linear combination of the ionic and covalent functions:

$$\psi = \alpha \phi_{\text{icn}} + \beta \phi_{\text{cov}}$$

where $\alpha$ determines the contribution of the two wave functions. When this is done, it is found that the new wave function is lower in energy than either of the contributing structures. This is a case of covalent-ionic resonance which will be discussed at greater length in the section on electronegativity.

Another type of resonance arises in the case of the carbonate ion. A simple Lewis structure suggests that the ion should have three $\pi$ bonds and one $\sigma$ bond. However, when we come to the placement of the $\sigma$ bond, it becomes obvious that there is no unique way to draw the $\sigma$ bond. There is no a priori reason for choosing one oxygen atom over the other two to receive the $\sigma$ bond. We also find experimentally that it is impossible to distinguish one oxygen atom as being in any way different from the other two.

We can draw three equivalent contributing structures for the carbonate ion:

Each of these structures may be described by a wave function $\phi_1$, $\phi_2$, or $\phi_3$. The actual structure of the carbonate ion is none of the above, but a resonance hybrid formed by a linear combination of the three canonical structures:

$$\psi = a\phi_1 + b\phi_2 + c\phi_3$$

There is no simple Lewis structure that can be drawn to picture the resonance hybrid, but the following gives a qualitative idea of the correct structure:

It is found that the energy of IV is lower than that of I, II, or III. It is common to speak of the difference in energy between I and IV as the resonance energy of the carbonate ion. One should realize, however, that the resonance energy arises only because our wave functions $\phi_1$, $\phi_2$, $\phi_3$ are rather poor descriptions of the actual structure of the ion. In a sense, then, the resonance energy is simply a measure of our ignorance of the true wave function. More accurately, the resonance energy and the entire phenomenon of resonance are merely a result of the overly restrictive approach we have adopted in valence bond theory. In insisting that a "bond" be a localized pair of electrons between two nuclei, we have made certain that we will not encounter a molecule or ion in which one or more pairs of electrons are delocalized.

In contrast, in molecules in which the electrons are localized, the valence bond theory often proves to be especially useful. In the carbonate ion, the energies of the three contributing structures are identical, and so all three contribute equally ($a = b = c$) and the hybrid is exactly intermediate between the three. In many cases, however, the energies of the contributing structures differ (the hydrogen molecule was an example), and in these cases we find that the contribution of a canonical structure is inversely proportional to its energy. If the energy of a structure is appreciably higher than those of the other two, we can then draw up a set of general rules for determining the possibility of contribution of a canonical structure.

Table 5.1

<table>
<thead>
<tr>
<th>Type of wave function</th>
<th>Energy (kJ mol$^{-1}$)</th>
<th>Distance (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncorrected, $\psi = \phi_{\text{icn}}$</td>
<td>24</td>
<td>90</td>
</tr>
<tr>
<td>Heitler-London</td>
<td>303</td>
<td>86.9</td>
</tr>
<tr>
<td>Addition of shielding</td>
<td>365</td>
<td>74.3</td>
</tr>
<tr>
<td>Addition of ionic contributions</td>
<td>388</td>
<td>74.9</td>
</tr>
<tr>
<td>Observed values</td>
<td>458.0</td>
<td>74.1</td>
</tr>
</tbody>
</table>

*McWeeny, R. Coulson's Valence; Oxford University: London, 1979; p 120.

Used with permission.

2 A 100-term function (see Footnote 3) has reproduced the experimental value to within 0.01 kJ mol$^{-1}$.

Finally, it should be noted that the XeF$_6$ molecule exhibits a definite tendency to donate a fluoride ion and form the XeF$_3^-$ cation, which is isostructural and isoionic with IF$_3$ as expected from the VSEPR model. The structure of solid XeF$_6$ is complex, with 144 molecules of XeF$_6$ per unit cell; however, there are no discrete XeF$_6$ molecules. The simplest way to view the solid is as pyramidal XeF$_3^-$ cations extensively bridged by "free" fluoride ions. Obviously, these bridges must contain considerably covalent character. They cause the xenon-containing fragments to cluster into tetrahedral and octahedral units (Fig. 6.15a,b). There are 24 tetrahedra and eight octahedra per unit cell, packed very efficiently as pseudospheres into a Cu$_3$Au structure (Fig. 6.15c). The structure thus provides us with no information about molecular XeF$_6$, but it does reinforce the idea that the VSEPR-correct, square pyramidal XeF$_3^-$ is structurally stable.

Another problem arises with alkaline halide molecules, MX$_2$. These molecules exist only in the gas phase—the solids are ionic lattices (cf. CaF$_2$, Fig. 4.3). Most MX$_2$ molecules are linear, but some, such as SrF$_2$ and BaF$_2$, are bent. If it is argued that the bonding in these molecules is principally ionic and therefore not covered by the VSEPR model, the problem remains. Electrostatic repulsion of the negative ions should also favor a 180° bond angle. At present, there is no simple explanation of these difficulties, but the phenomenon has been treated by means of Walsh diagrams (see page 218).

The preceding can be summed up in a few rules:

1. Electron pairs tend to minimize repulsions. Ideal geometries are:
   a. For two electron pairs, linear.
   b. For three electron pairs, trigonal.
   c. For four electron pairs, tetrahedral.
   d. For five electron pairs, trigonal bipyramidal.
   e. For six electron pairs, octahedral.
2. Repulsions are of the order LP-LP > LP-BP > BP-BP.
   a. When lone pairs are present, the bond angles are smaller than predicted by the VSEPR model. The phenomenon has been treated by means of Walsh diagrams (see page 218).
3. Double bonds occupy more space than single bonds.
4. Bonding pairs to electronegative substituents occupy less space than those to more electropositive substituents.

There are actually four phases known of solid xenon hexafluoride. All have several structural features in common, and the phase described here, phase IV or the cubic phase, is the easiest to describe.


1. The proposed canonical structure should have a maximum number of bonds, consistent, of course, with the other rules. In the carbon dioxide molecule, for example, the structure

\[ \text{O} = \text{C} = \text{O} \]

plays no appreciable role because of its much higher energy resulting from loss of the 1 bonding stabilization. In general, application of this rule is simply a matter of drawing Lewis structures and using good chemical sense in proposing contributing structures.

2. The proposed canonical structures must be consistent with the location of the atoms in the actual molecule (resonance hybrid). The most obvious consequence of this rule is the elimination of tautomers as possible resonance structures. Thus the following structures for phosphorous acid represent an equilibrium between two distinct chemical species, not resonance:

\[ \text{H}_3\text{O}_2\text{P} = \text{O} \quad \rightleftharpoons \quad \text{H}_2\text{O}_2\text{P} = \text{O} \]

A less obvious result of this criterion is that when contributing structures differ in bond angle, resonance will be reduced. Consider, for example, the following hypothetical resonance for nitrous oxide:

\[ \text{N}_2\text{O} \quad \rightleftharpoons \quad \text{N}^+\text{N}^-\text{O} \]

Aside from the fact that II is a strained structure and therefore less stable than I, it will not contribute to the resonance of \( \text{N}_2\text{O} \) because the bond angle is 180° in I and 60° in II. For any intermediate hybrid, the contribution of either I or II would be unfavorable because of the high energy cost when I is bent or when II is opened up.

A few words should be said about the difference between resonance and molecular vibrations. Although vibrations take place, they are oscillations about an equilibrium position determined by the structure of the resonance hybrid, and they should not be confused with the resonance among the contributing forms. The molecule does not "resonate" or "vibrate" from one canonical structure to another. In this sense the term "resonance" is unfortunate because it has caused unnecessary confusion by invoking a picture of "vibration." The term arises from a mathematical analogy between the molecule and the classical phenomenon of resonance between coupled pendulums, or other mechanical systems.

3. Distribution of formal charges in a contributing structure must be reasonable. Formal charge, which will be more fully explicated in the next section, may be defined as the charge an atom in a molecule would have if all of the atoms had the same electronegativity. Canonical forms in which adjacent like charges appear will probably be unstable as a result of the electrostatic repulsion. A structure such as \( A = B^+ - C^- - D^- \) is therefore unlikely to play a major role in hybrid formation.

In the case of adjacent charges which are not of the same sign, one must use some chemical discretion in estimating the contribution of a particular structure. This is best accomplished by examining the respective electronegativities of the atoms involved. A structure in which a positive charge resides on an electropositive element and a negative charge resides on an electronegative element may be quite stable, but the reverse will represent an unstable structure. For example, in the following two molecules

\[ \text{X} = \text{P} \quad \rightleftharpoons \quad \text{X} = \text{P} \quad \rightleftharpoons \quad \text{X} = \text{B} \]

canonical form II contributes very much to the actual structure of phosphoryl compounds, but contributes much less to \( \text{BF}_3 \), and, indeed, the actual contribution in compounds of this sort is still a matter of some dispute.

Furthermore, placement of adjacent charges of opposite sign will be more favorable than when these charges are separated. When adjacent, charges of opposite sign contribute electrostatic energy toward stabilizing a molecule (similar to that found in ionic compounds), but this is reduced when the charges are far apart.

4. Contributing forms must have the same number of unpaired electrons. For molecules of the type discussed previously, structures having unpaired electrons should not be considered since they usually involve loss of a bond

\[ \text{A} = \text{B} \quad \rightleftharpoons \quad \text{A} = \text{B} \]

and higher energy for structure II. We shall see when considering coordination compounds, however, that complexes of the type \( \text{M}_2\text{L}_4 \) (where \( \text{M} = \text{metal} \), \( \text{L} = \text{ligand} \) can exist with varying numbers of unpaired electrons but comparable energies. Nevertheless, resonance between such structures is still forbidden because the spin of electrons is quantized and a molecule either has its electrons paired or unpaired (an intermediate or "hybrid" situation is impossible).

These rules may be applied to nitrous oxide, \( \text{N}_2\text{O} \). Two structures which are important are

\[ \text{N}^+\text{N}^-\text{O} \quad \rightleftharpoons \quad \text{N}^+\text{N}^-\text{O} \]
little help in studying XeF_6 because the pentagonal bipyramidal structure was the first to be experimentally eliminated as a possibility. A number of other fluorine complexes with coordination number 7 are known: [ZnF_6]^-_, known in both pentagonal bipyramidal and capped trigonal prismatic forms; the [NiF_6]^-_ anion is a capped octahedron.

Determining the exact structure of the gaseous XeF_6 molecule proved to be unexpectedly difficult. It is known to be a slightly distorted octahedron. In contrast to the molecules discussed previously, however, the lone pair appears to occupy less space than the bonding pairs. The best model for the molecule (Fig. 6.13) appears to be a distorted octahedron in which the lone pair extends either through a face (C_s symmetry) or through an edge (C_2v symmetry).

The conformation of lowest energy appears to be that of C_s symmetry. Part of the experimental difficulties stems from the fact that the molecule is highly dynamic and probably passes through several conformations. In either of the two models shown in Fig. 6.13, the Xe-F bonds near the lone pair appear to be somewhat lengthened and distorted away from the lone pair; however, the distortion is less than would have been expected on the basis of the VSEPR model. That the latter model correctly predicted a distortion at all is quite amazing, considering the highly symmetrical octahedral molecule (all other hexafluorides such as SF_6 and UF_6 are perfectly octahedral) is a signal success, however.

The powerful technique of X-ray diffraction cannot be applied to the resolution of this question since solid XeF_6 polymerizes with a completely different structure (see below). However, the isoelectronic compound XeO(TeF_6) crystallizes as a simple molecular solid, so that it may be studied by X-ray diffraction. Each molecule has C_2v symmetry (for the oxygen coordination shell about the xenon) indicating a sterically active lone pair. The best model for the molecule (Fig. 6.13) appears to be experimentally consistent with this structure in XeF_6 as well.

Even more puzzling are the structures of anions isoelectronic with XeF_6. Raman spectroscopy indicates that the IF_7 anion, like XeF_6, has lower symmetry than octahedral, but that BrF_7^- is octahedral on the spectroscopic time scale. Both are fluxional on the NMR time scale. Anions such as SbF_5^-, TeF_6^- (X = Cl, Br, or I), and BrF_7^- have been assigned perfectly octahedral structures on the basis of X-ray crystallography. For these structures in which the lone pair is sterically inactive, it is thought that the pair resides in an s orbital. This could result from a static crowding of the ligands or the stability of the lower energy s orbital, or both. Sulfur and infrared spectroscopy have indicated, however, that these ions may either be nonoctahedral or extremely susceptible to deformation.

Complexes of arsenic(III), antimony(III), [electron configuration = (n - 1) d^5](aspx^3), and bismuth(III) [n - 2d^4, (n - 1) d^3] with polydentate ligands occupying six coordination sites have been found to have a stereochemically active lone pair. However, the dichotomy of behavior of the heavier elements that have a lone pair is reflected in the crystal chemistry of BiF_6. When forced into sites of high symmetry, the Bi^3+ ion responds by assuming a spherical shape; in crystals of lower symmetry the lone pair asserts itself and becomes stereochemically active. There appears to be no simple "best" interpretation of the stereochemistry of species with 14 valence electrons. Rather, it should be noted that there seem to be several structures of comparable stability and small forces may tip the balance in favor of one or the other. An example of the balance of these forces is the trans isomer of tetrachlorobis(tetramethylthiourea)tellurium(IV) which provides a very interesting story. This compound was synthesized and separated as orthorhombic crystals which contained centrosymmetric molecules consisting of approximately octahedral arrangements of four chlorine and two sulfur atoms about each tellurium atom. When, however, these crystals were examined several years later, it was found that they changed to a monoclinic form. When the X-ray structure was determined, it was found that the monoclinic crystals contained severely distorted molecules (Fig. 6.14a) with bond angles decreased to about 80°, but the orthoform changed to an orthorhombic form. Apparently the orthorhombic form contains molecules in which the lone pair has been forced into a stereochemically inert s orbital (as is TeO_2^-), while the monoclinic form has a stereochemically active lone pair presumably providing within the 106° bond angle (Fig. 6.14b). Consistent with this interpretation is the lengthening of the Te—S and Te—Cl bonds adjacent to the lone pair. Such lengthening is commonly found and may be interpreted in terms of the increased LP-BP repulsions. It is tempting to suggest that crystal structure forces the lone pair to be stereochemically inactive in the orthorhombic form and that the proclivity of the lone pair forces the crystal symmetry to change. However, this leads to oversimplify what must be a delicate balance of crystal packing forces and electronic effects.

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9. We shall see that the number of d electrons in a complex can alter its stability and geometry (Chapters 11 and 12). The examples given here were chosen to have a d^1 configuration.


13. The time scale of spectroscopic and other techniques is discussed in Table 8.5, and fluxional or rearranging molecules are discussed on pp 227-243 and in Chapter 15.


Both of these structures have four bonds and the charges are reasonably placed. A third structure

$$\begin{align*}
\text{IV} &: \equiv \equiv \\
\text{V} &: \equiv \equiv
\end{align*}$$

is unfavorable because it places a positive charge on the electronegative oxygen atom and also has adjacent positive charges.

Other possibilities are

$$\begin{align*}
\text{IV} &: \equiv \equiv \\
\text{V} &: \equiv \equiv
\end{align*}$$

and the cyclic structure discussed under Rule 2. This last structure has been shown above to be unfavorable. Likewise IV and V should be bent and are energetically unfavorable when forced to be linear to resonate with I and II. In addition, both have only three bonds instead of four and are therefore less stable. Furthermore, V has widely separated charges, but they are exactly opposite to those expected from electronegativity considerations.

It is almost impossible to overemphasize the fact that the resonance hybrid is the only structure which is actually observed and that the canonical forms are merely constructs which enable us to describe accurately the experimentally observed molecule. The analogy is often made that the resonance hybrid is like a mule, which is a genetic hybrid between a horse and a donkey. The mule is a mule and does not "resonate" back and forth between being a horse and a donkey. It is as though one were trying to describe a mule to someone who had never seen one before and had available only photographs of a jackass and a mare. One could then explain that their offspring, intermediate between them, was a mule. There is perhaps a better analogy, though one that will be unfamiliar to those not versed in ancient mythology: Consider a falcon (a real animal) described as a hybrid of Re (the falcon-headed Egyptian sun god) and a harpy (a creature with a woman's head and the body of a raptor), although neither of the latter has an independent existence.

The following formal charges:

$$Q_N = 5 - 6 = 5 - 4 - 1(4) = 0$$

$$Q_O = 5 - 4 = 5 - 0 - 1(8) = +1$$

$$Q_H = 1 - 1 = 1 - 0 - 1(2) = 0$$

For which the formal charges are

$$Q_N = 5 - 5 = 5 - 2 - 1(6) = 0$$

$$Q_H = 1 - 1 = 1 - 0 - 1(2) = 0$$

In the case of $\text{N}_2\text{O}$, the electronegativities of nitrogen and oxygen are different. In both cases, the calculated formal charges indicate the presence of real electrical charges on the atoms in question, though not necessarily exactly +1 or -1. Specifically, the charge density about the two nitrogen atoms is not the same.

To obtain the formal charge on an atom, it is assumed that all electrons are shared equally and that each atom "owns" one-half of the electrons it shares with neighboring atoms. The formal charge, $Q_F$, is then:

$$Q_F = N_M - N_m = N_N - N_{LP} = LN_{LP}$$

where $N_M$ is the number of electrons in the valence shell in the free atom and $N_m$ is the number of electrons "belonging to the atom in the molecule"; $N_{LP}$ and $N_{AP}$ are the numbers of electrons in unshared pairs and bonding pairs, respectively.

Applied to the Lewis structure of the phosphonium ion.

$$\begin{align*}
Q_P &= 5 - 4 = 5 - 0 - 1(8) = +1 \\
Q_H &= 1 - 1 = 1 - 0 - 1(2) = 0 \\
Q_O &= 1 - 1 = 1 - 0 - 1(2) = 0
\end{align*}$$

This is in contrast to the phosphine molecule.

$$\begin{align*}
Q_P &= 5 - 4 = 5 - 0 - 1(8) = +1 \\
Q_H &= 1 - 1 = 1 - 0 - 1(2) = 0
\end{align*}$$

For which the formal charges are

$$Q_P = 5 - 5 = 5 - 2 - 1(6) = 0$$

$$Q_H = 1 - 1 = 1 - 0 - 1(2) = 0$$

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$$Q_F = N_M - N_m = N_N - N_{LP} = LN_{LP}$$

where $N_M$ is the number of electrons in the valence shell in the free atom and $N_m$ is the number of electrons "belonging to the atom in the molecule"; $N_{LP}$ and $N_{AP}$ are the numbers of electrons in unshared pairs and bonding pairs, respectively.

Applied to the Lewis structure of the phosphonium ion.

$$\begin{align*}
Q_P &= 5 - 4 = 5 - 0 - 1(8) = +1 \\
Q_H &= 1 - 1 = 1 - 0 - 1(2) = 0 \\
Q_O &= 1 - 1 = 1 - 0 - 1(2) = 0
\end{align*}$$

This is in contrast to the phosphine molecule.

$$\begin{align*}
Q_P &= 5 - 5 = 5 - 2 - 1(6) = 0 \\
Q_H &= 1 - 1 = 1 - 0 - 1(2) = 0
\end{align*}$$

For which the formal charges are

$$Q_P = 5 - 4 = 5 - 0 - 1(8) = +1$$

$$Q_H = 1 - 1 = 1 - 0 - 1(2) = 0$$

To return now to nitrous oxide, $\text{N}_2\text{O}$, specifically structure I, we have a Lewis structure:

$$\begin{align*}
Q_N &= 5 - 6 = 5 - 4 - 1(4) = -1 \\
Q_O &= 5 - 4 = 5 - 0 - 1(8) = +1 \\
Q_O &= 6 - 6 = 6 - 4 - 1(4) = 0
\end{align*}$$

Likewise, structure II gives a +1 charge on $\text{N}_2$ and -1 on the oxygen. Recently, the concept of formal charge has been made more quantifiable by combining it with the idea of electronegativity to estimate the relative effects of each in.
bond angles (Fig. 6.10b). The molecule is indeed planar but distorted rather severely from a symmetrical trigonal arrangement (Fig. 6.10b). It is apparent that the oxygen atom requires considerably more room than the fluorine atoms. There are at least two steric reasons for this. First, the oxygen atom is double bonded to the carbon and the C=O bond length (120 pm) is somewhat less than that of C—F (155 pm); thus, the van der Waals repulsion of the oxygen atom will be greater. More important in the present case is the fact that the double bond contains two pairs of electrons, and whether viewed as a σ—p pair or two bent bonds, it is reasonable to assume that they will require more space than a single bonding pair.

This assumption is strengthened by other compounds with double bonds. In the OSF$_3$ molecule the doubly bonded oxygen atom seeks the more spacious equatorial position, and the fluorine atoms are bent away somewhat from the other two equatorial and the two axial positions (Fig. 6.11b). Further examples are listed in Table 6.1. Note that the behavior of the doubly bonded oxygen atom is in several ways similar to that of a lone pair. Both require more room than a single bonding pair, both seek the equatorial position, and both repel adjacent bonds, thereby distorting the structure. For example, compare the structure of OSF$_3$ (Fig. 6.11b) with that for SF$_4$ (Fig. 6.11a). However, Christe and Oberhammer's* cite one major difference: The lone pair in SF$_4$ is cylindrically symmetrical whereas the σ bond in O=SF$_3$ will have greater electron density in one plane than another. However, the plane of the σ bond can only be inferred from the bond angles, leading to a possible circularity in reasoning. More straightforward is the CH$_3$=SF$_2$ molecule (Fig. 6.11c). Because the hydrogen atoms lie in the C=S=O plane, we know that the σ bond involving a p orbital on the carbon atom must lie in the equatorial plane of the molecule. And the resulting repulsion between the σ electrons and the electron pairs bonding the equatorial fluorine atoms is dramatic: The F$_{eq}$—F$_{eq}$ angle has been reduced to 97°.  

No discussion of the VSEPR model of molecular structure would be complete without a brief discussion of some problems remaining. One interesting problem is the molecular structure of XeF$_6$. The simplest MO treatment of this molecule predicted that the molecule would be perfectly octahedral. In contrast, the VSEPR model considers the fact that there will be seven pairs of electrons in the valence shell (six bonding pairs and one lone pair) and predicts a structure based on seven-coordination. Unfortunately, we have little to guide us in choosing the preferred arrangement. Gillespie suggested three possibilities for XeF$_6$: a distorted pentagonal bipyramid, a distorted octahedron, or a distorted trigonal prism. The lone pair should occupy a definite geometric position and a volume as great as or greater than a bonding pair. Unfortunately, only three neutral fluoride molecules with seven bonding pairs are known: IF$_3$, ReF$_5$, and OsF$_5$. The structures are known with varying degrees of certainty, but all three appear to have approximate $D_6h$ symmetry, a distorted pentagonal bipyramid (Fig. 6.12). Unfortunately, knowing the MF$_7$ structures was of no help in deciding the preferred arrangement of the polar bond.

---

* Christe, K. O.; Oberhammer, H. Inorg. Chem. 1981, 20, 296. Note that the bond angles accepted by Christe and Oberhammer were somewhat different than those given here and were somewhat more favorable for their argument.

---

**Table 6.1**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>X—Y—X°</th>
<th>Molecule</th>
<th>X—Y—X°</th>
</tr>
</thead>
<tbody>
<tr>
<td>O=CF$_2$</td>
<td>108°</td>
<td>O=CF$_2$</td>
<td>94° ± 4°</td>
</tr>
<tr>
<td>O=SF$_3$</td>
<td>106°</td>
<td>O=SF$_2$</td>
<td>98°</td>
</tr>
<tr>
<td>O=PCl$_3$</td>
<td>103.3°</td>
<td>O=PCl$_3$</td>
<td>103.3°</td>
</tr>
<tr>
<td>O=SF$_3$</td>
<td>110.178.5°</td>
<td>O=SF$_3$</td>
<td>103.179°</td>
</tr>
<tr>
<td>O=IF$_3$</td>
<td>82.8°</td>
<td>O=IF$_3$</td>
<td>82°</td>
</tr>
</tbody>
</table>

* Y = central atom, C, S, P, I, Ge; X = halogen atom, Cl, F.
Hybridization consists of mixing or linear combination of the "pure" atomic orbitals in such a way as to form new hybrid orbitals. Thus we say that the single $2s$ orbital plus the three $2p$ orbitals of the carbon atom have combined to form a set of four spatially and energetically equivalent $sp^3$ hybrid orbitals. This is illustrated in Fig. 5.2 for the conceptually simpler case of the $sp$ hybrid formed from an $s$ orbital and a single $p$ orbital. Combination of the $s$ and $p$ orbitals causes a reinforcement in the region in which the signs of the wave function are the same, cancellation where the signs are opposite.

If we let $\psi_s$ and $\psi_p$ represent the wave functions of an $s$ and a $p$ orbital, then we combine them to make two equivalent orbitals as follows:

$$\psi_{sp} = \sqrt{\frac{1}{2}} (\psi_s + \psi_p)$$  \hspace{1cm} (5.16)

$$\psi_{sp^3} = \sqrt{\frac{1}{4}} (\psi_s + \psi_p + \psi_s - \psi_p)$$  \hspace{1cm} (5.17)

where $\sqrt{1}$ is the normalizing coefficient and $\psi_{sp}$ and $\psi_{sp^3}$ are the new $d$ orbital ($4d$ or $6d$) or $sp^3$ orbitals.

Mathematically, the formation of $sp^3$ or tetrahedral orbitals for methane is more complicated but not basically different. The results are four equivalent hybrid orbitals, each containing one part $s$ to three parts $p$ in each wave function, directed to the corners of a tetrahedron. As in the case of $sp$ hybridization, the hybridization of $s$ and $p$ has

$$\text{ Fig. 5.2 Formation of } sp^3 \text{ hybrid orbitals by the addition and subtraction of angular wave functions.}$$

The existence of this extra valence state excitation energy may be clearer if the reverse process is considered. (In a thought experiment) four hydrogen atoms are removed from methane but the carbon is not allowed to change in any way, the resulting spins would be perfectly randomized. Energy would then be released if the spins were allowed to become parallel. See McWeeny, R. Coulson's Valence, Oxford University Press, London, 1979, pp. 110, 201-203, 208-209. It should be noted that unlike $sp^3$, etc., $sp^2$ is not an observable spectroscopic state but is calculated by adding promotion energies related to the electron spins.
The Structure and Reactivity of Molecules

Fig. 6.6 (a) The pentafluorotellurate(IV) anion. Approximately octahedral arrangement of bonding and nonbonding electrons. (b) Experimentally determined structure. The tellurium atom is below the plane of the fluorine atoms. [From Mastin, S. H.; Ryan, R. R.; Asprey, L. S., J. Am. Chem. Soc. 1970, 92, 2100-2103. Reproduced with permission.]

Fig. 6.7 The tetrachloroiodate(III) ion. (a) Octahedral arrangement of bonding and nonbonding electrons with lone pairs cis to each other, (b) Octahedral arrangement of bonding and nonbonding electrons with lone pairs trans to each other, (c) Experimentally determined structure.

Nitrogen dioxide (C₃), nitrite ion (O₂⁻), and nitryl ion (NO). The three species, NO₂, NO₃, and NOV⁺, show the effect of steric repulsion of bonding and nonbonding electrons. The Lewis structures are

\[
\begin{align*}
\text{NO}₂ & :\text{N}::\text{O}::\text{O}::\text{N}: \\
\text{NO}_3 & :\text{N}::\text{O}::-\text{O}::-\text{O}:-\text{N}:
\end{align*}
\]

The nitryl ion, NOV⁺, is isoelectronic with carbon dioxide and will, like it, adopt a linear structure with two σ bonds (Fig. 6.8a). The nitrite ion, NO₃, will have one σ bond, stereochemically inactive, two π bonds, and one lone pair. The resulting structure is therefore expected to be trigonal, with 120° σπ bonds to a first approximation. The lone pair should be expected to expand at the expense of the bonding pairs, however, and the bond angle is found to be 115° (Fig. 6.8b).

The nitryl ion, NOV⁺, is a free radical, i.e., it contains an unpaired electron. It may be considered to be a nitrite ion from which one electron has been removed from the least electronegative atom, nitrogen. Instead of having a lone pair on the nitrogen, it has a single electron in an approximately trigonal orbital. Since a single electron would be expected to repel less than two, the bonding electrons can move so as to open up the bond angle and reduce the repulsion between them (Fig. 6.8c).

Phosphorus trichlorides (C₃). The importance of electron repulsions near the nucleus of the central atom is nicely shown by the bond angles in phosphorus trichloride molecules: PF₃ = 97.7°, PCl₃ = 100.3°, PBr₃ = 101.0°, PI₃ = 102°. The immediate inclination to ascribe the opening of the bond angles to van der Waals repulsions between the halogens must be rejected. Although the van der Waals radii increase F < Cl < Br < I, the covalent radii and hence the P—X bond lengths also increase in the same order. The two effects cancel each other (see Problem 6.15). The important factor appears to be the ionization of the P—X bond.

The more electronegative fluorine atom attracts the bonding electron pairs away from the phosphorus nucleus and allows the lone pair to expand while the P—F bond angle closes. Reduced bond angles in nonmetal fluorides are commonly observed. For the small atoms nitrogen and oxygen, where the VSEPR interactions seem to be especially important, the fluorides have smaller bond angles than the hydrides (NF₃ = 102.3°, NH₃ = 107.2°, OF₂ = 103.4°, OH₂ = 104.3°). Gillespie has discussed the effect of substituent electronegativity and pointed out that the expansion of lone pairs relative to bonding pairs may be viewed simply as an example of the extreme effect when the nonexistent "substituent" on the lone pair has no electronegativity at all (see Fig. 6.9).

Carbonyl fluoride (C₂). Fluorine and oxygen atoms are about the same size and similar in electronegativity; therefore we might expect OCF₂ to have a rather symmetrical structure. There are no lone pairs on the carbon atom, so to a first approximation we might expect the molecule to be planar with approximately 120° bond angles. However, resonance has been omitted to simplify the discussion. (c) The effect of the unpaired electron, half of a lone pair, in nitrogen dioxide.

Fig. 6.8 (a) The linear nitryl ion, NOV⁺, (b) The effect of the lone pair in the nitrite ion, NO₃⁻. Resonance has been omitted to simplify the discussion. (c) The effect of the unpaired electron, half of a lone pair, in nitrogen dioxide.

Fig. 6.9 Effect of decreasing electronegativity of X on the size of a bonding pair of electrons: (a) electronegativity X > A, (b) electronegativity X = A, (c) electronegativity X < A. (From Gillespie, R. J., J. Chem. Educ. 1970, 47, 18. Reproduced with permission.)
resulted in one lobe of the hybrid orbital being much larger than the other (see Fig. 5.3). Hybrid orbitals may be pictured in many ways: by several contour surfaces (Fig. 5.3), a single, outer contour surface (Fig. 5.4a); cloud pictures (Fig. 5.4b); or by simpler, diagrammatic sketches which ignore the small lobe of the orbital and picture the larger lobe (Fig. 5.4c). The latter, though badly distorted, are commonly used in drawing molecules containing several hybrid orbitals.

It is possible to form a third type of s-p hybrid containing one s orbital and two p orbitals. This is called an sp2 or trigonal (tr) hybrid. It consists of three identical orbitals, each of which does not differ appreciably in shape from Fig. 5.3 and is directed toward the corner of an equilateral triangle. The angles between the axes of the orbitals in a trigonal hybrid are thus all 120°.

Although promotion and hybridization are connected in the formation of methane from carbon and hydrogen, care should be taken to distinguish between them. Promotion involves the addition of energy to raise an electron to a higher energy level in order that the two additional bonds may form. It is conceivable that after promotion the carbon atom could have formed three bonds with the three p orbitals and the fourth with the s orbital. That carbon forms tetrahedral bonds instead is a consequence of the greater stability of the latter, not a necessary result of promotion. Thus, although promotion and hybridization often occur together, either could occur without the other.

A second point to be made with regard to hybrids is the source of the driving force resulting in hybridization. Statements are often made to the effect that "methane is tetrahedral because the carbon is hybridized sp3." This is very loose usage and gets the cart before the horse. The methane molecule is tetrahedral because the energy of the molecule is lowest in that configuration, principally because of increased bond energies and decreased repulsion energies. For this molecule to be tetrahedral, VB theory demands that sp3 hybridization take place. Thus it is incorrect to attribute the shape of a molecule to hybridization—the latter prohibits certain configurations and allows others but does not indicate a preferred one. For example, consider the following possibilities for the methane molecule:

\[
\text{I: } \text{sp}^3 \\
\text{II: sp}^2 + p \\
\text{III: sp} + p^2 \\
\text{IV: } T + p^3 \\
\text{V: sp} + p^3
\]

The first three geometries involve the tetrahedral, trigonal, and digonal hybrids discussed above and the fourth involves the use of pure s and p orbitals as discussed on page 149. The last structure contains three equivalent bonds at mutual angles of 60° and a fourth bond at an angle of approximately 145° to the others. It is impossible to construct sp3 hybrid orbitals with angles less than 90°, and so structure V is ruled out. In this sense it may be said that sp3 hybridization does not "allow" structure V, but it may not be said that it "chooses" one of the others. Carbon hybridizes sp, sp2, and sp3 in various compounds, and the choice of sp3 in methane is a result of the fact that the tetrahedral structure is the most stable possible.

Although we shall not make explicit use of them, the reader may be interested in the form of the s-p hybrids we have seen.9

\[
\phi_{sp} = \sqrt{2} \phi_s + \sqrt{2} \phi_p \\
\phi_{sp} = \sqrt{2} \phi_s - \sqrt{2} \phi_p \\
\phi_{sp} = \sqrt{2} \phi_s + \sqrt{2} \phi_p \\
\phi_{sp} = \sqrt{2} \phi_s - \sqrt{2} \phi_p \\
\psi_{sp} = \psi_s + \psi_p \\
\psi_{sp} = \psi_s - \psi_p \\
\psi_{sp} = \psi_s + \psi_p \\
\psi_{sp} = \psi_s - \psi_p \\
\psi_{sp} = \psi_s + \psi_p \\
\psi_{sp} = \psi_s - \psi_p \\
\psi_{sp} = \psi_s + \psi_p \\
\psi_{sp} = \psi_s - \psi_p
\]

The percent s and p character is proportional to the squares of the coefficients. Taken from Hsu, C. Y.; Orchin, M. J. Chem. Educ. 1973, 50, 114-118.

9 The percent s and p character is proportional to the squares of the coefficients. Taken from Hsu, C. Y.; Orchin, M. J. Chem. Educ. 1973, 50, 114-118.
As a general rule, we can state that the lone pair will always occupy a greater angular volume than bonding electrons. Furthermore, if given a choice, the lone pair tends to go to that position in which it can expand most readily. Consider, for example, the following molecules, where if in each case we consider only the bonding electrons, we obtain wrong predictions concerning the geometry of the molecules. For example, BrF$_3$ would be trigonal, ICl$_4$ tetrahedral, IF$_4$ trigonal bipyramidal, and SF$_4$ tetrahedral. In fact, none of these molecules has the structure just assigned to it. If, however, we include the lone pairs, we can predict not only the approximate molecular shape but also distortions which will take place.

**Sulfur tetrafluoride** (C$_3$). The molecule SF$_4$ has ten electrons in the valence shell of sulfur, four bonding pairs and one nonbonding pair. In order to let each pair of electrons have as much room as possible, the approximate geometry will be a trigonal bipyramid, as in PF$_3$. However, the lone pair can be arranged in one of two possible ways, either equatorially (Fig. 6.4a) or axially (Fig. 6.4b). The lone pair is in an experimentally derived structure is shown in Fig. 6.4c. The lone pair is in an equatorial position and tends to repel the bonding pairs and cause them to be bent equatorially. We back away from the position occupied in an undistorted trigonal bipyramid. We can rationalize the adoption of the equatorial position by the lone pair by noting that in this position it encounters only two 90° interactions (with the axial bonding pairs), whereas in the alternative structure it would encounter three 90° interactions (with the equatorial bonding pairs). Presumably the 120° interactions are sufficiently relaxed that they play no important role in determining the most stable arrangement. This is consistent with the fact that repulsive forces are important only at very small distances. In any event, lone pairs always adopt positions which minimize 90° interactions.

**Bromine trifluoride** (C$_3$). The BrF$_3$ molecule also has ten electrons in the valence shell of the central atom, in this case three bonding pairs and two lone pairs. Again, the approximate structure is trigonal bipyramidal with the lone pairs occupying equatorial positions. The distortion from lone pair repulsion causes the axial fluorine atoms to be bent away from a linear arrangement so that the molecule is a slightly "bent T" with bond angles of 86° (Fig. 6.5a).

**Dichloroiodate(I) anion** ($\text{Cl}_2\text{IO}_4^-$). The ($\text{Cl}_2\text{IO}_4^-$) anion has a linear structure as might have been supposed naively. However, note that three lone pairs are presumably still stereochemically active, but by adopting the three equatorial positions they cause no distortion (Fig. 6.5b). [A note on bookkeeping for ions: Add 7 electrons (I) + 2 electrons (2Cl) + 1 electron (ionic charge) = 10 = 5 pairs.]

**Pentafluorotellurate(IV) anion** ($\text{TeF}_5^-$). In the ($\text{TeF}_5^-$) ion the tellurium atom has twelve electrons in its valence shell, five bonding pairs and one nonbonding. The most stable arrangement for six pairs of electrons is the octahedron which we should expect for a first approximation. Repulsion from the single lone pair should cause the adjacent fluorine atoms to move upward somewhat (Fig. 6.6a). The resulting structure is a square pyramid with the tellurium atom 40 pm below the plane of the four fluorine atoms (Fig. 6.6b).

**Tetrachloroiodate(III) anion** ($\text{ICl}_4^-\text{IO}_3^-$). The ($\text{ICl}_4^-\text{IO}_3^-$) ion is isoelectronic with the TeF$_5$ ion with respect to the central atom. In this case, however, there are four bonding pairs and two lone pairs. In an undistorted octahedron, all six points are equivalent, and the lone pairs could be adjacent, or cis (Fig. 6.7a); or trans (Fig. 6.7b), opposite to one another. In the cis arrangement the lone pairs will compete with each other for volume into which they can expand at the expense of the bonding pairs. Since the lone pairs are not seen in a normal structural determination, the resulting arrangement of atoms is square planar (Fig. 6.7c).
It is not necessary to limit hybridization to $s$ and $p$ orbitals. The criteria are that the wave functions of the orbitals being hybridized must be of appropriate symmetry (Chapter 3) and be similar in energy. If the orbitals are not close in energy, the wave function of the hybrid will be unsuit for bonding because the electron density would be spread too thinly. In practice this means that hybrids are formed among orbitals lying in the same principal energy level or, occasionally, in adjacent energy levels.

Some hybrid orbitals containing $s$, $p$, and $d$ orbitals are listed in Table 5.2. The structural aspects of various hybrid orbitals will be discussed in Chapter 6, but the bond angles between orbitals of a given hybridization are also listed in Table 5.2 for reference.

Most sets of hybrid orbitals are equivalent and symmetric, that is, four $sp^3$ orbitals directed to the corners of a regular tetrahedron, six $sp^2$ orbitals to the corners of an octahedron, etc. In the case of $sp^2$ hybrids the resulting orbitals are not equivalent. In the trigonal bipyramidal arrangement three orbitals directed trigonally form one set of equivalent orbitals (these may be considered $sp^2$ hybrids) and two orbitals directed linearly (and perpendicular to the plane of the first three) form a second set of two (these may be considered $dp$ hybrids). The former set is known as the equatorial orbitals and the latter as the axial orbitals. Because of the nature of the different orbitals involved, bonds formed from the two sets are intrinsically different and will have different properties even when bonded to identical atoms. For example, in molecules like PF$_5$ bond lengths differ for axial and equatorial bonds (see Chapter 6).

Even in the case of $s$-$p$ orbitals it is not necessary that all the orbitals be equivalent. Consider the water molecule, in which the $H-O-H$ angle is 104.5°, which does not correspond to any of the hybrids described above, but lies between the 109.5° angle for $sp^2$ and 90° for pure $p$ orbitals. Presumably the bonding orbitals in water are approximately tetrahedral orbitals but contain a little more $p$ character, which correlates with the tendency of the bond angle to diminish toward the 90° of pure $p$ orbitals. The driving forces for this effect will be discussed in Chapter 6.

The relationship between $p$ or $s$ character and bond angle will also be discussed in Chapter 6. For now we need only consider the possibility of $s$-$p$ hybridization other than $sp$, $sp^2$, and $sp^3$. If we take the ratio of the $s$ contribution to the total orbital complement in these hybrids, we obtain 50%, 33%, and 25% $s$ character, respectively, for these hybrids. A pure $s$ orbital would be 100% $s$, and a $p$ orbital would have 0% $s$ character. Since hybrid orbitals are constructed as linear combinations of $s$ and $p$ orbital wave functions,

$$\phi = a\psi_s + b\psi_p,$$  

(5.25)

there is no constraint that $a$ and $b$ must have values such that the $s$ character is exactly 25%, 33%, or 50%. A value of 20% $s$ character is quite acceptable, for example, and indeed this happens to be the value in water. When the hybridization is defined as above, the $\%$ $s$ character is always the complement of $\%$ p, in the case of water, 80%.

We may make the generalization that the strength of a bond will be roughly proportional to the extent of overlap of the atomic orbitals. Both pure $s$ and pure $p$ orbitals provide relatively inefficient overlap compared with that of hybrid orbitals. The relative overlap of hybrid orbitals decreases in the order $sp > sp^2 > sp^3 > p$. The differences in bonding resulting from hybridization effects on overlap can be seen in Figure 5.3. The C—H bond in acetylene is shorter and stronger than in hydrocarbons having less $s$ character in the bonding orbital. The hybridization in the hydrocarbons listed in Table 5.3 is dictated by the stoichiometry and stereochemistry. In molecules where variable hybridization is possible, various possible hybridizations, overlaps, and bond strengths are possible. Other things being equal, we should expect molecules to maximize bond energies through the use of appropriate hybridizations.

A second approach to bonding in molecules is known as the molecular orbital (MO) theory. The assumption here is that if two nuclei are positioned at an equilibrium distance, and electrons are added, they will go into molecular orbitals that are in many ways analogous to the atomic orbitals discussed in Chapter 2. In the atom there are $s$, $p$, $d$, $f$, ... orbitals determined by various sets of quantum numbers and in the molecule we have $s$, $p$, $d$, $f$, ... orbitals determined by quantum numbers. We should expect to find the Pauli exclusion principle and Hund's principle of maximum multiplicity obeyed in these molecular orbitals as well as in the atomic orbitals.

When we attempt to solve the Schrödinger equation to obtain the various molecular orbitals, we run into the same problem found earlier for atoms heavier than hydrogen. We are unable to solve the Schrödinger equation exactly and therefore must make some approximations concerning the form of the wave functions for the molecular orbitals.

Of the various methods of approximating the correct molecular orbitals, we shall discuss only one: the linear combination of atomic orbitals (LCAO) method. We assume that we can approximate the correct molecular orbitals by combining the atomic orbitals of the atoms that form the molecule. The rationale is that most of the time the electrons will be near and hence "controlled" by one or the other of the two nuclei, and when this is so, the molecular orbital should be very nearly the same as the atomic orbital for that atom. The basic process is the same as the one we employed in constructing hybrid atomic orbitals except that now we are combining orbitals on different atoms to form new orbitals that are associated with the entire molecule.
because the aluminum atom can accept an additional pair of electrons (Lewis acid, see Chapter 9) in its unused $p$ orbital and rehybridize from $sp^2$ to $sp^3$. We should expect the bond angles about the aluminum to be approximately tetrahedral except for the strain involved in the $Al-Br-Al-Br$ four-membered ring. Since the average bond angle within the ring must be $90^\circ$, we might expect both the aluminum and bromine atoms to use orbitals which are essentially purely $p$ in character for the ring in order to reduce the strain. The structure of the $Al_3Br_6$ molecule is shown in Fig. 6.1h.

Although the discussions of the preceding molecules have been couched in valence bond terms (Lewis structures, hybridization, etc.), recall that the criterion for molecular shape (rule 2 above) was that the $a$ bonds of the central atom should be allowed to get as far from each other as possible: $2$ at $180^\circ$, $3$ at $120^\circ$, $4$ at $109.5^\circ$, etc. This is the heart of the VSEPR method of predicting molecular structures, and it is, indeed, independent of valence bond hybridization schemes, although it is most readily applied in a VB context.

The source of the repulsions that maximize bond angles is not completely clear. For molecules such as $CO_2$, $CH_3OH$, or $OF_2$, we might suppose that van der Waals repulsions (analogous to the Born repulsions in ionic crystals, Chapter 4) among, for example, the three methyl groups might open the bond angles to the maximum possible value of $120^\circ$. In the next section we shall see that nonbonding pairs of electrons (one pair) are at least as effective as bonding pairs (or bonded groups) in repulsion, and so attention focuses on the electron pairs themselves. Although a number of theorists have been advanced, the consensus seems to be that the physical force behind VSEPR is the Pauli force: Two electrons of the same spin cannot occupy the same space. However, it should be noted that there has been some disagreement over the matter. Nevertheless, we shall see, the VSEPR model is an extremely powerful tool for predicting molecular structures.

When we investigate molecules containing lone (unshared) electron pairs, we must take into account the difference between the bonding electrons and the nonbonding electrons. First, before considering hybridization and the energies implicit in the bonding rules (Chapter 3) let us consider the simplest possible viewpoint. Consider the water molecule in which the oxygen atom has a ground state electron configuration of $1s^22s^2p^6$: The unpaired electrons in the $p_x$ and $p_y$ orbitals may now be paired with electrons on two hydrogen atoms to give $H_2O$. Since the $p_z$ and $p_y$ orbitals lie at right angles to one another, maximum overlap is obtained with an $H—O—H$ bond angle of $90^\circ$. The experimentally observed bond angle in water is, however, about $104.5^\circ$, much closer to a tetrahedral angle. Inclusion of repulsion of positive charges on the adjacent hydrogen atoms (resulting from the fact that the oxygen does not share an electron equally with the hydrogen) might cause the bond angle to open up somewhat, but cannot account for the large deviation from $90^\circ$. Not only must the $H—H$ repulsions be taken into consideration, but also every other energetic interaction in the molecule: all repulsions and all changes in bond energies as a function of angle and hybridization. It is impossible to treat this problem in a rigorous way, mainly as a result of our ignorance of the magnitudes of the various energies involved; however, certain empirical rules have been formulated.

First, as we have seen in examples on the previous pages, bond angles in molecules tend to open up as much as possible as a result of the repulsions between the electrons bonding the substituents to the central atom. Repulsions between unshared electrons on the central atom and other unshared electrons or bonding electrons will affect the geometry. In fact, it is found that the repulsions between lone pair electrons are greater than those between the bonding electrons. The order of repulsive energies is lone pair—lone pair $> $ lone pair—bonding pair $> $ bonding pair—bonding pair. This result comes from the absence of a second nucleus at the distal end of the lone pair which would tend to localize the electron cloud in the region between the nucleus. Because the lone pair does not have this second nucleus, it is attracted only by its own nucleus and tends to occupy a greater angular volume (Fig. 6.2).

The difference in spatial requirements between lone pairs and bonding pairs may perhaps be seen most clearly from the following example. Consider an atom or ion with a noble gas configuration such as $C_6^+$, $N_7^-$, $O_8^-$, $F_9^-$, or $Ne_0^{12}p^6$. Assume that the eight electrons in the outer shell occupy four equivalent tetrahedral orbitals. Now let a proton interact with one pair of electrons to form an $X—H$ bond ($H_2O^-$, $NH_2^+$, $OH_2^-$, $HF$, $NeH_2^+$). The proton will polarize the pair of electrons to which it attaches in the same way that a proton or other small, positive ion polarizes an anion (Fajans' rules, Chapter 4). Electron density will be removed from the vicinity of the nucleus of the first atom and attracted toward the hydrogen nucleus. The remaining, nonbonding pairs may thus expand at the expense of the bonding pair. Addition of a second proton produces two polarized, bonding pairs and two expanded lone pairs ($H_2O_2^-$, $NH_2OH$, $H_2O_2^+$). A third proton forms $H_2O_3^-$, $NH_2OH$, and $H_2O_2^+$ with one expanded lone pair. A fourth proton produces $CH_2$, $NH_4^+$, and $H_2O_2^+$ in which all four pairs of electrons have been polarized toward the hydrogen nuclei, are once more equivalent, and hence directed at tetrahedral angles.

From this point of view, the water molecule can be considered to be hybridized tetrahedrally to a first approximation. Since the two lone pairs will occupy a greater angular volume than the two bonding pairs, the angle between the latter two is reduced somewhat (from $109.5^\circ$ to $104.5^\circ$), allowing the angle between the lone pairs to open up slightly. The series methane, $CH_4$ (no lone pairs, bond angle = $106^\circ$); ammonia, $NH_3$ (one lone pair, bond angle = $107^\circ$); and water, $H_2O$ (two lone pairs, bond angle = $104^\circ$) illustrates an isoelectronic series in which the increasing requirements of the nonbonding pairs reduce the bond angle (Fig. 6.3).
therefore combine the atomic orbitals \( \psi_a \) and \( \psi_b \) on atoms A and B to obtain two molecular orbitals:

\[
\psi_a = \psi_A + \psi_B \quad (5.26)
\]
\[
\psi_a' = \psi_A - \psi_B \quad (5.27)
\]

The one-electron molecular orbitals thus formed consist of a bonding molecular orbital (\( \psi_a \)) and an antibonding molecular orbital (\( \psi_a' \)). If we allow a single electron to occupy the bonding molecular orbital (as in \( \text{H}_2 \), for example), the approximate wave function for the molecule is

\[
\psi = \psi_{a(1)} = \psi_{a(1)} + \psi_{a(1)}' \quad (5.28)
\]

For a two-electron system such as \( \text{H}_2 \), the total wave function is the product of the wave functions for each electron:

\[
\psi = \psi_A \psi_B = \left[ \psi_{a(1)} \right] \left[ \psi_{a(1)}' \right] \quad (5.29)
\]

\[
\psi = \psi_A \psi_B = \left[ \psi_{a(1)} \right] \left[ \psi_{a(1)}' \right] \quad (5.30)
\]

The results for the MO treatment are similar to those obtained by VB theory. Equation 5.30 is the same (when rearranged) as Eq. 5.3 except that the ionic terms (\( \psi_A \psi_B \) and \( \psi_B \psi_A \)) are weighted as heavily as the covalent ones (\( \psi_{a(1)} \psi_{a(1)}' \)).

This is not surprising, since we did not take into account the repulsion of electrons in obtaining Eq. 5.29. This is a general result: Simple molecular orbitals obtained in this way from the linear combination of atomic orbitals (LCAO-MO theory) tend to exaggerate the ionicity of molecules, and the chief problem in adjusting this simple method to make the results more realistic consists of taking into account electron correlation. As in the case of VB theory it is possible to optimize the wave function by the addition of correcting terms. Some typical results for the hydrogen molecule are listed in Table 5.4.

### Table 5.4

<table>
<thead>
<tr>
<th>Type of Wave Function</th>
<th>Energy (kJ mol(^{-1}))</th>
<th>Distance (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncorrected, ( \psi_a + \psi_b )</td>
<td>200</td>
<td>85</td>
</tr>
<tr>
<td>Addition of shielding</td>
<td>337</td>
<td>73</td>
</tr>
<tr>
<td>MO, SCF limit</td>
<td>349</td>
<td>74</td>
</tr>
<tr>
<td>Observed values</td>
<td>458.0</td>
<td>74.1</td>
</tr>
</tbody>
</table>


The two orbitals \( \psi_a' \) and \( \psi_b' \) differ from each other as follows. In the bonding molecular orbital the wave functions for the component atoms reinforce each other in the region between the nuclei (Fig. 5.5a, b), but in the antibonding molecular orbital they cancel, forming a node between the nuclei (Fig. 5.5d). We are, of course, interested in learning of the electron distribution in the hydrogen molecule, and will therefore be interested in the square of the wave functions:

\[
\psi_a^2 = \psi_A^2 + 2\psi_A \psi_B + \psi_B^2 \quad (5.31)
\]
\[
\psi_a'^2 = \psi_A^2 - 2\psi_A \psi_B + \psi_B^2 \quad (5.32)
\]

The difference between the two probability functions lies in the cross term \( 2\psi_A \psi_B \). The integral \( \int \psi_a \psi_b \, dV \) is known as the overlap integral, \( S \), and is very important in bonding theory. In the bonding orbital the overlap is positive and the electron density between the nuclei is increased, whereas in the antibonding orbital the electron density between the nuclei is decreased. (See Fig. 5.5c, e.) In the former case the nuclei are shielded from each other and the attraction of both nuclei for the electrons is enhanced. This results in a lowering of the energy of the molecule and is therefore a bonding situation. In the second case the nuclei are partially bared toward each other and the electrons tend to be in those regions of space in which mutual attraction by
The Structure and Reactivity of Molecules

and no nonbonding electrons on the carbon atom, and so the preferred orientation is for the π bonds to form on opposite sides of the carbon atom. This will require hybridization of the 2s and 2p orbitals to form a trigonal hybrid, with a bond angle of 120°.

3. Once the structure of the σ-bonded molecule has been determined, π bonds may be added as necessary to complete the molecule. In carbon dioxide, the πs and πp orbitals on the carbon atom were unused by the σ system and are available for the formation of π bonds. A complete structure for carbon dioxide would thus be as shown in Fig. 6.1a.

These simplified VSEPR rules may seem a far cry from the more elegant application of symmetry and molecular orbitals to the beryllium ion (Chapter 5), or the BH₃ molecule (Problem 6.37). Although the molecular orbital approach can rationalize these structures, the direct application of the VSEPR rules is by far the easier way to approach a new structure.

Fig. 6.1 Some simple molecular structures in which all electrons are on the central atom from bonding pairs: (a) carbon dioxide, with two π σ bonds (solid lines) and two π σ bonds; (b) trimethylborane, with three π σ bonds; (c) chloroform, with three π σ bonds; (d) phosphorus oxyfluoride, with four approximately π σ bonds plus one p π σ bond; (e) phosphorus pentfluoride, with five π σ bonds; (f) sulfur hexafluoride, with six π σ bonds; (g) ammonium tetrafluoroborate: each ion has four π σ bonds; (h) aluminum bromide dimer.

Trimethylborane (D₃h). 2 We may assume that the methyl groups will have their usual configuration found in organic compounds. The Lewis structure of (CH₃)₃B will place six electrons in the valence shell of the boron atom, and in order that the electron pair be as far apart as possible, the methyl groups should be located at the corners of an equilateral triangle. This results in sp², or trigonal (D₃h) hybridization for the boron atom (Fig. 6.1b).

Phosgene (C₂O₂). A Lewis structure for CO₂ has eight electrons about the carbon, but one pair forms the π bond of the double bond, so again an sp², or trigonal, hybridization will be the most stable (Fig. 5.1f).

Phosphorus oxyfluoride (C₃v). Two Lewis structures can be drawn for the PF₃ molecule.

To a first approximation, the three fluorine atoms and the single oxygen atom will be bonded to the phosphorus atom with a bond from sp³ tetrahedral orbitals. One of the five 3d orbitals on the phosphorus atom also can overlap with a 2p orbital on the oxygen atom (Fig. 6.1d) and form a fifth bond, d₃p₃, further stabilizing the molecule.

Phosphorus pentfluoride (D₅h). A Lewis structure for the PF₅ molecule requires 10 electrons in the valence shell of the phosphorus atom and the use of 3s, 3p, and 3d orbitals and five σ π bonds. It is impossible to form five bonds in three dimensions such that they are all equidistant from one another, but the trigonal bipyramidal (Fig. 6.1e) and square pyramidal arrangements tend to minimize repulsions. Almost every five-coordinate molecule (coordination compounds excepted) which has been carefully investigated has been found to have a trigonal bipyramidal structure. The structure of the PF₅ molecule is shown in Fig. 6.1e (sp²d hybrid). The bonds are of two types: axial, the linear F—P—F system; and equatorial, the three P—F bonds forming a trigonal plane.

Sulfur hexafluoride (O₃h). Six sulfur–fluorine σ bonds require 12 electrons in the valence shell. Six equivalent bonds require an octahedron and so sulfur will be hybridized sp³d² as shown in Fig. 6.1f.

Ammonium tetrafluoroborate (T₄h). Both the ammonium (NH₄⁺) and tetrafluoroborate (BF₄⁻) ion are isoelectronic with the methane molecule and we might therefore reasonably expect them to have similar structures. Indeed, all four bonds are equivalent, and since the electrons avoid each other as much as possible, the most stable arrangement is a tetrahedron (Fig. 6.1g).

Aluminum bromide (D₅h). For the molecule AIBr₃, a structure similar to that of trimethylborane would be expected with 120° bond angles. Experimentally, however, it is found that aluminum bromide is a dimer, AIBr₂. This is readily explainable as a result of the tendency to maximize the number of bonds formed since AIBr₃ contains four bonds per aluminum atom. This is possible.

The point group symmetry of each molecule is given in parentheses. See Chapter 3.
both nuclei is severely reduced. This is a repulsive, or antibonding, situation. An electron density map for the hydrogen molecule ion, $H_2^+$, is shown in Fig. 5.6 illustrating the differences in electron densities between the bonding and antibonding conditions. We have postponed normalization of the molecular orbitals until now. Because $<j|^2 = 1$ for the probability of finding an electron somewhere in space, the integral of Eq. 5.31 becomes

$$\int \psi_2^2 \, dr = \int \psi_A^2 \, dr + \int \psi_B^2 \, dr + 2 \int \psi_A \psi_B \, dr$$

where $N_v$ is the normalizing constant. If we let $S$ be the overlap integral, $\int \psi_A \psi_B \, dr$, we have

$$\int \psi_2^2 \, dr = \left( \int \psi_A^2 \, dr + \int \psi_B^2 \, dr + 2S \right)$$

Now since the atomic wave functions $\psi_A$ and $\psi_B$ were previously normalized, $\int \psi_A^2 \, dr$ and $\int \psi_B^2 \, dr$ each equal one. Hence

$$N_2^2 = \frac{1}{2 + 2S}$$

and

$$N_2 = \sqrt{\frac{1}{2 + 2S}}$$

(N.35)

(N.36)

(N.37)

For most simple calculations the value of the overlap integral, $S$, is numerically rather small and may thus be neglected without incurring too great an error. This simplifies the algebra considerably and is sufficiently accurate for most purposes. With complete neglect of overlap, our molecular wave functions become

$$\psi_0 = \sqrt{\frac{1}{2}} (\psi_A + \psi_B)$$

and

$$\psi_2 = \sqrt{\frac{1}{2}} (\psi_A - \psi_B)$$

The idea of "complete neglect of overlap" refers only to the omission of the mathematical value of the overlap integral in the normalization calculation. Note, however, that "good overlap" in the qualitative sense is necessary for good bonding because the covalent energy, $\Delta E_c$, is proportional to the extent that the atomic orbitals overlap. If overlap is neglected in the calculations, the stabilization and destabilization of bonding and antibonding orbitals are equal (Fig. 5.7), and the value for both normalization constants is $(Eqs. 5.36$ and 5.37) $N_2 = N_0 = 0.71$. If the overlap is explicitly included in the calculations, the normalization coefficients are $N_2 = 1.11$ and $N_0 = 0.56$. Other molecules have smaller overlap integrals than $H_2$ and so the effect is less.

As we have seen from Eqs. 5.31 and 5.32 the only difference between the electron distribution in the bonding and antibonding molecular orbitals and the atomic orbitals is in those regions of space for which both $\psi_A$ and $\psi_B$ have appreciable values, so that their product $(S = \int \psi_A \psi_B \, dr)$ has an appreciable nonzero value. Furthermore, for bonding, $S > 0$; and for antibonding, $S < 0$. The condition $S = 0$ is termed nonbonding and corresponds to no interaction between the orbitals. That $S$ serves as a criterion for bonding, antibonding, and nonbonding conditions is consistent with our earlier assertion that bond strength depends on the degree of overlap of atomic orbitals. In general, we should expect that bonds will form in such a way as to maximize overlap.

In $s$ orbitals the sign of the wave function is everywhere the same (with the exception of small, intramolecular regions for $n > 1$), and so there is no problem with matching the sign of the wave functions to achieve positive overlap. With $p$ and $d$ orbitals, however, there are several possible ways of arranging the orbitals, some resulting in positive overlap, some in negative overlap, and some in which the overlap is exactly zero (Fig. 5.8). Bonding can take place only when the overlap is positive.
electrons would each of these three species have? Would you expect the nonbonding electron pairs on nitrogen or those on oxygen to be more reactive? Explain.

5.26 Construct a qualitative molecular orbital diagram for ClO₂ and compare it to the one presented in Figure 5.31 for NO₂.

5.27 Return to Problem 2.25. Answer it now in terms of group electronegativity.

5.28 The methyl group is usually considered to be electron-donating with regard to hydrogen, yet its electronegativity is not lower than hydrogen but slightly higher. Explain. (Hint: Think specifically about situations in which the methyl group is a good donor.)

5.29 You may have learned in organic chemistry that the acidity of acids R—C(O)OH depends upon χ,R. Discuss in terms of R = H, CH₃, and CH₂Cl₂.

5.30 The FSeO₃ group is extremely electronegative. On the basis of the ¹H NMR chemical shifts (Fig. 5.36) of methyl compounds CH₃X, Lentz and Seppelt have suggested that this group may be even more electronegative than fluoride. Discuss.

![Fig. 5.36](Translated from the original paper: Correlation of the ¹H chemical shift of methyl compounds CH₃X with the electronegativity (Allred-Rochow) of the group X. Extrapolation to the OSeF₃ group gives an electronegativity slightly greater than that of fluorine. (From Huppmann, P.; Lentz, D.; Seppelt, K. Z. Anorg. All. Chem. 1981, 472, 26-32. Reproduced with permission.)]

In this chapter a few simple rules for predicting molecular structures will be investigated. We shall examine first the valence shell electron pair repulsion (VSEPR) model, and then a purely molecular orbital treatment.

**Valence Shell Electron Pair Repulsion Theory**

We begin by considering the simplest molecules—those in which the electrons on the central atom are all involved in bonds. It should be kept in mind that each molecule is a unique structure resulting from the interplay of several energy factors and that the following rules can only be a crude attempt to average the various forces.

1. First, from the electronic configuration of the elements, determine a reasonable Lewis structure. For example, in the carbon dioxide molecule, there will be a total of 16 valence electrons to distribute among three atoms:

   ![Lewis structure](a) or ![Lewis structure](b)

   Note that a Lewis structure says nothing about the bond angles in the molecule since both (a) and (b) meet all the criteria for a valid Lewis structure.

2. A structure should now be considered which lets all the electron pairs in the valence shell of the central atom(s) get as far away from each other as possible. In the usual σ-π treatment this usually means ignoring the π bonds temporarily since they will follow the σ bonds. In carbon dioxide there will be two σ bonds

---

It may occur to the reader that it is always possible to bring the orbitals together in such a way that the overlap is positive. For example, in Fig. 5.8g, if negative overlap is obtained, one need only invert one of the atoms to achieve positive overlap. This is true for diatomic molecules or even for polyatomic linear molecules. However, when we come to cyclic compounds, we no longer have the freedom arbitrarily to invert atoms to obtain proper overlap matches. One example will suffice to illustrate this.

There is a large class of compounds of formula \((\text{PNX}_2)^n\) (X = F, Cl, Br), containing the phosphazene ring system (see Chapter 16). The trimer, \(\text{P}_3\text{N}_3\text{X}_6\), is illustrated in Fig. 5.9. Note the resemblance to benzene in the alternating single and double bonds. Like benzene, the phosphazene ring is aromatic, that is, the \(\sigma\) electrons are delocalized over a conjugated system with resonance stabilization. The description of the \(\pi\) bonding in the phosphazene ring, which involves \(p\) orbitals on the nitrogen atoms and \(d\) orbitals on the phosphorus atoms, has been a matter of considerable debate. One view is illustrated in Fig. 5.10, in which the phosphazene ring has been split open and arranged linearly for clarity. We start on nitrogen atom number one (N₁) and assume an arbitrary assignment of the positive and negative lobes of the \(p\) orbital. The phosphorus atom \(\pi\) bonds through its \(d\) orbitals, and so for the P₁ atom we draw a

---

Fig. 5.8 Arrangement of atomic orbitals resulting in positive (a-f), negative (g-i), and zero (m-o) overlap.

Fig. 5.9 Comparison of bonding in the ring systems of (a) benzene and (b) hexachlorotriphosphazene.

Fig. 5.10 Overlap of the orbitals in the \(p-p\) \(\pi\) system in benzene (a) and the \(p-d\) \(\pi\) system in the phosphazene ring (b). Note the mismatch of orbital symmetry in the latter.
5.1 Draw Lewis structures for CS₂, PF₅, SnH₄, HONH₃⁺.

5.2 Draw Lewis structures for H₂CO, HNO₂, NO₂, Be(CH₃)₃.

5.3 Draw Lewis structures for BF₃, SF₅, XeF₅, PF₅, IF₅.

5.4 Show that there is no mismatch of the sign of the wave function in the π system of (PNC)₂, in contrast to (PNC)₃.

5.5 Write the MO electron configuration for the NO⁻ ion.
   a. What is the bond order?
   b. Will the bond length be shorter or longer than in NO?
   c. How many unpaired electrons will be present?
   d. Will the unpaired electrons be concentrated more on the N or the O? Explain.

5.6 Consider the hypothetical dioxygen peroxide, O₂O₂⁻, discussed in Chapter 4. If this compound did exist, what would be the electronic structures of the ions? Discuss bond orders, bond lengths, and unpaired electrons.

5.7 The resonance of BF₃ (page 145) is still a matter of some dispute because one chemist will postulate too many bonds in structure II (favorably), another will point to F⁻ (unfavorably), both as structures for which charges completely rule out resonance.

5.8 Write resonance structures, including formal charges, for O₃, SO₂, NO₂.

5.9 The assumption was made that the carbon-carbon σ bond in CH₂=CH₂ is the same as that in CH₃CH₃. In reality, it is probably somewhat stronger. Discuss.

5.10 The NO₂ molecule was discussed on page 145. Consider the isoelectronic NO₂⁻ molecule. Would you expect it to be more stable or less stable than NO₂? Why? Does CO₂ have the CO₂⁻ arrangement rather than COO⁻?

5.11 The cyanate ion, OCN⁻, forms a stable series of salts, but many fulminate, CNO⁻, are explosive (L. Fulman, to finish). Explain. (For a lead, see page 145; for a slightly different approach, see Pauling, L. J. Chem. Educ. 1975, 51, 577.)

5.12 Calculate the electronegativity of hydrogen from the ionization potential and the electron affinity.

5.13 In later chapters you will find examples of the stabilization of covalent bonds through lone resonance energy. For now, show its importance by predicting whether the molecules N₂X₂ (X = hydrogen or halogen) are stable, that is, whether the reaction

\[
N₂ + 2X \rightarrow 2NX
\]

is exothermic. Assume that neither ammonia nor any of the nitrogen halides has yet been synthesized, so you are permitted to look up bond energies for N₂X₂, N₂⁻, and X⁻X (Appendix E), but you must predict the bond energy of N₂⁻X⁻X.

5.14 Which do you expect to be more acidic:

\[
\text{CH}_3\text{OH} \text{ or } \text{CH}_2=\text{OH}\]

Explain. (See Cook, A. G.; Mason, G. W. J. Org. Chem. 1972, 37, 3342-3345.)

5.15 In Table 5.6 the electronegativities of the noble gases are, as a group, the highest known, being higher even than those of the halogens. Yet we all know that the noble gases do not accept electrons from elements of low electronegativity:

\[
\text{Na} + \text{A} \rightarrow \text{Na}^+\text{A}^-
\]

Discuss the meaning of the electronegativities of the noble gases.

5.16 In discussing ionic resonance, AB ↔ A⁺B⁻, where:

\[
\phi = \alpha_{\text{ionic}} + \beta_{\text{covalent}}
\]

Pauling assumed that \( \phi_{\text{ionic}} \) made a negligible contribution if \( x_A = x_B \). The bond energy of C₂H₂ is 240 kJ mol⁻¹ and the bond length is 1.39 pm. In the C₂ molecule, \( x_A = x_B \). Show by means of a Born-Haber-type calculation that the canonical structure, O²C⁻⁻, cannot contribute appreciably to the stability of the molecule. (You may check your answer with Pauling, L. The Nature of the Chemical Bond, 3rd ed.; Cornell University: Ithaca, NY, 1960; p 73.)

5.17 The energy necessary to break a bond is not always constant from molecule to molecule. For example:

\[
\text{NC} = \text{NCl} + \text{Cl} \quad \Delta H = -375 \text{ kJ mol}^{-1}
\]

\[
\text{ONCl} \rightarrow \text{NO} + \text{Cl} \quad \Delta H = 158 \text{ kJ mol}^{-1}
\]

Suggest a reason for the difference of ~200 kJ mol⁻¹ between these two enthalpies.

5.18 From what you know of the dependence of ionization energies, electron affinities, and electronegativities, would you expect the addition of some character to a hybrid to raise or lower the electronegativity? For example, will sulfur be more electronegative when hybridized sp² or sp³?

5.19 The dipole moment of H—C=C—Cl is in the direction −. Explain, carefully.

5.20 The legend to Fig. 5.20 says: "The isomers CCl₃ and the bond length is 199 pm. In the Cl₂ molecule, \( x_A = x_B \). Explain by means of a Born-Haber-type calculation that the canonical structure, O²C⁻⁻, cannot contribute appreciably to the stability of the molecule. (You may check your answer with Pauling, L. The Nature of the Chemical Bond, 3rd ed.; Cornell University: Ithaca, NY, 1960; p 73.)

5.21 Look at Figs. 5.14 and 5.15 carefully. Identify:
   a. the nodal planes responsible for the symmetry of the MOs (i.e., sigma, pi, etc.).
   b. any changes in electron density that you can ascribe to bonding versus antibonding situations.
   c. Oxygen is more electronegative than carbon and Fig. 5.18a indicates that there is more electron density on oxygen than on carbon in carbon monoxide. Yet the dipole moment of CO is quite small (0.373 x 10⁻²⁴ C m; 0.112 D) and it is known that the oxygen atom is the positive end of the dipole. Explain. Hint: Does a comparison with the isoelectronic disulphides molecule (Fig. 5.18b) help?

5.22 The dipole moment of H—C≡C—Cl is in the direction −. Explain, carefully.

5.23 Using the MO treatment of BeH₂ (page 175) as a starting point, write linear combinations of molecular orbitals for the molecular orbitals in CO₂.


5.25 The HOMO (a₁) of NO₂⁺ is somewhat antibonding. On this basis, what predictions would you make about the N—O bond lengths in NO₂⁻, NO₂⁺, and NO₂⁻? How many unpaired...
Molecular Orbital Theory

Symmetry of Molecular Orbitals

Molecular Orbitals in Homonuclear Diatomic Molecules

Some of the possible combinations of atomic orbitals are shown in Fig. 5.11. Those orbitals which are cylindrically symmetrical about the internuclear axis are called \( \sigma \) orbitals, analogous to an \( s \) orbital, the atomic orbital of highest symmetry. If the internuclear axis lies in a nodal plane, a \( \pi \) bond results. In \( \delta \) bonds (Chapter 16) the internuclear axis lies in two mutually perpendicular nodal planes. All antibonding orbitals (identified with an * ) possess an additional nodal plane perpendicular to the internuclear axis and lying between the nuclei. In addition, the molecular orbitals may or may not have a center of symmetry. Of particular interest in this regard are \( \pi_p \) orbitals, which are ungerade, and \( \pi^*_p \) orbitals, which are gerade.

Molecules containing two atoms of the same element are the simplest molecules to discuss. We have already seen the results for the hydrogen molecule (page 157; Fig. 5.7) and for the linear combination of \( s \) and \( p \) orbitals (Fig. 5.8). We shall now investigate the general case for molecular orbitals formed from two atoms having atomic orbitals \( 1s, 2s, 2p, 3s, \) etc.

There are two criteria that must be met for the formation of bonding molecular orbitals, that is, orbitals that are more stable (lower in energy) than the contributing atomic orbitals. One is that the overlap between the atomic orbitals must be positive. Furthermore, in order that there be effective interaction between orbitals on different atoms, the energies of the atomic orbitals must be approximately the same. For now we will assume that molecular orbitals will form from corresponding orbitals on the two atoms (i.e., \( 1s + 1s, 2s + 2s, \) etc.). We shall soon see that under some circumstances this assumption will have to be modified. When we combine the atomic orbitals in this way, the energy levels shown in Fig. 5.12 are obtained. The appropriate combinations are:

\[
\begin{align*}
\sigma_{1s} &= 1s_A + 1s_B \\
\sigma_{2s} &= 2s_A - 2s_B \\
\sigma_{2p_x} &= 2p_{x_A} + 2p_{x_B} \\
\sigma_{2p_y} &= 2p_{y_A} - 2p_{y_B} \\
\sigma_{2p_z} &= 2p_{z_A} + 2p_{z_B} \\
\sigma^*_{1s} &= 1s_A - 1s_B \\
\sigma^*_{2s} &= 2s_A - 2s_B \\
\sigma^*_{2p_x} &= 2p_{x_A} - 2p_{x_B} \\
\sigma^*_{2p_y} &= 2p_{y_A} + 2p_{y_B} \\
\sigma^*_{2p_z} &= 2p_{z_A} - 2p_{z_B}
\end{align*}
\]

The \( \sigma \) and \( \sigma^* \) orbitals correspond to the molecular orbitals seen previously for the hydrogen molecule. The atomic \( 2s \) orbitals form a similar set of \( \sigma \) and \( \sigma^* \) orbitals. The \( \sigma_{1s} \) and \( \sigma_{2s} \) can form \( \sigma \) bonds from direct ("head on") overlap of the \( 1s \) and \( 2s \) orbitals and two \( \pi \) bonds from parallel overlap of the \( 1s \) and \( 2s \) orbitals. Because the overlap is greater in the former case, we should expect the covalent energy to be greater also (page 153), and \( \sigma \) bonds are generally stronger than \( \pi \) bonds. Hence the \( \sigma_{2s} \) orbital is stabilized (lowered in energy) more than the \( \pi_{2s} \) orbitals, and conversely the corresponding antibonding orbitals are raised accordingly. By analogy with atomic electron configurations, we can write molecular electron configurations. For \( H_2 \) we have

\[
H_2 = \sigma^2_{1s}
\]
For many reasons, chemists would like to be able to estimate the charges on the constituent atoms in a molecule. There have been many attempts to do this, but none has proved to be completely successful. The ideal way would be to solve the wave equation for a molecule without the use of any simplifying assumptions, and then to calculate the electron distribution. Such ab initio calculations are possible for small molecules but become increasingly difficult as the number of atoms increases. Even when the calculations are possible, there is not complete agreement among chemists as to the best way of apportioning the charge density among the atoms in the molecule.

Several workers have suggested semiempirical methods based on electronegativity for the estimation of charge. Only one method will be discussed here. Sanderson has proposed that when a bond forms between two atoms electron density will shift from one atom to the other until the electronegativities have become equalized. Initially the more electronegative element will have a greater attraction for electrons (Fig. 5.34), but as the electron density shifts toward that atom it will become negative and lend to attract electrons less. Conversely, the atom which is losing electrons becomes somewhat positive and attracts electrons better than it did when neutral. This process will continue until the two atoms attract the electrons equally, at which point the electronegativities will have been equalized and charge transfer will cease (Fig. 5.35):

\[ x_A = a_A + b_A \delta_A = x_B = a_B - b_B \delta_B \]  \hspace{1cm} (5.84)

\[ \delta_A = \frac{a_B - a_A}{b_A + b_B} \]  \hspace{1cm} (5.85)

The partial charges in the HCl molecule may be estimated with Eq. 5.85 by using the appropriate \( a \) and \( b \) values from Table 5.6:

\[ a_H = 7.17, \quad b_H = 12.84, \quad a_C = 12.15, \quad b_C = 11.55. \]

\[ \delta_C = \frac{12.15 - 7.17}{11.55 + 12.84} = 0.20 \]  \hspace{1cm} (5.86)

The charges estimated by this method is often different from a similar estimate based on dipole moments. If the total ionization energy (including the electron affinity) were the only energy involved in the charge distribution, Eq. 5.85 would be rigorously correct. In a molecule, however, other energy terms are important. The exchange energy associated with the overlap of orbitals will be reduced if the charge transfer is too great. The Madelung energy (so named because of resemblance to that found in ionic crystals) resulting from the electrostatic attraction of \( A^+ \) for \( B^- \) (within the molecule) tends to increase ionicity. These energies tend to cancel each other in effect because they work in opposite directions, so Eq. 5.85 can be considered a useful, qualitative approximation.

Although there is no universal agreement on the "real" charges in molecules, various attempts have been made to improve upon simple electronegativity calculations. One method is to estimate the exchange and Madelung energies by simple bonding models, and then to use them to adjust the values obtained by the electronegativity equalization method. This modification has been found to correlate well with some ab initio calculations for some simple molecules.

There is a maxim that when there are many treatments for a disease, none of them is completely adequate. The same idea could be applied to electronegativity in view of the many attempts to define and quantify it. Nevertheless, bond energies, polarities, and the inductive effect are fundamental to much of inorganic, organic, and physical chemistry, hence the efforts applied to electronegativity theory. While there is as yet no complete agreement on all aspects of electronegativity, defining it some way in terms of the energies of the valence electrons is generally accepted as the best approach, although the last word has undoubtedly not yet been said on the matter.
Bonding Models in Inorganic Chemistry: 2. The Covalent Bond

1. Molecules containing one to four electrons. We have already seen the He molecule which has only two electrons in the \( 1s \) orbital. Two bonding electrons constitute a chemical bond. The molecular orbital theory does not restrict itself to even numbers of bonding electrons, and so the bond order is given as one-half the difference between the number of bonding electrons and the number of antibonding electrons:

\[
\text{Bond order} = \frac{1}{2}(N_b - N_a)
\]

The molecule \( \text{He}_2 \) is unknown because the number of antibonding electrons (2) is equal to the number of bonding electrons (2) and the net bond order is zero. With no bond energy to overcome the dispersive tendencies of entropy, two helium atoms in a "molecule" will not remain together but fly apart. If it existed, molecular helium would have the electron configuration:

\[
\text{He}_2 = \sigma_1^2 \sigma_2^2
\]

If helium is ionized, it is possible to form diatomic helium molecules, \( \text{He}^+ \). Such a molecule will contain three electrons, two bonding and one antibonding, for a net bond order of one-half. Such a species, although held together with only about one-half the bonding energy of the hydrogen molecule, should be expected to exist. In fact it does, and it has been observed spectroscopically in highly energetic situations sufficient to ionize the helium. That it is not found under more familiar chemical conditions is, for example, 

2. Lithium and beryllium. Two helium atoms contain 6 electrons. Four will fill the \( \sigma_1 \) and \( \sigma_2^* \) orbitals with no bonding. The last two electrons will enter the \( \pi_2 \) orbital, giving a net bond order of one in the \( \text{Li}_2 \) molecule. The electron configuration will be:

\[
\text{Li}_2 = \sigma_1^2 \sigma_2^2 \pi_2^2
\]

Using Fig. 5.12 as a guide, we can proceed to build up various diatomic molecules in much the same way as the aufbau principle was used to build up atoms.

3. Oxygen, fluorine, and neon. Three of these molecules can be treated with the same energy diagram that we have been using for other diatomic molecules of the second-row elements. As we shall see shortly, the intervening molecules, \( \text{Be}_2, \text{C}_2, \) and \( \text{N}_2 \), require additional considerations, which lead to an alteration in the relative energies of the molecular orbitals.

The oxygen molecule was one of the first applications of molecular orbital theory in which it proved more successful than valence bond theory. The molecule contains sixteen electrons. Four of these lie in the \( \sigma_1 \) and \( \pi_x \) orbitals, which cancel each other and may thus be ignored. The next four electrons occupy \( \sigma_2 \) and \( \sigma_2^* \) orbitals and also contribute nothing to the net bonding. The remaining eight electrons occupy the \( \pi_y, \pi_z \) and \( \sigma^* \) levels giving as the electron configuration:

\[
\text{O}_2 = \pi_y^2 \pi_z^2 \sigma^*^2
\]

However, examination of the energy level diagram in Fig. 5.12 indicates that the \( \sigma^* \) level is doubly degenerate from the two equivalent \( \sigma \) orbitals, \( \sigma_1 \) and \( \sigma_2 \), and...
phosphorus, and sulfur do not fit well into such simple schemes. This is because the hybrids are often some nonintegral mix of \( s \) and \( p \) character. Methods have been proposed for determining hybridizations from bond angles, but they are approximate at best (see Chapter 6). Recently, Bratseh\(^{49} \) has suggested a purely numerical rule based on an extension of the hybrid properties of the early, well-behaved elements in each row. Elements with group numbers, \( N = 1\) (IA, 1), \( 2\) (IIA, 2), \( 3\) (IIIA, 3), and \( 4\) (IVA, 14) form hybrids of the type \( sp^{x-1}\). For the nonmetals to the right of the periodic table, Bratseh suggests working hybridizations of nitrogen, Group VA (15) = \( sp^2\), carbon, oxygen, Group VIA (16) = \( sp^3\), and \( 17\) % \( s \) character, etc. These values are in reasonable agreement with estimates from bond angles, and the electronegativity values thus obtained are consistent with electronegativities obtained by other methods. These values have been listed in Table 5.6, but other hybridizations are listed as well. A value of \( 20\% \) \( s \) character might be best for nitrogen in ammonia, but in the ammonium ion, the nitrogen atom is isoelectronic with the carbon in methane, and the hybridization must be \( sp^3\).

It is often convenient to have an estimate of the inductive ability of a substituent group. As we have seen previously, we cannot use a single value of carbon to represent the electronegativity of carbon in both \( CH_3 \) and \( CF_3 \). The electronegativities of these two groups will be the electronegativity of carbon as it is adjusted by the presence of three hydrogen or three fluorine atoms. Estimation of group electronegativities has been approached from a variety of ways. Organic chemists have developed sets of substituent constants from kinetic data\(^{49} \) and these have proven useful in certain inorganic systems as well. Other values have been obtained from physical measurements of electronic effects, and calculated directly from atomic electronegativities.\(^{51} \) Some comparative values are listed in Table 5.7. We need not go into the details of the various methods, but note that there is general agreement, and that two simple rules-of-thumb hold for group electronegativities: (1) The inherent group electronegativity, \( \chi_0 \) is approximated by the simple average of the inherent atomic electronegativities. (2) The charge coefficient, \( \chi \), is an average as well, but inversely proportional to the number of atoms in the group. Thus the electronegativity of a group is given by:

\[
\chi = \chi_0 + \frac{\sum a_i}{n} + \frac{\sum b_i}{n^2} \chi_0 \tag{S.83}
\]

It is intuitively reasonable that these values should be an average over the \( n \) values of the \( i \)th...\( n \)th atom. In the same way, the charge coefficient should be inversely proportional (i.e., the charge capacity should be directly proportional) to the number, \( n \), of atoms over which the charge may be spread. This is the most important property of group electronegativities: Groups are "superatoms" capable of absorbing a large amount of positive or negative charge. This means that groups can donate or accept charge better than would be indicated by their inherent electronegativities (\( \chi \) values) alone. For example, the methyl group is slightly, though not significantly, more electronegative than hydrogen. Yet the methyl group is generally considered a better donor than the hydrogen atom. It is the greater charge capacity, which results from the ability to spread the charge around that allows the methyl group to donate more electron density than the smaller hydrogen atom:

\[
\begin{align*}
\text{H}^+ & \quad \to \quad \text{H}^+ \\
\text{H}^+ & \quad \to \quad \text{H}^+
\end{align*}
\]


\(^{51}\) For methods of calculating group electronegativities from Mulliken-Slater electronegativity values of the constituent atoms, see Bratseh, S. G. J. Chem. Educ. 1985, 62, 101-103.
Hund's rule of maximum multiplicity predicts that the two electrons entering the \(2p\) level will occupy two different orbitals, so the electronic configuration can be written more explicitly as

\[
\text{O}_2 = \text{KK} \sigma_2^2 \pi_2^2 \pi_3^2 \pi_4^2 \pi_5^2 \pi_6^2
\]

This has no effect on the bond order, which is still two [(16 - 2)] as anticipated by valence bond theory. The difference lies in the paramagnetism of molecular oxygen resulting from the two unpaired electrons. (In this regard \(\text{O}_2\) is analogous to atomic carbon in which the last two electrons remained unpaired by entering different, degenerate orbitals.) The simple valence bond theory predicts that all electrons in oxygen will be paired; in fact, the formation of two bonds demands that the maximum number of electrons be paired. This is the first case of several we shall encounter in which the stress placed on paired bonding electrons is exaggerated by the valence bond theory. The molecular orbital theory does not require such pairing as it merely counts the number of bonding versus antibonding electrons. The experimentally measured paramagnetism of \(\text{O}_2\) confirms the accuracy of the MO treatment.

For the fluorine molecule, there will be a total of 18 electrons distributed:

\[
\text{F}_2 = \text{KK} \sigma_2^2 \pi_2^4 \sigma_3^2 \sigma_4^2 \sigma_5^2 \sigma_6^2
\]

The net bond order is one, corresponding to the \(\sigma\) bond, and agreeing with the valence bond picture. The addition of two more electrons to form the \(\text{Ne}_2\) molecule will result in filling the last antibonding orbital, the \(\pi_6^2\) orbital. This will reduce the bond order to zero and \(\text{Ne}_2\), like \(\text{He}_2\), will not exist.

**4. Boron, carbon, and nitrogen.** According to Fig. 5.12, the \(\text{B}_2\) molecule would be predicted to have a single \(\sigma\) bond and be diamagnetic. Experimentally the \(\text{B}_2\) molecule is found to have two unpaired electrons. The \(\text{C}_{2s}\) molecule would be predicted to have an electron configuration \(\text{KK} \sigma_2^4 \pi_2^4 \sigma_3^2 \pi_6^4\), and be paramagnetic. The experimental evidence indicates that the ground state of \(\text{C}_2\) is diamagnetic.

The problem here is that in constructing Fig. 5.12 mixing was allowed only between orbitals on atoms A and B that were identical in energy. Actually, mixing will take place between all orbitals of proper symmetry, inhibited only by the fact that if the energy mismatch between orbitals is large, mixing will be reduced. We are therefore justified in dismissing mixing between the \(2s\) and \(2p\) orbitals. The energy difference between the \(2s\) and \(2p\) orbitals is less and varies with the effective nuclear charge. With a larger \(Z^*\), as in fluorine, the energy difference is greater and mixing may again be neglected. The difference in energy between the \(2s\) and \(2p\) levels dramatically increases from about 200 kJ mol\(^{-1}\) in the lithium atom to about 2500 kJ mol\(^{-1}\) in fluorine. In the case of the elements to the left of the series, the lower effective nuclear charge allows the \(2s\) and \(2p\) orbitals to come sufficiently close to mix. This phenomenon is the equivalent of hybridization in the valence bond theory.

Another way to view this phenomenon is to ignore \(s-p\) mixing in the initial construction of molecular orbitals but then recognize that molecular orbitals of the same symmetry will interact if they are close enough in energy. Thus the \(\sigma_2(2s)\) and \(\pi_2(2p)\) molecular orbitals in a molecule such as \(\text{B}_2\) will interact. As a result, the lower-energy orbital \(\sigma_2(2s)\) will be stabilized while the higher-energy one \(\pi_2(2p)\) will become less stable. This leads to a reversal in the energy ordering of the \(\sigma_2(2p)\) and \(\pi_2(2p)\) molecular orbitals (Fig. 5.13) compared to the case for molecules such as \(\text{F}_2\), where essentially no mixing occurs. There will also be some interaction between the \(\pi_2(2p)\) and \(\sigma_6(2p)\) orbitals, with the lower-energy orbital becoming stabilized and the higher-energy orbital being destabilized. However, because these orbitals do not correspond to each other closely in energy, the interaction will be negligible. Note in Fig. 5.13 that \(\text{N}_2\) is no longer appropriate to use labels such as \(2s\) and \(2p\) to identify the origins of molecular orbitals, so we merely label them according to their symmetry number them in order from the most to the least stable. Thus \(\sigma_2(2s)\) becomes \(\sigma_2\), \(\sigma_2(2p)\) becomes \(\pi_6\), etc.

The magnetic properties of \(\text{B}_2\) and \(\text{C}_2\) provide strong experimental verification that their electron configurations are based on Fig. 5.13 rather than on Fig. 5.12. For \(\text{N}_2\) (fourteen electrons), either diagram would predict a triple bond (one \(\sigma\) and two \(\pi\)) and diamagnetism, consistent with physical measurements. Experimental evidence supporting one configuration over the other for \(\text{N}_2\) has been sought in photoelectron spectroscopy. The method involves ionizing electrons in a molecule or atom by subjecting them to radiation of appropriate energy. When ionizing photons in the ultraviolet range are used, valence-level electrons are ejected, whereas X rays can be used to ionize inner, core electrons. The energy of the impinging photons is known from their frequency \((E = hv)\), and the kinetic energy \((E_k)\) of the ejected electrons can be measured.
Electronegativity

Not all chemists would agree with this statement. Pauling's discussions of the subject for the details of the methods he used.\(^\text{45}\) but an outline follows.

Pauling assumed that if the CIF bond were completely covalent, its bond energy would be simply the average of the Cl and F bond energies:

\[
\frac{242 + 158}{2} = 200 \text{ kJ mol}^{-1}
\]

(8.80)

The ionic resonance energy is the difference between the experimental bond energy of CIF, 255 kJ mol\(^{-1}\), and the calculated value, 200 kJ mol\(^{-1}\), or 55 kJ mol\(^{-1}\). Pauling defined the difference in electronegativity between chlorine and fluorine as the square root of the ionic resonance energy.\(^\text{43}\)

\[
\sqrt{55} = 0.76
\]

(8.81)

This may be compared with the tabular value for the difference in electronegativities of fluorine and chlorine, 3.98 − 3.16 = 0.82, which is based on many experimental data, not just the single calculation illustrated here. Once again, the details of the calculation are not particularly important since Pauling’s method of obtaining electronegativity data is probably mainly of historical interest.\(^\text{44}\) The concept of covalent-ionic resonance is still quite useful, however. Unfortunately, as alternative methods of treating electronegativity have developed, the fact that a bond with partial ionic character can be stronger than either a purely covalent or purely ionic bond has often been overlooked. Energies associated with electronegativity differences can be useful in accounting for the total bonding energies of molecules.

Other Methods of Estimating Electronegativity

Many other methods have been suggested for determining the electronegativity values of the elements. Only one general method will be discussed here. It is to consider electronegativity to be some function of size and charge. These methods differ among themselves only in the choice of function (energy, force, etc.) and the method of estimating the effective charge. Pauling and Allred–Rochow defined electronegativity as the electrostatic force exerted by the nuclei on the valence electrons. They used effective nuclear charges obtained from Slater’s rules\(^\text{46}\) and obtained the formula:

\[
\chi_A = \left(3590 \frac{Z^2}{r^4}\right) + 0.744
\]

(8.82)

where \(r\) is the covalent radius (pm). The Allred–Rochow scale has been widely accepted as an alternative to Pauling’s thermochemical method for determining electronegativities. Allred–Rochow values are listed in Table 5.6.

Another definition that is based on size and charge, but in a unique way, is the definition of Sanderson,\(^\text{47}\) which is based on relative electron density. This method has never been accepted widely, although Sanderson has applied it successfully to a variety of problems.\(^\text{48}\) and his values were the first to illustrate the interesting electronegativity properties of the posttransition elements (see Chapter 18).

Values for each of the electronegativity systems discussed here are listed in Table 5.6. With more than one valid system available, the choice of the “best” one is not always easy. We can arbitrarily divide the various methods into two groups. One consists of the methods that depend on orbital energies; the Mulliken–Jaffe theory, density functional theory, and the spectroscopic theory. They may be termed “theoretical” or “absolute” scales because they are based on the fundamental orbital energies of isolated atoms. The other scales are “empirical” and “relative” because they utilize experimentally obtained data such as enthalpies of formation, covalent radii, etc. Both types of systems have advantages. In general, the energy scales are more satisfying because they are, in a sense, more fundamental and basic. The empirical methods also have an advantage, resulting directly from their method of derivation. In other words, variables such as hybridization, etc., are often “built in” as long as the atom under consideration is in a fairly typical environment. Each of the empirical methods has advantages and disadvantages, adherents and detractors, and they do not really differ greatly among themselves. If the situation is sufficiently nonspecific to make it necessary to use an empirical system, it probably will not make a great deal of difference which is chosen. However, one must be consistent and avoid picking the value for one element from Pauling, another from Allen, and a third from Allred–Rochow. By judicious mixing of systems like this, one could probably “prove” anything! Choosing the appropriate hybridization for use with Mulliken–Jaffe electronegativities sometimes presents problems. Only the elements to the left in the periodic table have strong covalent hybridizations assignable by structure. Thus few would argue with an assumption of sp\(^3\) for boron in its tricovalent compounds, and organic chemistry is based on the successful assumption of dinitrogen (sp\(^2\)), trigonal (sp\(^3\)), and tetrahedral (sp\(^4\)) hybridizations for carbon. However, the hybridizations of nitrogen, oxygen, phos-
The difference between these two quantities (IE) is the amount of energy that must be provided to overcome the attraction of the nuclei for the ionized electron:

\[ IE = E_{\text{ion}} - E_{\text{atom}} \quad (5.41) \]

The technique thus can provide valuable information regarding energies of occupied molecular orbitals in a molecule since, by Koopmans' theorem, IE is the energy of an atomic or molecular orbital. The theorem assumes that orbital energies are the same in the ion (N2 + in this case) produced in the photoelectron experiment as in the original molecule. The photoelectron spectrum of N2 shows that the IE values for the 5σ and 1π electrons are about 15.6 and 16.7 eV, respectively, giving –15.6 and –16.7 eV as the orbital energies and suggesting that sufficient s-p mixing (or molecular orbital interaction) occurs in this molecule to make the 5σ level higher in energy than the 1π. However, ab initio calculations reveal that these two levels are quite close in energy and may undergo a reversal in their respective orders during the photoionization process. In other words, the Koopmans approximation cannot be assumed to hold for N2.

Some molecular orbital results for first- and second-row diatomic molecules, as well as relevant experimental data, are summarized in Table 5.5.

### Table 5.5

<table>
<thead>
<tr>
<th>Molecular orbital predictions</th>
<th>Experimental data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecule</td>
<td>Electrons</td>
</tr>
<tr>
<td>H₂</td>
<td>2</td>
</tr>
<tr>
<td>H₂O</td>
<td>4</td>
</tr>
<tr>
<td>Li₂</td>
<td>6</td>
</tr>
<tr>
<td>Be₂</td>
<td>8</td>
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<tr>
<td>B₂</td>
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<td>C₂</td>
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<td>O₂</td>
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</tr>
<tr>
<td>F₂</td>
<td>18</td>
</tr>
<tr>
<td>Ne₂</td>
<td>20</td>
</tr>
</tbody>
</table>

※ See discussion of bond energies in Appendix E.

### Further support for the MO descriptions presented in the preceding section comes from investigation of the bond lengths in some diatomic molecules and ions. For example, consider the oxygen molecule. As we have seen previously, it has a double bond resulting from two σ-bonding electrons, four π-bonding electrons, and two

Electron Density in Molecules Li₂

through F₂

Molecular Orbitals in Heteronuclear Diatomic Molecules

n-antibonding electrons. The bond length is 121 pm. Addition of two electrons to the oxygen molecule results in the well-known peroxide ion, O₂⁻:

\[ O₂ + 2e⁻ → O₂⁻ \quad (5.42) \]

According to Fig. 5.12 these two electrons will enter the π orbitals, decreasing the bond order to one. Since the compressive forces (bond energy) are reduced and the repulsive forces (antibonding electron repulsions) remain the same, the bond length is increased to 149 pm. If only one electron is added to an oxygen molecule, the superoxide ion, O₂⁻, results. Because there is one less antibonding electron than in O₂⁻, the bond order is 1 and the bond length is 126 pm.

Furthermore, ionization of O₂ to a cation:

\[ O₂ → O₂⁺ + e⁻ \quad (5.43) \]

causes a decrease in bond length to 112 pm. The electron ionized is a π antibonding electron and the bond order in O₂⁺ is 1.

The nitric oxide molecule, NO, has a bond length of 115 pm and a bond order of 2. Ionization to the nitrosyl ion, NO⁺, removes an antibonding π electron and results in a bond order of three (isoelectronic with N₂) and a shortening of the bond length to 106 pm. In contrast, addition of an electron (to a π orbital) causes a decrease in bond order and an increase in bond length.

The fact that the formation of the nitrosyl ion results from the removal of an antibonding electron makes the ionization energy (IE) for the reaction

\[ NO → NO⁺ + e⁻ \quad (5.44) \]

taller than it is for the unbound atoms of nitrogen (IE = 1402 kJ mol⁻¹) and oxygen (IE = 1314 kJ mol⁻¹). The nitrosyl ion is thus stabilized and exists in several compounds, such as NO⁺HSO₃ and NO⁺BF₄⁻.

A comparison of the ionization energies of molecular oxygen and nitrogen illustrates the same point. The ionization energy of molecular nitrogen is 1035 kJ mol⁻¹, greater than that of atomic nitrogen, in agreement with Fig. 5.13 that a (and therefore more stable) electron is removed. In contrast, the ionization energy of molecular oxygen is 1164 kJ mol⁻¹, less than that of atomic oxygen. In this case the ionized electron is removed from an antibonding orbital, requiring less energy.

The approximate shapes of molecular orbitals have been given previously (Fig. 5.11). These give a general idea of the electron distribution in diatomic molecules. Wahl has computed electron density contours for the molecular orbitals of diatomic molecules for H₂ to Ne₂. Some examples are shown in Figs. 5.14 and 2.15. Note particularly that: (1) bonding orbitals cause an increase in electron density between the nuclei; (2) antibonding orbitals have nodes and reduced electron density between nuclei; and (3) inner shells (1s in Li, for example) are so contracted from the higher effective nuclear charge that they are nearly spherical with almost no overlap and thus contribute little to the overall bonding. We are thus justified in ignoring these core electrons in determining the molecular electron configuration (page 163).

In developing a molecular orbital description for heteronuclear diatomics, we need to take into account the fact that different types of atoms have different capacities to attract electrons. The ionization potential of fluorine is considerably greater than that
Electronegativity

The electronegativity of the nitrogen atom increases as the $s$ character of the hybridization increases, and hence its polarity decreases.

Another interesting case has been found by Streitwieser and coworkers. It has been found that strained ring systems of the type shown in Fig. 5.33 are much more reactive at position $1$ than at position $2$ in reactions involving loss of positive hydrogen. The strain in the four-membered ring results in the use of more $p$ character in these bonds by the $C_4$ atom (the shaded orbitals in Fig. 5.33). The corresponding increased $s$ character in the carbon to $C_1$ causes a greater electronegativity, an induced positive charge, and a greater acidity of the hydrogen atom. In the related pyridine derivative with a nitrogen atom in place of $C_4$, the same phenomenon is seen in reduced electron density on the nitrogen atom and reduced basicity compared to the unconstrained analogue.

The electronegativity of an atom can vary in response to the partial charge induced by substituent atoms or groups. For example, methyl iodide hydrolyzes as expected for alkyl halides, but trifluoromethyl iodide gives unusual products:

\[
\begin{align*}
\text{CH}_3\text{I} + \text{OH}^- & \rightarrow \text{CH}_3\text{OH} + \text{I}^- \quad \text{(5.75)} \\
\text{CF}_3\text{I} + \text{OH}^- & \rightarrow \text{CF}_3\text{H} + \text{IO}^- \quad \text{(5.76)}
\end{align*}
\]

Pauling observed that bonds between dissimilar atoms are almost always stronger than might have been expected from the strength of bonds of the same elements when bonded in homonuclear (nonpolar) bonds. For example, the bond energy of chlorine...
of lithium. Likewise, the electron affinity of fluorine is strongly exothermic but that of lithium is much less so, and some metals have endothermic electron affinities. A bond between lithium and fluorine is predominantly ionic, consisting (to a first approximation) of transfer of an electron from the lithium atom to the fluorine atom. Hydrogen is nature in contrast to the bonds discussed previously (page 167). Charge density

Fig. 5.14 Electron density contours for (a) H₂; (b) Li⁺; (c) Li⁺ na core; (d) Li⁺ na; (e) Li⁺ total electron density. [From Wahl, A. C. Science 1966, 151, 961. Reproduced with permission.]

Molecular Orbital Theory

Fig. 5.15 Electron density contours for various orbitals in the O₂ molecule. (a) σ₂; (b) σ₂, (c) σ₂, (d) σ₂, (e) π₂, (f) total electron density. [From Wahl, A. C. Science 1966, 151, 961. Reproduced with permission.]

distributions for these molecules are shown in Fig. 5.16, which may be compared with the nonpolar, homonuclear bonds in Figs. 5.14 and 5.15. Cross-sectional density profiles of several homonuclear and heteronuclear molecules are shown in Fig. 5.17. Although LiF gives an appearance of being (again, to a first approximation) an ion pair, in HF the hydrogen atom is deeply embedded in the electron cloud of the fluorine ion as predicted by Fajans' rules (Chapter 4).
### Table 5.6

<table>
<thead>
<tr>
<th>Element</th>
<th>Pauling</th>
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### Figure

**Variation of Electronegativity**

Two recent approaches should be mentioned. In one, Parr and others have followed Mulliken by defining electronegativity in terms of ionization energy and electron affinity. They have also advanced the idea of electronegativity in terms of density functional theory. This is a close parallel to the Mulliken-Jaffe system in its emphasis upon the first and second derivatives of the ionization potential-electron affinity energy curves. In addition, it provides quantum mechanical support for the intuitively appealing idea of electronegativity equalization (see page 194). It differs only in the extent of those using this method have tended to use ground state values instead of valence state values.

More recently Allen has proposed that electronegativity be defined in terms of the average one-electron energy of valence shell electrons in ground-state free atoms which may be obtained spectroscopically. This quantity is termed the configuration energy:

$$ CE = \frac{m_p + n_p}{m + n} $$

where $e_p$ and $e_n$ are the energies and numbers of electrons in the $p$ and $s$ orbitals of the valence shell, respectively. The result is another strong argument for defining electronegativity ($\chi_{Pauling}$) in terms of orbital energy. This system of electronegativity has been successfully applied to periodic properties of the elements such as covalent, ionic, and ionic bonding; atomic radius; multiple bonding; oxidation states; and the unique properties of carbon and hydrogen. Note, however, that these energies are not valence state energies, nor does the calculation include electron affinities. This prevents application to the effect of charge asymmetry (hardness and softness) as related to electronegativity or to the variability of electronegativity with hybridization (see below). On the other hand it presents an unambiguous measure of an atom's average electronegativity. Further efforts to apply the method to transition metals and to changes in oxidation states will probably be forthcoming.

The articles by Allen cited above are also recommended as the most recent review of various aspects of electronegativity theories and for the idea that electronegativity is the third dimension of the periodic chart.

Although electronegativity is often treated as though it were an invariant property of an atom, we have seen that it depends on two properties: valence state (hybridization) and atomic charge. Hybridization affects electronegativity because of the lower energy and hence greater electron-attracting power of s orbitals. We might expect the electronegativity of an atom to vary slightly with hybridization, with those orbitals having greater s character being more electronegative. Some results of the variation in electronegativity.

---


$V^+$ = $V^{2+}$ (from ref. a).

$A_{25} = \frac{(\text{rad})}{\mu m} = 6.37$ (from ref. a).

$A_{14} = \frac{(\text{rad})}{\mu m} = 6.27$ (from ref. a).

**Electronegativity**

Variation of Electronegativity
The treatment of heteronuclear bonds revolves around the concept of electronegativity. This is simultaneously one of the most important and one of the most difficult problems in chemistry. In the previous discussion of molecular orbitals it was assumed that the atomic orbitals of the bonding atoms were at the same energy. In general, this will be true only for homonuclear bonds. Heteronuclear bonds will be formed between atoms with orbitals at different energies. When this occurs, the bonding electrons will be more stable in the presence of the nucleus of the atom having the greater attraction (greater electronegativity), that is, the atom having the lower atomic energy levels. They will thus spend more time nearer that nucleus. The electron cloud will be distorted toward that nucleus (see Fig. 5.16) and the bonding MO will resemble that AO more than the AO on the less electronegative atom.

Consider the carbon monoxide molecule, CO, isoelectronic with the N₂ molecule. Oxygen is more electronegative than carbon, so the bonding electrons are more stable if they can spend a larger proportion of their time in the region of the oxygen nucleus. The electron density on the oxygen atom is greater than that on the carbon atom in contrast to the symmetrical distribution in the N₂ molecule (Fig. 5.18). For homonuclear diatomic molecules we have seen that the molecular orbitals are

\[ \Phi_a = \Psi_a + \Psi_b \]  
\[ \Phi_b = \Psi_b - \Psi_a \]

Both orbitals contribute equally. Now if one atomic orbital is lower in energy than the other, it will contribute more to the bonding orbital:

\[ \Psi_a = b \Psi_a + a \Psi_b \]

where \( b > a \) if atom B is more electronegative than atom A. Conversely, the more stable orbital contributes less to the antibonding orbital:

\[ \Psi_a = b \Psi_a - a \Psi_b \]
### Table 5.6: Electronegativities of the Elements (Continued)

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In carbon monoxide the bonding molecular orbitals will resemble the atomic orbitals of oxygen more than they resemble those of carbon. The antibonding orbitals resemble the least electronegative element more, in this case carbon (see Fig. 5.19). This results from what might be termed the conservation of orbitals. The number of molecular orbitals obtained is equal to the total number of atomic orbitals combined, and each orbital must be used to the same extent. Thus, if the carbon atomic orbital contributes less to the bonding molecular orbital, it must contribute more to the antibonding molecular orbital. The energy level diagram for CO is shown in Fig. 5.20.

Note carefully the bond order: The $1\pi$ and $3\pi$ MOs are essentially nonbonding. The bond order, as in the $N_2$ molecule is three.

A second feature of heteronuclear molecular orbitals which has been mentioned previously is the diminished covalent energy of bonds formed from atomic orbitals of different energies. This may be shown qualitatively by comparing Fig. 5.21 with Fig. 5.22. This can be seen even more readily in Fig. 5.23, in which the electronegativity difference between atoms A and B is so great as to preclude covalent bonding. In this case the bonding MO does not differ significantly from the atomic orbital of B, and so transfer of the two bonding electrons to the bonding MO is indistinguishable from the simple picture of an ionic bond; the electron on A has been transferred completely to B.

This extreme situation in which the energy level of B is so much lower than that of A that the latter cannot contribute to the bonding may be visualized as follows: If the energy of atomic orbital B is very much lower than A, the electron will spend essentially all of its time in the vicinity of nucleus B. Although this may be a very stable situation, it hardly qualifies as a covalent bond or sharing of electrons. In this case, the sharing of electrons has been drastically reduced, and the covalent energy is negligible. All chemical bonds lie somewhere on the spectrum defined by Figs. 5.21-5.23. There has been some confusion in the literature concerning the strength of bonds in situations such as shown in Figs. 5.22 and 5.23. Because good energy match is necessary for a large $\Delta E$, and good covalent bonding, some workers have concluded that Figs. 5.22 and 5.23 represent increasingly weak bonding. This is not true, for the...
Recent Advances in Electronegativity Theory

The advances in recent years have been more evolutionary than revolutionary. Increasingly, Mulliken's original idea of expressing electronegativity in terms of the energy of valence electrons has come into favor, and the other definitions in terms of orbital energies or algebraic relationships of size and charge have been viewed as useful approximations when orbital energies are not available. In addition, the relationship between electronegativity and acidity and basicity, always intimate, has been extended further (see Chapter 9).

\[ b = \frac{dE}{dQ} = \frac{d\alpha}{dQ} = IE - EA \]  
\[ b = \frac{1}{\alpha} \] (5.79)

Large, soft, polarizable atoms have low values of \( b \), and small, hard, nonpolarizable atoms tend to have higher values. An atom with a large charge coefficient will charge electronegativity much more rapidly than one with a lower value of \( b \). Thus a small atom (low \( \kappa \), large \( b \)) has only a limited ability to donate or absorb electron density before its electronegativity changes too much for further electron transfer to take place. One of the most important examples is the very electronegative but very small fluorine atom. Although initially very electronegative when neutral, it rapidly becomes "saturated" as it accepts electron density (note how quickly the slope flattens out between -0.4 and -0.6), and beyond -0.7, it is necessary "to push" to get more electron density onto a fluorine atom. This is closely related to the comparatively low electron affinity of fluorine (Chapter 3).

The charge capacity effect is responsible for the well known inductive effect of alky groups (see page 196). It is also important in hard and soft acid-base theory (see Chapter 9), and causes several other unexpected effects. It is basically a polarization effect in which larger atoms and groups can acquire or donate large amounts of electron density without unfavorable energy changes.

The advances in recent years have been more evolutionary than revolutionary. Increasingly, Mulliken's original idea of expressing electronegativity in terms of the energy of valence electrons has come into favor, and the other definitions in terms of orbital energies or algebraic relationships of size and charge have been viewed as useful approximations when orbital energies are not available. In addition, the relationship between electronegativity and acidity and basicity, always intimate, has been extended further (see Chapter 9).

\[ V_{\text{Pauling}} = V_{\text{Sanderson}} \]

Table 5.6

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<th>Allred-Rochow</th>
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<th>Pauling scale</th>
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</tbody>
</table>

The advances in recent years have been more evolutionary than revolutionary. Increasingly, Mulliken's original idea of expressing electronegativity in terms of the energy of valence electrons has come into favor, and the other definitions in terms of orbital energies or algebraic relationships of size and charge have been viewed as useful approximations when orbital energies are not available. In addition, the relationship between electronegativity and acidity and basicity, always intimate, has been extended further (see Chapter 9).

\[ V_{\text{Pauling}} = V_{\text{Sanderson}} \]
loss of covalent bonding may be compensated by an increase in ionic bonding, which, as we have seen previously, can be quite strong. In fact, the total of ionic and covalent bonding may make a very strong bond in the intermediate situation shown in Fig. 7.22. (Note that the ionic contribution to the bonding does not appear in these figures.) In fact, the strengthening of a polar bond over a corresponding purely covalent one is an important phenomenon.

A second example of a heteronuclear diatomic molecule is hydrogen chloride. In this molecule the attraction of the chlorine nucleus for electrons is greater than that of the hydrogen nucleus. The energies of the 3s and 3p orbitals on the chlorine atom are less than that of the 1s orbital on hydrogen as a result of the imperfection of the much larger nuclear charge of chlorine. The molecular orbitals for the hydrogen chloride molecule are illustrated in Fig. 5.24. There is one σ bond holding the atoms together. The remaining six electrons from chlorine occupy nonbonding orbitals, which are almost unchanged atomic orbitals of chlorine. These nonbonding molecular orbitals correspond to the lone pair electrons of valence bond theory. They represent the two p orbitals on the chlorine atom that lie perpendicular to the bond axis. They are therefore orthogonal to the hydrogen 1s orbital (Fig. 5.8) and have a net overlap of zero with it. As such, they cannot mix with the hydrogen orbital to form bonding and antibonding molecular orbitals. The third nonbonding MO is the second of the hybridized atomic orbitals resulting from some s–p mixing. If the mixing were complete (50% s character, which is far from the case in HCl), it would be the second di orbital directed away from the bond. Since little mixing of the s orbital of the chlorine into the bonding MO occurs, the third lone pair is a largely s orbital, a distorted sphere of electron density with the major portion behind the chlorine atom.

Although mixing of s and p orbitals is represented in Fig. 5.24 as a separate step preceding the formation of molecular orbitals, the entire process can be combined into a single step. For example, the bonding molecular orbital in hydrogen chloride may be considered to be formed as

\[ \psi_{\sigma} = a\phi_y + b\phi_y + c\psi_x \]  

(5.49)

where \( \phi_y \), \( \phi_y \), and \( \psi_x \) are the atomic orbitals on the chlorine (3s and 3p) and hydrogen (1s) atoms. Now \( a \) and \( b \) can be varied relative to each other in such a way that any amount of p character can be involved in the molecular orbital. For example, if \( a = 0 \), the chlorine atom uses a pure p orbital, and if \( a^2 + b^2 = 1 \), the p character will be 75% (an "sp^2 hybrid" in VB terminology). As of, the relative weighting of \( a \) and \( b \) versus \( c \) indicates the relative contributions of chlorine versus hydrogen wave functions to the bonding molecular orbital.

The linear molecule BeH_2 will serve as our first example of a trisatomic species. The molecular orbitals for this molecule are constructed from the 1s orbitals on the hydrogen atoms (labeled H and H') and the 2s and one of the 2p orbitals of beryllium (the one directed along the H—Be—H bond axis). The remaining two 2p orbitals of beryllium cannot enter into the bonding because they are perpendicular to the molecular axis and thus have zero overlap with the hydrogen orbitals. Because four atomic orbitals enter into the bonding, we anticipate the formation of four molecular orbitals. As always, the bonding molecular orbitals are formed by linear combination of the atomic orbitals to give maximum overlap. Prior to forming molecular orbitals, we can combine the orbitals of the two hydrogen atoms into group orbitals that are consistent with the linear geometry of the molecule and with the symmetries of the atomic orbitals on beryllium. The group orbitals are formed by simply taking linear combinations of the 1s orbitals on H and H'. There are only two possibilities, so the group orbitals correspond to \( \psi_1 + \psi_2 \) and \( \psi_1 - \psi_2 \). The first one is appropriate for overlap with the beryllium 2s orbital, which is everywhere positive. The second one will form a bonding MO by overlapping with the 2p orbital of beryllium, which has one positive and one negative lobe. The antibonding orbitals will be formed by opposite combinations, which give nodes between the bonded atoms. The molecular orbitals can be represented as

\[ \psi_{\sigma} = \alpha\psi_1 + \beta(\psi_2 + \psi_3) + \gamma\psi_4 \]  

(5.50)

\[ \psi_{\pi} = \alpha\psi_1 + \beta(\psi_2 - \psi_3) + \gamma\psi_4 \]  

(5.51)

\[ \psi_{\sigma} = \alpha\psi_1 + \beta(\psi_2 + \psi_3) - \gamma\psi_4 \]  

(5.52)

\[ \psi_{\pi} = \alpha\psi_1 + \beta(\psi_2 - \psi_3) - \gamma\psi_4 \]  

(5.53)

The parameters \( \alpha \), \( \beta \), \( \gamma \), and \( \delta \) are weighting coefficients, which are necessary because of differences in electronegativity between Be and H.

The energies of the BeH_2 molecular orbitals are shown in Fig. 5.25 and their electron density boundary surfaces are sketched in Fig. 5.26. Both of the bonding molecular orbitals are delocalized over all three atoms. This is a general result of the MO treatment of polyatomic molecules. Note that the lowest-energy orbital, the 1\( \sigma \), is not shown in either Fig. 5.25 or 5.26. It would be formed from the 1\( \sigma \) orbital on beryllium, which interacts very little with the hydrogen orbitals because of the large energy difference between them. This molecular orbital is therefore nonbonding and is essentially indistinguishable from the beryllium 1\( \sigma \) atomic orbital.

The nitride ion, NO_3^-, is an example of a nonlinear trisatomic species with \( \pi \) as well as \( \sigma \) bonds. In the valence bond description of the ion, resonance structures are used to allow for the distribution of the \( \pi \) electrons over all three atoms. The molecular orbitals of the chlorine atom use a pure p orbital, but if \( a^2 + b^2 = 1 \), the p character will be 75% (an "sp^2 hybrid" in VB terminology). As of, the relative weighting of \( a \) and \( b \) versus \( c \) indicates the relative contributions of chlorine versus hydrogen wave functions to the bonding molecular orbital.
that if the energy curve (see Fig. 5.32) is used in this form, the Mulliken definition of electronegativity is equal to the slope of the curve as it passes through the origin.

\[ E = \alpha q + (\beta q)^2 \]

\[ \chi = \frac{dE}{dq} = \alpha + 2\beta q \]  

This formulation provides clear intuitive perspective: It indicates that an atom will be highly electronegative if it releases much energy (because its energy curve is steep) as it acquires electron density; another atom will be less electronegative because its curve is less steep and, when combined with the more electronegative atom, it does not cost as much energy climbing its own energy curve. A molecule of CIF will exist as Cl⁺F⁻, and it will be more stable than the hypothetical nonpolar CIF molecule.

The relationship between the Mulliken definition and that of Jaffe can be shown quite simply. Taking Eq. 5.62 and substituting \( q = 1 \), we know that the energy, \( E \), of the system will be that of the +1 cation, or the first ionization energy. Likewise for \( q = -1 \), the energy will be the negative of the electron affinity, so:

\[ \text{IE}_+ = E_{+1} = \alpha(1) + \beta(1)^2 \]  

\[ -\text{EA}_- = E_{-1} = \alpha(-1) + \beta(-1)^2 \]  

Subtracting Eq. 5.65 from Eq. 5.64 gives:

\[ \text{IE}_+ + \text{EA}_- = 2\alpha \]  

which yields \( \alpha \) as the Mulliken electronegativity (Eq. 5.59).

Fig. 5.32 Ionization energy-electron affinity curves for chlorine and chlorine. The electronegativities are given by the slopes of these curves. This figure is an enlarged portion of Fig. 5.15.

\[ \frac{dE}{dq} = a + b \delta \]

in which the partial charge, \( \delta \), replaces the ionic charge, \( q \), and the constants have been changed for convenience. The importance of this equation lies in illustrating the large effect that charge can have on the electronegativity of an atom. Intuitively, one would expect an atom with a positive charge to be more electronegative than that same atom with a negative charge.
Molecular Orbital Theory

The orbital treatment provides an alternate approach that does not require resonance structures because electrons are automatically delocalized as the method is applied. We can consider the σ system in NO₂ to consist of two N—O single bonds formed by overlap of sp² hybrid orbitals on nitrogen and oxygen. Also part of the σ network will be four pairs of electrons in nonbonding orbitals that are essentially oxygen sp² hybrids. (These are the oxygen lone pairs in the valence bond description.) Remaining on the nitrogen and oxygen atoms are parallel p orbitals (Fig. 5.27). These orbitals will interact to form bonding and antibonding combinations:

\[ \psi_b = \alpha_o + \alpha_y + \beta_o \]  
\[ \psi_a = \alpha_o + \alpha_y - \beta_o \]  
\[ \psi_c = \beta_o - \beta_y \]  

(5.54)

(5.55)

(5.56)

As in the cases we have seen before, the bonding orbital yields a concentration of electron density between the atoms and the antibonding orbital has nodes between the atoms (Fig. 5.28). There is a third combination possible:

(5.57)

Fig. 5.27 Sigma bonds and lone pairs in the nitrite ion, NO₂⁻.

Fig. 5.28 Atomic orbitals (left) and resulting molecular orbitals (right) in the nitrite ion: (a) bonding and (b) antibonding.

Hybridization is, of course, completely unnecessary when using molecular orbital theory, but is a convenience here since we are primarily concerned with the σ system. The VB and MO treatments of the σ system are not significantly different in their results.
Electronegativity

Linus Pauling first defined electronegativity and suggested methods for its estimation. Pauling’s definition has not been improved upon: the power of an atom in a molecule to attract electrons to itself. It is evident from this definition that electronegativity is not a property of the isolated atom (although it may be related to such properties) but rather a property of an atom in a molecule, in the environment and under the influence of surrounding atoms. One must also note that the “power to attract” is merely another way of describing the “reluctance to release” electrons from itself to a more electronegative element.

Pauling based his scale on thermochemical data. We shall examine his methods shortly, but we may note that his scale is an arbitrary one chosen so that hydrogen is given a value of about 2 and the most electronegative element, fluorine, has a value of about 4:

\[
\begin{align*}
H &= 2.2 \\
Li &= 1.0 \\
Be &= 1.6 \\
B &= 2.0 \\
C &= 2.5 \\
N &= 3.0 \\
O &= 3.4 \\
F &= 4.0 \\
Na &= 0.9 \\
Mg &= 1.3 \\
Al &= 1.6 \\
Si &= 1.9 \\
P &= 2.2 \\
S &= 2.6 \\
Cl &= 3.2
\end{align*}
\]

There are other scales that have absolute units, and whereas it might seem at first glance that an absolute scale would be preferable, the Pauling scale has a familiarity and attendant literature that no absolute scale can come close to matching. Familiarity as a virtue should not be discounted in unthinking attempts to “standardize” things. Several times workers have reported erroneous electronegativity values in electron volts or in MJ mol\(^{-1}\). They would have instantly noticed and rejected if they had converted their values to the Pauling scale. A value of 3.3 for fluorine stands out like the proverbial sore thumb.

Consider Pauling’s approach to the treatment of a molecule of hydrogen chloride, which is usually represented today as H\(^+\)Cl\(^-\).

The use of + and - to represent partial charges in a polar molecule is relatively recent. Pauling would have pictured it as

\[
\begin{align*}
\text{H}^+\text{Cl}^- &\quad \text{H}^+\text{Cl}^- \\
\text{I} &\quad \text{II} &\quad \text{III}
\end{align*}
\]

where the wave function of the resonance hybrid would be

\[
\psi = a_1\psi_1 + a_2\psi_2 + a_3\psi_3
\]

where \(x, y,\) and \(z\) are weighting coefficients and \(\psi_1, \psi_2,\) and \(\psi_3\) are labels for contributing canonical forms I, II, and III. If chlorine is more electronegative than hydrogen, contributing form II will be important as well as form I (HCl is predominantly covalent), but form III, which places a positive charge on the chlorine atom, makes a negligible contribution. Pauling assumed that resonance would stabilize the molecule of HCl and that the greater the contribution of II, the more polar the molecule and the greater its stability. Soon after Pauling published his first paper on electronegativity, Mulliken suggested a method for estimating how much each of the forms I, II, and III would contribute to the hybrid and used it to establish the electronegativity scale that bears his name.

The method of treating electronegativities that has the simplest theoretical basis is the Mulliken–Jaffe system. Recall that canonical forms that are low in energy and stable contribute the most to the resonance hybrid, and that high-energy forms contribute little. Mulliken suggested that two energies associated with an atom should reflect a measure of its electronegativity: (1) the ionization energy, as a measure of the difficulty of removing an electron (or, more generally, electron density) to form a positive species; (2) the electron affinity, as a measure of the tendency of an atom to form a negative species. Structure II is stable because chlorine has a high electron affinity and hydrogen has a low ionization energy for a nonmetal. Structure III is unstable because chlorine has a high ionization energy and hydrogen has a low electron affinity. Mulliken’s definition of electronegativity is given simply as

\[
\chi = \frac{IE + EA}{2}
\]

or, when the energies are in electron volts (the most common unit used in the past), putting the values on the Pauling scale:

\[
x_m = 0.336 \left[ \frac{IE + EA}{2} - 0.615 \right]
\]

or, when the energies are in MJ mol\(^{-1}\):

\[
x_m = 3.48 \left[ \frac{IE + EA}{2} - 0.0602 \right]
\]

Now it should be recalled that the first ionization energy and the electron affinity are merely two of the multiple ionization potentials—electron affinity energies that fit a polynomial equation (see Chapter 2) that is quite close to being quadratic (the coefficients of the higher order terms are small). Jaffe and coworkers have pointed out


**Reduction of**

**Carrying out the**

**As we have seen pictorially in this chapter, in order for a bond to form, the**

**By again referring to the**

**Continuing in a similar fashion with the**

**The atomic orbitals on nitrogen contributing to the bonding will be the outer shell**

**By a similar analysis, the nitrogen orbitals capable of participating in**

**22 Whereas the pictorial approach used here for deriving the oxygen group orbitals and determining**

**Molecular Orbital Theory**
that have $a_1$ and $b_2$ symmetries. Taking the $a_1$ category first, we find a total of five orbitals (two from nitrogen and three oxygen group orbitals), which will result in five molecular orbitals. In estimating the relative energies of these molecular orbitals, we should bear in mind that two factors will promote stabilization of a bonding molecular orbital formed from two interacting orbitals: favorable overlap and similarity in energy. The degree to which these two factors are present or absent will determine whether a molecular orbital is bonding (with an antibonding counterpart) or essentially nonbonding. Thus we would predict (on the basis of a rather large energy gap) that the $(s + s)$ oxygen group orbital and the nitrogen $a_1$ orbitals will lead to an $a_1$ molecular orbital that is only slightly bonding. Overlap and energy match are more favorable for

The $a_2$ orbitals (four in all), we conclude that the nitrogen orbitals of this symmetry will overlap to yield a slightly bonding MO with the $(s - s)$ group orbital and a distinctly bonding MO with the $(p_x - p_y)$ group orbital. The $(s + p_y)$ group orbital will be essentially nonbonding and there will be one antibonding MO. Finally, the nitrogen $\pi$ orbital will combine with the $(p_x + p_y)$ group orbital to form bonding and antibonding $\pi$ MOs.

Of the twelve molecular orbitals constructed, the nine that are lowest in energy will be occupied by the valence electrons in NO$_2^-$ ions. The electrons in the lowest level $a_1$ and $b_2$ orbitals are only slightly bonding and may be thought of as lone pairs on the oxygen atoms. The Lewis structure for NO$_2^-$ includes three additional lone pairs on the nitrogen atom. In the MO picture, they are the electrons in the $e_1$ orbitals, which we have already identified as essentially nonbonding — and those in the $a_1$ orbital, which is strictly nonbonding because the $a_1$ group orbital has no symmetry match on nitrogen. The nonbonding electron pair that is shown in the Lewis structure as residing on nitrogen corresponds to the pair in the highest occupied molecular orbital (HOMO) in the MO diagram. The final result, then, for our molecular orbital description is two $\sigma$ bonds, one $\pi$ bond, and six~
Various imperfections can lead to semiconductivity in analogous ways. For example, nickel(II) oxide may be doped by lithium oxide (see Fig. 7.12). The NiO ions now behave as holes as they are reduced and produce new Ni$^{2+}$ ions at adjacent sites. These holes can migrate under a potential (indicated by the signs on the extremes of the series of nickel ions):

\[ (+)\text{Ni}^{2+} \ldots \ldots \text{Ni}^{2+} \ldots \ldots \text{Ni}^{2+} \ldots \ldots (-) \]

\[ (+)\text{Ni}^{2+} \ldots \ldots \text{Ni}^{2+} \ldots \ldots \text{Ni}^{2+} \ldots \ldots (-) \]

\[ (+)\text{Ni}^{2+} \ldots \ldots \text{Ni}^{2+} \ldots \ldots \text{Ni}^{2+} \ldots \ldots (-) \]

The range of possibilities for semiconduction is very great, and the applications to the operation of transistors and related devices have revolutionized the electronics industry, but an extensive discussion of these topics is beyond the scope of this text. See Hofmann, R. Solids and Surfaces, VCH: New York, 1988, for a clear discussion of solid state chemistry and physics in chemist's language for this structure as well as many others. This discussion may also be found in Hoffmann, R.; Zheng, C. J. Phys. Chem. 1985, 89, 1775-1811. Reproduced with permission.

The ThCr$_2$Si$_2$ Structure Type

More than 400 compounds of AB$_2$X$_3$ stoichiometry adopt the ThCr$_2$Si$_2$ type structure. In these A is typically an alkali, alkaline earth, or rare earth metal; B may be a transition metal or a main-group metal. X is a group VA (N, P, As, Sb, Bi), a transition metal (B = Mn, Fe, Co, Ni, Cu), and phosphorus (see Table 7.2). These compounds are isomorphous and crystallize in the ThCr$_2$Si$_2$ structure with space group P6/mmm. The unit cell (Fig. 7.28) consists of eight A$^{2+}$ ions at the corners of a rectangular parallelepiped plus one

![Fig. 7.28 Unit cell of an alkaline earth (A)/transition metal (B)/phosphide (P) of the ThCr$_2$Si$_2$ type structure.](image)

The distances listed in Table 7.2 are indicated. [Modified from Hoffmann, R.; Zheng, C. J. Phys. Chem. 1985, 89, 1775-1811. Reproduced with permission.]

### Table 7.2

<table>
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<tr>
<th>Compound</th>
<th>r$_{\text{A}-\text{P}}$ (Å)</th>
<th>r$_{\text{B}-\text{P}}$ (Å)</th>
<th>r$_{\text{A}-\text{B}}$ (Å)</th>
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<td>245</td>
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<td>229</td>
<td>230</td>
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<tr>
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<tr>
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<td>336</td>
<td>226</td>
<td>243</td>
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</tbody>
</table>


The specific example for this section is described in an article with the same title as the heading above; see Footnote 34.

In crystallography, as in systematic botany and zoology, the type is merely a "name-bearer"—something to which a name may be attached unambiguously. It is not necessarily the typical species in the everyday meaning of the word (= representative, usual). Although this can cause some initial confusion, note that the overall stoichiometry and the total number of $r$ and $p$ electrons (as given by the Roman numeral group numbers) are the same in both Th$^{3+}$Cr$_2$Si$_2$ and Th$^{4+}$Si$_2$.
Jahn-Teller distortions are expected in $\text{ML}_4$ complexes configurations for which Table 11.21 is relevant. 

### Table 11.21

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Ground-state term</th>
<th>Jahn-Teller distortion?</th>
</tr>
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</tr>
<tr>
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<td>$t_{2g}$</td>
<td>Yes</td>
</tr>
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<td>$t_{2g}$</td>
<td>No</td>
</tr>
<tr>
<td>$d^4$</td>
<td>$e_g$ (high spin)</td>
<td>Yes</td>
</tr>
<tr>
<td>$d^5$</td>
<td>$e_g$ (high spin)</td>
<td>No</td>
</tr>
<tr>
<td>$d^6$</td>
<td>$e_g$ (low spin)</td>
<td>Yes</td>
</tr>
<tr>
<td>$d^7$</td>
<td>$A_2g$ (high spin)</td>
<td>Yes</td>
</tr>
<tr>
<td>$d^8$</td>
<td>$A_2g$ (low spin)</td>
<td>No</td>
</tr>
<tr>
<td>$d^9$</td>
<td>$E_g$ (low spin)</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Basic insight into the nature of the Jahn-Teller effect can be obtained by returning to an orbital picture. Consider Fig. 11.47a in which the two ligands on the $z$ axis of an octahedral complex have moved away from the central metal. In so doing, they have reduced their interaction with the metal $d$ orbitals that have a $z$ component, i.e., the $d_{x^2}$, $d_{yz}$, and $d_{zx}$. As a result, these orbitals are stabilized. Because of the “center-of-gravity” rule, the orbitals without a $z$ component, the $d_{x^2}$ and $d_{y^2}$, will be raised a corresponding amount. It is not possible, a priori, to predict the magnitude of these splittings because the extent of distortion cannot be predicted. However, we can say that the splitting of the strongly antibonding $e_g$ orbitals ($\Delta_e$) will be significantly larger than that of the $t_{2g}$ orbitals ($\Delta_t$) because the latter are either nonbonding or are involved in weaker $\sigma$ interactions with the ligands. Also, both $\Delta_e$ and $\Delta_t$ will be relatively small with respect to $\Delta_o$, so we are justified in regarding the distortion as a perturbation of an octahedral geometry.

The Jahn-Teller theorem per se does not predict which type of distortion will take place other than that the center of symmetry will remain. The $z$ ligands can move out as in the example discussed above or they can move in. For a “$z$-out” distortion, the splitting pattern is similar to that observed for a “$z$-in,” but the energy ordering within the $t_{2g}$ and $e_g$ levels is inverted (see Fig. 11.47b).

Consider a complex that is subject to Jahn-Teller distortion, $[\text{TiCl}_4]^{2-}$. The $\text{Ti}^{3+}$ ion is a $d^1$ species and the $d^0$ ground term which arises from it in an octahedral field is split into $T_{1u}$ and $T_{2g}$ terms. The $T_{1u}$ term is the ground state and, because it is triply degenerate, the Jahn-Teller theorem would predict a distortion. The structure of $[\text{TiCl}_4]^{2-}$ does show a slight compression of the axial ligands at low temperature, but this is thought to be due to packing forces rather than the Jahn-Teller effect. Evidence for a Jahn-Teller distortion is seen, however, in the electronic spectrum of the complex. There are two absorption peaks separated by approximately 1400 cm$^{-1}$, one resulting from excitation of an electron from the ground state ($T_{1u}$) to the excited $T_{2g}$ state and the other to the excited $A_{2g}$ state (Fig. 11.48). This assignment is supported by EPR results, which are consistent with a tetragonal compression. For some $d^1$ complexes, the Jahn-Teller splitting is not of sufficient magnitude to produce well-defined...
body-centered A\(^1\) ion. The transition metal atoms (B\(^2\)) and the phosphorus atoms occur in [B—P—P—B] layers, each in a square array such that each metal atom is surrounded by a tetrahedron of phosphorus "ligands":

![Diagram of tetrahedron](https://example.com/diagram.png)

Note the capping phosphorus atom atop the square pyramid. It is coordinated to four metal atoms, all on one side, highly unusual for an ion. However, if we ask whether this is an extraordinarily strong structure for a metal ion, we note that it is not at all unusual for sulfur (cf. SF\(_4\), Fig. 6.4). Although currently unknown for phosphorus in a simple molecule, a similar structure would be expected for the inelegant :PF\(_7\) anion if it existed.

If we examine the distances listed in Table 7.2, some interesting facts emerge. For a given metal A, the A—P distance is constant as we might expect for an ionic alkaline earth metal—phosphide bond. Furthermore, these distances increase calcium < strontium < barium in increments of about 15 pm (cf. Table 7.2). However, the B—P distances vary somewhat more with increasing orbital density (Mo, Ca larger; Ni, Fe, Co smaller). Most interesting, however, is the larger variability in the P—P distance from about 380 pm (Mn, Fe) to 225 pm (Cu). As it turns out, the lower limit of 225 pm (Cu) is a typical value for a P—P bond (Table 6.1, Appendix E) and 380 pm is approximately twice the van der Waals radius of phosphorus.

Furthermore, there is a steady reduction of this distance as one progresses across the transition series. All of this is consistent with the hypothesis that this is an electronic (covalent) effect.

Before examining these electronic effects, we should delve a little more deeply into the theory and terminology of solid state chemistry than was done on pages 269-272. Specifically, if there is an infinite array of identical orbitals (say H\(_1\)v) represented by \(\langle \psi_n \rangle = \langle \psi_0 \rangle + \langle \psi_1 \rangle + \langle \psi_2 \rangle + \langle \psi_3 \rangle + ...\) related by translational symmetry and spaced at a given distance \(a\), then we can have linear combinations, \(\langle \psi_k \rangle = \sum_{n=0}^{N} e^{ikna} \langle \psi_n \rangle\) where \(\langle \psi_n \rangle\) is the basic function of the nth orbital, \(i = \sqrt{-1}\), and \(k\) is the base of natural logarithms. The linear combinations, \(\langle \psi_k \rangle\), are called Bloch functions and \(k\) is an index that indicates which combination (irreducible representation) is involved. To return to the previous discussion of the analogy between bond structure and a molecule of molecular orbitals, consider two values for \(k\).

\[
\psi_0 = \sum_{n=0}^{N} e^{ikna} \langle \psi_n \rangle
\]

From simple MO theory, we expect that this nodeless function will be the most bonding state.\(^{33}\) It thus represents the bottom of the band.

\[
\psi_{\text{val}} = \psi_0 + \psi_1 + \psi_2 + \psi_3 + \psi_4
\]

This is the most antibonding state. These two define the bottom and the top of the band. The situation is the same as we have seen previously for lithium, whether there are two, eight, or a mole of hydrogen atoms in metallic polyhydrogens.\(^{33}\) Now what we

\[\text{Footnote 26}\]

\[\text{Footnote 27}\]

\[\text{Footnote 28}\]

\[\text{Footnote 29}\]
Tetragonal Distortions from Octahedral Symmetry

We have seen that the electronic spectra of octahedral ML₆ and tetrahedral ML₄ complexes may be analyzed with the aid of appropriate correlation, Orgel or Tanabe-Sugano diagrams. When we move away from these highly ordered cubic structures to complexes having lower symmetries, spectra generally become more complex. A general consequence of reducing the symmetry is that energy levels that were degenerate in the more symmetric geometry are split. With more energy levels, the number of possible transitions increases and so does the number of spectral bands. In this section we will examine departures from octahedral symmetry in six-coordinate complexes.

There are a number of circumstances that can lead to a symmetry that is less than octahedral in a six-coordinate complex. One is simple replacement of some of the ligands of an ML₆ molecule or ion with ligands of another type. For example, if we replace two L groups to give either cis- or trans-MX₃L₄, the symmetry becomes C₂ᵥ or Dᵥ, respectively. More subtle alterations in symmetry frequently occur in complexes having bidentate or chelating ligands. For instance, the chelated complexes [Cr(en)₃]³⁺ and [Cr(ox)₃]⁻ are not perfectly octahedral. Because of the rings associated with the bidentate ligands, these complexes belong to the lower symmetry point group Dᵥ. Nevertheless, the perturbation is slight enough that we were able to successfully analyze the spectra of these complexes (Fig. 11.13) as though they were purely octahedral, and the expected absorptions for a symmetrical [CrL₆]³⁺ species were observed. However, if one of the ethylenediamine ligands of [Cr(en)₃]³⁺ is replaced with two F⁻ ligands to give trans-[Cr(en)₂F₂]⁺, the change in symmetry is drastic enough that to treat the new complex as pseudooctahedral is no longer valid; rather, it must be analyzed as a tetragonal (D₄ᵥ) species. The alteration in energy levels that accompanies this progression from octahedral to tetragonal symmetry is shown in Fig. 11.45. Each of the triply degenerate T terms is split into two new terms (an E and an A or B), with the result that six transitions are now expected instead of three. The four lowest energy absorptions for trans-[Cr(en)₂F₂]⁺ are shown in Fig. 11.46. A fifth band appears as a shoulder in the charge transfer region and the sixth has been calculated (Table 11.20).

![Fig. 11.45 Alteration of energy levels for a d⁹ ion as the symmetry of its environment changes from octahedral (O₆) to tetragonal (Dᵥ₃)].

![Fig. 11.46 Electronic spectrum of trans-[Cr(en)₂F₂]⁺; transition frequencies are given in Table 11.20. (Modified from Dubicki, L.; Hitchman, M. A.; Day, P. Inorg. Chem. 1970, 9, 188-209. Used with permission.)](image)

11.46. A fifth band appears as a shoulder in the charge transfer region and the sixth has been calculated (Table 11.20).

Tetragonal distortion from octahedral symmetry often occurs even when all six ligands of a complex are the same. Two L groups that are trans to each other are found to be either closer to or farther from the metal ion than are the other four ligands. A distortion of this type actually is favored by certain conditions described by the Jahn-Teller theorem. The theorem states that for a nonlinear molecule in an electronically degenerate state, distortion must occur to lower the symmetry, remove the degeneracy, and lower the energy.⁴⁷ We can determine which octahedral complexes

![Table 11.20](image)

**Table 11.20**

<table>
<thead>
<tr>
<th>Observed frequency (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>18,500</td>
<td>2B₁g</td>
</tr>
<tr>
<td>21,700</td>
<td>2B₁g</td>
</tr>
<tr>
<td>25,300</td>
<td>2B₁g</td>
</tr>
<tr>
<td>29,300</td>
<td>2B₁g</td>
</tr>
<tr>
<td>41,000 (shoulder)</td>
<td>2A₂g</td>
</tr>
<tr>
<td>43,655 (calculated)</td>
<td>2A₂g(P)</td>
</tr>
</tbody>
</table>

have drawn previously as a block to represent the aggregation of a very large number of orbitals (cf. Figs. 7.19-7.21 with the simplified diagrams here):

![Diagram of orbitals]

the physicist plots as an energy function:

![Energy graph]

This graph conveys the same important information given by the energy level diagram: The number of states (molecular orbitals) generated by the linear combination of atomic orbitals in Eq. 7.3 is not evenly distributed over the energy range, but is densest at the bottom and top. The number of states in the interval \( E + dE \) is known as the density of states (DOS):

![DOS graph]

As can be readily seen, the density of states at any given energy is inversely proportional to the slope of the energy function at that energy.

The density of states for this type of system may be worked out qualitatively rather easily.

We shall make some simplifications. First, we shall assume that in the compound \( \text{BaMn}_2\text{P}_2 \) the barium occurs as simple cations having no covalent interactions with the remaining atoms. Then we shall let the phosphorus atoms interact with the metal atoms as though we were dealing with a discrete, tetrahedral, molecular complex of the sort \([\text{Mn(PR}_3)_4]^+\). In such a situation, molecular orbital theory gives a set of four bonding MOs \( (\zeta_1 + \zeta_2) \) which come from the atomic \( 4s \) and \( 4p \) orbitals of the metal and the phosphorus lone pair orbitals of the same symmetry:

![MO diagram]

The orbitals which are principally nonbonding metal \( 3d \) in character are split into an \( e \) set and a \( t_2 \) set. The latter splitting will be discussed at some length in Chapter 11 and need not concern us too much at present. Finally, there are the \( \zeta_1 \) and \( \zeta_2 \) antibonding orbitals.

Correspondingly, we can calculate the band structure and density of states for the extended \( \text{Mn}_2\text{P}_2^2 \) layer (Fig. 7.29). We have seen previously (Chapter 5) that if the interacting AOs are distinctly separate in energy, we can treat the resulting MOs as though they came essentially from only the AOs of a given energy. We thus can look at the DOS for the extended \( \text{Mn}_2\text{P}_2^2 \) layer and find the origin of the bands. The lowest \((- 19 \text{ eV})\) corresponds to the \( \zeta_2 \) orbital of the isolated complex and comes from the manganese \( 4s \) orbital and the phosphorus \( 3p \) orbitals. The next \((- 15 \text{ eV})\) corresponds to manganese \( 4p \) and phosphorus \( 3s \). It is possible to decompose these bands into the relative contribution of manganese and phosphorus (Fig. 7.30) and, as we should expect from the lower electronegativity of manganese, these bands are dominated by the phosphorus. In contrast to these two bands which are mostly phosphorus but partly manganese, at higher energies (between \(- 13 \) and \(- 8 \text{ eV}\)) we find that the electron density is almost entirely on the manganese. In isolated metal complexes these are the approximately nonbonding metal \( 3d \) orbitals.

This turns out to be an oversimplification; we have seen that there is no such thing as a perfectly ionic bond, but the simplification does not cause serious errors (see Footnote 34).

Discrete tetrahedral \([\text{Mn(PR}_3)_4]^+\) complexes have apparently not been prepared, but \([\text{Mn(PR}_3)_4]^+\) consists of distorted tetrahedral molecules. As we shall see (Chapter 11) phosphine complexes with large positive charges on the transition metal will be less stable than when there is more electron density on the metal, as in the \([\text{Mn(PR}_3)_4]^+\) layer. The present MO discussion and the MO diagram above anticipate the discussion of molecular orbital theory in complexes in Chapter 11 and may most profitably be read again after reading that chapter.

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Footnote 34: For the complete discussion, see Hoffmann, R.; Zhang, C. J. Phys. Chem. 1985, 89, 6175-6181.
obscured by a charge transfer band), it is still possible to evaluate \( B' \).

If only two transitions are observed (as, for example, in Fig. 11.13b where \( v_1 \) is obscured by a charge transfer band), it is still possible to evaluate \( B' \) by other methods. Once values for \( \Delta \) and \( B' \) have been determined, it is possible to estimate all of the transition frequencies for a complex. The appropriate relationships for high spin octahedral \( d^2 \) and \( d^6 \) and tetrahedral \( d^2 \) and \( d^3 \) species are:

\[
v_1 = A_{3u} \rightarrow T_{2e} = \Delta
\]

\[
v_2 = A_{1u} \rightarrow T_{2g}(F) = 7.5B' + 1.5\Delta - \frac{1}{2}[225\beta^2 + (\Delta)^2 - 18.0\beta \Delta] \quad \text{(11.22)}
\]

\[
v_3 = A_{2u} \rightarrow T_{1u}(P) = 7.5B' + 1.5\Delta + \frac{1}{2}[225\beta^2 + (\Delta)^2 - 18.0\beta \Delta] \quad \text{(11.23)}
\]

These equations, which can be solved by iterative processes, lead to accurate estimates of transition frequencies (Table 11.19) and quite satisfactory fitting of spectra. Parallel equations for octahedral \( d^8 \) complexes are:

\[
v_1 = \Delta + 4B' = 86.2\Delta \quad \text{(11.25)}
\]

\[
v_2 = \Delta + 2B' = 2B' \Delta \quad \text{(11.26)}
\]

### Table 11.19

<table>
<thead>
<tr>
<th>Energy level diagram</th>
<th>Calculated (cm(^{-1}))</th>
<th>Experimental (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_{2g}(F) )</td>
<td>34,400</td>
<td>34,400</td>
</tr>
<tr>
<td>( T_{2g}(P) )</td>
<td>22,400</td>
<td>22,700</td>
</tr>
<tr>
<td>( T_{1u}(P) )</td>
<td>24,000</td>
<td>24,000</td>
</tr>
<tr>
<td>( T_{1u}(F) )</td>
<td>38,100</td>
<td>46,500</td>
</tr>
</tbody>
</table>

* This transition is not experimentally observed because it is masked by the charge transfer transition.

### References


Now, what can we say about the phosphorus-phosphorus interaction between layers? Comparing the layer structure of $\text{MnP}_2^{2+}$ with the unit cell in Fig. 7.28, we see that the 3-D structure of $\text{BaMnP}_2$ consists of alternating $\text{MnP}_2^{2+}$ and $\text{Ba}^{2+}$ layers. This brings the apical phosphorus atoms of one layer close to those of the next layer, and they interact along the $z$ axis. If we look at the DOS for a single $\text{MnP}_2^{2+}$ layer (Fig. 7.30), but now inquire as to the contribution of the phosphorus $3p_z$ orbitals, we see that most (70%) of it is in a rather narrow band at $-15$ eV (Fig. 7.31). The narrowness of a band is an indication of its localization; these are the lone pairs that were postulated on the basis of the $\text{PF}_7$ analogue (page 278). If these orbitals are completely filled, the lone pairs on adjacent layers will repel each other. If half filled, they could form inter-layer covalent bonds. When the layers come together, we expect the $3p_z$ orbitals to interact strongly with shifts to higher (antibonding) energies and lower (bonding) energies. In fact, all orbitals of the system with $z$ components will interact, but only the $3p_z$ orbitals will be sufficiently close to have much overlap.

The three-dimensional (total) DOS is illustrated in Fig. 7.32. We see a low-lying band at $-16.5$ eV corresponding essentially to a $\text{P-P}$ bonding interaction and...
The spectrum of any octahedral $d^6$ complex can be assigned with the help of Fig. 11.42. For high spin species such as [CoFJ$^3-$, the only spin allowed transition is $^5T_2g \rightarrow ^1E_g$ and only one absorption should be observed. Indeed the blue color of this complex results from an absorption centered at 13,100 cm$^{-1}$.

For low spin Co$^{3+}$ complexes there are two spin allowed transitions at relatively low energies: $^1A_g \rightarrow ^1T_2g$ and $^1A_g \rightarrow ^1T_2g$. There are additional spin allowed transitions at higher energies, but they generally are masked by totally allowed transitions and hence are not observed. Because the slope of $^1T_2g$ changes more rapidly than that of $^1T_2g$, the two observed peaks will be further apart in energy at larger values of $\Delta$. The spectra of yellow [Co(en)$_2$]$^{3+}$ and green [Co(ox)$_2$]$^{3+}$ (Fig. 11.43) confirm these expectations.

Fitting an observed spectrum to its corresponding Tanabe-Sugano diagram enables one to obtain the value of $\Delta$ for a complex. In addition, it is possible to evaluate

---

**Table 11.18**

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Ion</th>
<th>$\beta$</th>
<th>$\gamma$</th>
</tr>
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<tbody>
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<td>$3d^2$</td>
<td>Ti$^{2+}$</td>
<td>718</td>
<td>2629</td>
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<td></td>
<td>V$^{3+}$</td>
<td>861</td>
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<td></td>
<td>Cr$^{4+}$</td>
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<td>4238</td>
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<td>Sc$^{3+}$</td>
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<td></td>
<td>V$^{3+}$</td>
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<td>Fe$^{2+}$</td>
<td>720</td>
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<td>620</td>
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<td>Cr$^{0}$</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>Co$^{0}$</td>
<td>600</td>
<td></td>
</tr>
</tbody>
</table>

---

another at ~6 eV that is essentially a P-P antibonding interaction. If only the lower band is filled, we shall have P-P bands between layers; if both are filled there will be nonbonding (van der Waals) contacts.

We must now compare how these bands lie with respect to the energies of the electrons in the bands arising from the metal 3d orbitals. The bottom and top of the 3d band and the Fermi level change as one progresses across the transition series:

$$\begin{array}{c}
\text{Mn} & \text{Fe} & \text{Co} & \text{Ni} & \text{Cu} \\
\text{bottom of }d\text{ band} & \text{top of }d\text{ band} & \text{bottom of }d\text{ band} & \text{top of }d\text{ band} & \text{bottom of }d\text{ band} \\
\end{array}$$

There are two factors involved. The fraction of the band filled with electrons increases with each increase in atomic number and addition of a valence electron. At the same time, the level and width of the band decreases as a result of the increase in effective atomic number. (Recall that d electrons shield poorly.) The overall result is a slow time, the level and width of the band decrease as a result of the increase in effective orbitals. The bottom and top of the 3d electrons in the bands arising from the metal 3d orbitals.

We note an interesting difference between early and late transition metals:

$$\begin{array}{c}
\text{Mn} & \text{Fe} & \text{Co} & \text{Ni} & \text{Cu} \\
\text{P} & \text{P} & \text{P} & \text{P} & \text{P} \\
\text{levels of }P & \text{levels of }P & \text{levels of }P & \text{levels of }P & \text{levels of }P \\
\end{array}$$

The P-P band is always filled, corresponding to a P—P bond (225 pm) in the copper compound. At the other extreme, the P-P* band is also filled, giving an antibonding interaction in addition. Thus, overall, there is a nonbonded interaction between the two phosphorus atoms and so we should not be surprised that the P—P distance is approximately twice the van der Waals radius of phosphorus (2 x 185 pm = 370 pm).

We can view the progression from Mn to Cu as a redox tuning of the occupancy of these energy levels:

$$\text{Mn} \rightarrow \text{Fe} \rightarrow \text{Co} \rightarrow \text{Ni} \rightarrow \text{Cu}$$

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In order to treat fully the problem of interpretation of spectra, it is common to use diagrams provided by Tanabe and Sugano,\(^4\) which provide an alternative means of depicting the variation of term energies with field strength. Tanabe-Sugano diagrams include both weak and strong fields and hence are more comprehensive than Orgel diagrams. They are similar to correlation diagrams but are more useful for extracting quantitative information.

A simplified version of the Tanabe-Sugano diagram for \(d^5\) octahedral complexes is shown in Fig. 11.42.\(^4\) The ground state is always taken as the absolute in these diagrams with the energies of the other states being plotted relative to it. Inter-electronic repulsion is expressed in terms of the Racah parameters \(B\) and \(C\), which are linear combinations of certain coulomb and exchange integrals pertaining to the uncomplexed ion.\(^5\) Accurate evaluation of these integrals is in general not feasible and so these factors are instead treated as empirical parameters and are obtained from the spectra of free ions. The parameter \(B\) is usually sufficient to evaluate the difference in energy between states of the same spin multiplicity; however, both parameters are necessary for terms of different multiplicity. A relationship that will prove to be quite useful in analyzing spectra is that the difference in energy between a free ion ground state \(F\) term and an excited \(P\) term of the same spin multiplicity (as found for \(d^2\), \(d^3\), and \(d^4\) configurations) is \(15B\). Energy \((E)\) and field strength are expressed on a Tanabe-Sugano diagram in terms of the parameter \(B\) as \(EF\) and \(DB\), respectively. In order to represent the energy levels with any accuracy, it is necessary to make some assumptions about the relative values of \(C\) and \(B\). The ratio \(C/B\) for the diagram in Fig. 11.42 is 4.8. For most transition metal ions \(B\) can be estimated as approximately 1000 \(cm^{-1}\) and \(C = -4B\). More precise values are given in Table 11.18.

At weak octahedral fields, the ground state for a \(d^5\) complex is \(^{2}T_{2g}\), which originates from the free ion \(^2D\) term (Fig. 11.42). Among the excited terms at the weak-field limit is a \(^{4}A_{2g}\) (from the free ion \(^4S\)) which falls precipitously in energy with increasing \(A\), eventually displacing \(^{2}T_{2g}\) as the ground term at \(DB = 20\). At this point spin pairing takes place, resulting in a discontinuity in the diagram, marked by the vertical line. From this boundary on, the low spin \(^{4}A_{2g}\) term remains the ground state.

A complete set of Tanabe-Sugano diagrams is given in Appendix G.

\(^4\) Occasionally the Slater-Condon-Shortley parameters \(F_2\) and \(F_4\) are used instead. Their relation to the Racah parameters is \(B = F_3 = 5F_2\) and \(C = 3F_2\).
Some of the high-temperature superconductors examined to date: (1) The structures can be derived by stacking different amounts and sequences of rock-salt and perovskite-like layers of metal and oxygen; (2) superconductivity occurs in the CuO$_2$ layers: (3) the similarity in energy between the copper 3d and oxygen 2p levels causes them to mix extensively in the electronic band at the Fermi level; (4) the non-CuO$_2$ layers (part of the CuO$_2$ chains in the 1-2-3 compounds, the TiO and BiO layers in others) furnish electron density that tunes the electronic state of the CuO$_2$ layers.\(^{45}\) Detailed discussion of superconductivity theory or of band theory applied to these crystals is beyond the scope of this text.
Complexes observed in various types of electronic transitions in molecular orbitals we encountered earlier (Chapter 5) and it leads to an identical (tetrahedral) and \( \lg \) (octahedral) levels. Mixing of terms exactly parallels the mixing because a tetrahedral field is, in effect, a negative octahedral field. The diagram also illustrates the effects of mixing of terms. As a general rule, terms having identical multiplicity for a particular configuration is with spin-orbit coupling and John–Teller distortions, often lead to more complex spectra than predicted with the spin selection rule.

Another popular way of representing ground and excited states of the same multiplicity for a particular configuration is with Orgel diagrams. Like correlation diagrams, they portray the energies of states as a function of field strength; however, Orgel diagrams are much simpler because excited states of multiplicities different from that of the ground state are omitted and only weak field cases are included. An Orgel diagram for Co\(^{2+}\) (d\(^6\)) in tetrahedral and octahedral ligand fields is shown in Fig. 11.39. Once again, we see the inverse relationship between the two symmetries, which arises because a tetrahedral field \( t_{2g} \) in effect, a negative octahedral field. The diagram also illustrates the effects of mixing of terms. As a general rule, terms having identical symmetry will mix, with the extent of mixing being inversely proportional to the energy difference between them. For Co\(^{2+}\) the terms involved are the two \( ^4T_{1g} \) (tetrahedral) and \( ^4T_{2g} \) (octahedral) levels. Mixing of terms exactly parallels the mixing of molecular orbitals we encountered earlier (Chapter 5) and it leads to an identical result: The upper level is raised in energy while the lower level falls. This is represented in the Co\(^{2+}\) diagram as diverging lines for the pairs of \( ^4T_{1g} \) and \( ^4T_{2g} \) levels; the condition of no mixing is shown as dashed lines. Note that for the tetrahedral case in the absence of mixing, the two \( ^4T_{1g} \) terms gradually approach each other in energy as the field strength increases while just the opposite is true for octahedral complexes. As a result, the extent of mixing is greater for tetrahedral complexes.

Orgel diagrams provide a convenient means of predicting the number of spin allowed absorption bands to expect in a UV/visible spectrum for a complex. From Fig. 11.39, it is clear that a complex of Co\(^{2+}\) (or any other d\(^2\) ion) should produce a spectrum with three absorptions. A more general Orgel diagram pertaining to high spin octahedral or tetrahedral complexes of metals with two to eight d electrons is shown in Fig. 11.40.

Up to this point we have considered two central issues involved in interpreting electronic spectra of transition metal complexes—the number and intensities of spectral lines. There is a third important spectral feature, the widths of observed bands, which we have not yet discussed. Consider again the visible spectrum for some metal-to-ligand charge transfer bands in molecules with unsaturated ligands particularly with organic ligands.
7.1 Find the spinel exceptions to the structure field map in Fig. 7.4.

7.2 Predict the structures of the following (i.e., to what mineral classes do they belong?):
   a. MgCrO$_4$
   b. K$_2$MgF$_4$

7.3 Rationalize the fact that the rutile field lies above and to the right of the zircon field (Fig. 7.5) from what you know about these structures. Does this insight enable you to predict anything about the silicon dioxide structure?

7.4 With regard to each of the following, does it make any difference whether one uses correct radii, such as empirically derived Shannon-Prewitt radii, or whether one uses theoretically reasonable but somewhat misassigned traditional radii?
   a. prediction of the interionic distance in a new compound, MX.
   b. calculation of the radius ratio in M$_3$X.
   c. calculation of the enthalpy of formation of a hypothetical compound, MX$_3$.
   d. construction of a structure field map as shown in Figs. 7.4 and 7.5.

7.5 Why is graphite a good conductor whereas diamond is not? (Both contain infinite lattices of covalently bound carbon atoms.)

7.6 It was stated casually (page 275) that the energy levels of gallium are above those of germanium and, later, that those of arsenic lie below those of germanium. Can you provide any arguments, data, etc., to substantiate this?

7.7 Cadmium sulfide is often used in the photometers of cameras to measure the available visible light. Suppose you were interested in infrared photography. Using Fig. 7.25, suggest some compounds that might be suitable for an infrared photocell.

7.8 Using Fig. 7.25, calculate the wavelength of light at which photoconduction will begin for a CdS light meter. If you are interested in black and white photography, can you tell why this wavelength is particularly appropriate?

7.9 A very important photographic reaction is the photolytic decomposition of silver bromide described approximately by the following equation:

\[ \text{AgBr(s)} \rightarrow \text{Ag(s)} + \text{Br}_2(g) \]

Assuming that the enthalpy of the reaction described in the equation can be equated with the energy of the photon, use a Born-Haber cycle to calculate the wavelength of light that is sufficiently energetic to effect the decomposition of silver bromide. What are some sources of error in your estimate?

7.10 There are two structures illustrated by figures in this chapter that are not identified as being the same, although they depict the same crystal structures. Examine all the crystal structures in this chapter and identify the two figures that are the same structure.

7.11 Convince yourself that if there were no defect vacancies in the 1-2-3 superconducting slab, the empirical formula would be Ba$_2$Cu$_3$O$_7$.

7.12 If you are certain that the true formula of the 1-2-3 superconductor is YBa$_2$Cu$_3$O$_8$, with $0.2 < b < 0.4$, what does this imply concerning the copper atoms?

---

7.13 To follow up on Problem 7.12, the band structure arising from the copper 3d orbitals has been calculated to be:

\[
\begin{align*}
&\sigma_\sigma \\
&\pi - \pi^* \\
&\text{The } \sigma^* - \pi^* \text{ band lies in the } \text{CuO}_2 \text{ layers (ab plane between the Bi and } V \text{ atoms), and the } \sigma^* - \pi \text{ band lies along the } \text{CuO}_2 \text{ (CuO}_2 - \text{CuO}_2 - | \text{ chains (b axis between adjacent Bi atoms). What can you say about the electron density on the different Cu atoms? (See Footnotes 40, 47.)}
\end{align*}
\]

7.14 Stishovite is a dense, metastable polymorph of SiO$_2$ with a C.N. = 6 for silicon. It forms at pressures above 8.5 GPa. In the meteoritic impact vs. volcanism controversy over the nonconformity at the Cretaceous-Tertiary boundary ("What killed the dinosaurs?") the presence of stishovite at the K/T boundary has been used as an argument in favor of meteoritic impact rather than volcanic activity (See McHone, J. P.; Nieman, R. A.; Lewis, C. F.; Yates, A. M. Science 1989, 247, 1182–1184). Discuss the possible changes involved in the quartz-to-stishovite phase transitions in terms of heat and pressure, and how they relate to meteorites vs. volcanoes. (See also Sigurdsson, H.; O'_connor, S.; Arthur, M. A.; Braddock, T. J.; Zachos, J. C.; van Fossen, M.; Chinomoto, J. E. T. Nature, 1991, 349, 482-487.)

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\[^{49}\text{Burdett, J. K. In Perspectives in Coordination Chemistry; Williams, A. F.; Floriani, C.; Merbach, A. E., Eds.; VCH: New York, 1992.}\]
\[^{50}\text{Whangbo, M.-H.; Pouget, M.; Rena, M. A.; Williams, J. M. Inorg. Chem. 1987, 26, 1879, 1831, 1832.}\]
\[^{52}\text{Burdett, J. K. In Perspectives in Coordination Chemistry; Williams, A. F.; Floriani, C.; Merbach, A. E., Eds.; VCH: New York, 1992.}\]
Selection rules reflect the restrictions on state changes available to an atom or molecule. Any transition in violation of a selection rule is said to be “forbidden,” but as we shall see, some transitions are “more forbidden than others” (to paraphrase George Orwell). We shall not pursue the theoretical bases of the rules in any detail but merely outline simple tests for their application.

The first selection rule, known as the Laporte rule, states that the only allowed transitions are those with a change of parity: gerade to ungerade (g → u) and ungerade to gerade (u → g) are allowed, but not g → g and u → u. Since all singlet orbitals have gerade symmetry in centrosymmetric molecules, this means that all d-d transitions in octahedral complexes are formally forbidden. This being true, it may seem strange that UV/visible spectroscopy for such complexes is even possible. In fact, optical spectroscopy is not only possible but has been an important source of experimental support for current bonding theories for complexes. The key element here is that there are various mechanisms by which selection rules can be relaxed so that transitions can occur, even if only at low intensities. For example, unsymmetrical vibrations of an octahedral complex can temporarily destroy its center of symmetry and allow transitions that would otherwise be Laporte forbidden. Such vibronic (vibrational-electronic) transitions will be observable, though weak (the number of molecules in an unsymmetrical conformation at any instant will be a small fraction of the total). Typically, molar absorptivities for octahedral complexes are in the range of 1 to 10 L mol⁻¹ cm⁻¹. In practical terms, this means that if you made up a 0.10 M solution of a typical ML₆ complex and obtained its UV/visible spectrum, the d-d absorptions probably would be observable. On the other hand, a 0.10 M solution of a substance such as benzene, which has fully allowed transitions, would yield absorption peaks that would be grossly off scale.

In tetrahedral complexes, there is no center of symmetry and thus orbitals have no g or u designation. However, the atomic orbitals from which the e and t₂ orbitals are derived do have parity properties that have a bearing on the molecular orbitals. The nonbonding e orbitals are purely metal d atomic orbitals (Fig. 11.21) and hence retain their g character even in the complex. The t₂ molecular orbitals, on the other hand, are formed from atomic d (gerade) and p (ungerade) orbitals. Through this d–p mixing, which imparts some p character to the t₂ level in the complex, the Laporte selection rule is relaxed. As a result, extinction coefficients for tetrahedral complexes are about 10² greater than those for octahedral complexes, ranging from 10³ to 10⁴ L mol⁻¹ cm⁻¹.

A second selection rule states that any transition for which ΔS ≠ 0 is forbidden; i.e., in order to be allowed, a transition must involve no change in spin state. Looking at the correlation diagram for a d⁴ configuration in an octahedral field (Fig. 11.35), we note that the ground state has a multiplicity of 3 (S = 1) and that there are three excited states with this same multiplicity: T₁₈⁰, T₁₈¹, and T₁₈² (from the 3P). Thus we can envision three transitions that are spin allowed:

$$
\begin{align*}
T₁₈⁰ & \rightarrow T₁₈¹ \\
T₁₈¹ & \rightarrow T₁₈² \\
T₁₈² & \rightarrow T₁₈(P)
\end{align*}
$$

Transitions from T₁₈⁰ to any of the single excited states are spin forbidden. A d⁴ octahedral complex should, therefore, give rise to an electronic spectrum consisting of three absorptions. This will be true whether the field is weak or strong. However, it should be observed that as the field strength increases, the separation between the triplet ground and excited states becomes larger. Thus with increasing field strength, transition energies become higher and spectral bands are shifted toward the UV region. For blue [V(H₂O)₆]³⁺, two of the three expected absorptions are observed in the visible region (Fig. 11.38a). The transition to the T₁₈¹ state occurs at 17,500 cm⁻¹ and the transition to the T₁₈² state is found at 25,700 cm⁻¹. The transition to T₁₈² is calculated to be at 36,000 cm⁻¹, but because it is of low intensity and is in the high energy portion of the spectrum where it is masked by many totally allowed transitions, it is not observed. In the solid state [V(H₂O)₆]³⁺, this transition is seen at 38,000 cm⁻¹.

The d⁴ correlation diagram (Fig. 11.37b) is particularly interesting. The ground state (T₁₈²) is the only state on the diagram with a multiplicity of 6. This means that for a d⁴ octahedral complex, all transitions are not only Laporte forbidden but also spin forbidden. Absorptions associated with doubly forbidden transitions are extremely weak, with extinction coefficients several hundred times smaller than those for singly forbidden transitions. It is understandable, then, that dilute solutions of Mn(II) are colorless and only with a substantial increase in concentration is the characteristic faint pink color of [Mn(H₂O)₆]²⁺ observable (Fig. 11.38b).

The spin selection rule breaks down somewhat in complexes that exhibit spin-orbit coupling. This behavior is particularly common for complexes of the heavier transition elements with the result that bands associated with formally spin forbidden transitions (generally limited to ΔS = 1; gain enough intensity to be observed. Table 11.16 summarizes band intensities for various types of electronic transitions, including all allowed charge transfer absorptions, which will be discussed later in the chapter.

If one's goal is merely to predict the number of spin-allowed transitions expected for a complex, a complete correlation diagram is not needed. It is only necessary to know the number of excited states having the same multiplicity as the ground state.

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439 11. Coordination Chemistry: Bonding, Spectra, and Magnetism

Electronic Spectra of Complexes
In the preceding chapters attention has been called to the importance of the forces between atoms and ions in determining chemical properties. In this chapter these forces will be examined more closely and comparisons made among them. The important aspects of each type of force are its relative strength, how rapidly it decreases with increasing distance, and whether it is directional or not. The last property is extremely important when considering the effects of a force in determining molecular and crystal structures. Because distance is an important factor in all interaction energies, a brief discussion of interatomic distances should precede any discussion of energies and forces.

**Chemical Forces**

**Van der Waals Radii**

If two noble gas atoms are brought together with no kinetic energy tending to disrupt them, they will “stick” together. The forces holding them together are the weak London dispersion forces discussed in a later section (pages 299-300). The interatomic distance will be such that the weak attractive forces are exactly balanced by the Pauli repulsive forces of the closed shells. If the two noble gas atoms are identical, one-half of the internuclear distance may be assigned to each atom as its nonbonded or van der Waals radius, as well as the vague term atomic radii. This plethora of radii is a reflection of the necessity of specifying what is being measured by an atomic radius. Nevertheless, it is possible to simplify the tecksent of atomic radii without causing unwarranted errors.

Although the van der Waals radius of xenon appears to be closer to 170 pm than the accepted value of 220 pm obtained from solid xenon, the explanation is that the xenon is reduced in size because electron density is shifted to the more electronegative fluorine atom. In addition, the partial charges induced (Xe$^{5+}$, F$^{-}$) may cause the xenon and fluorine atoms to attract each other and approach more closely.

Although we must therefore expect van der Waals radii to vary somewhat dependent upon the environment of the atom, we can use them to estimate nonbonded distances with reasonable success. Table 8.1 lists the van der Waals radii of some atoms.

**Ionic Radii**

Ionic radii are discussed thoroughly in Chapters 4 and 7. For the present discussion it is only necessary to point out that the principal difference between ionic and van der Waals radii lies in the difference in the attractive force, not the difference in repulsion. The interionic distance in LiF, for example, represents the distance at which the repulsion of a He core (Li$^{+}$) and a Ne core (F$^{-}$) is balanced by the strong electrostatic or Madelung force. The attractive energy for LiF$^{-}$ is considerably over 500 kJ mol$^{-1}$ and the London energy of He-Ne is of the order of 4 kJ mol$^{-1}$. The forces in the LiF crystal are therefore considerably greater and the interionic distance (201 pm) is less than expected for the addition of He and Ne van der Waals radii (300 pm).

**Covalent Radii**

The internuclear distance in the fluorine molecule is 142 pm, which is shorter than the sum of two van der Waals radii. The difference obviously comes from the fact that the electron clouds of the fluorine atoms overlap extensively in the formation of the F-F bond whereas little overlap of the van der Waals radii occurs between the molecules.

---

An inverse relationship also exists between fields of octahedral and tetrahedral symmetries. We saw earlier in this chapter that crystal fields of these two symmetries produce inverse splitting patterns for one-electron $d$ orbitals. This relationship also holds when electron-electron repulsions are added to the picture; any free-ion term will be split into the same new terms (except for $g$ and $u$ designations, which are inappropriate for tetrahedral complexes) by tetrahedral and octahedral fields, but the energy ordering will be opposite for the two symmetries.

Correlation diagrams for $d^2$ to $d^{10}$ octahedral and tetrahedral complexes are shown in Fig. 11.37. By taking advantage of the hole formalism and the octahedral-tetrahedral inversion, all seven configurations in both geometries can be represented with just four diagrams. In each diagram (except the one for $d^5$), free ion terms are shown in the center, with $d^0$ octahedral and $d^{10}$ tetrahedral splittings on the left and the $d^{10}$ octahedral and $d^0$ tetrahedral splittings on the right. Field strength increases in both directions outward from the center. Only lower energy terms are included. A feature that is common to all of the diagrams is that as the magnitude of the ligand field increases, a number of energy level crossovers occur. A general rule that governs all such crossovers is that they always involve states of different symmetry and spin multiplicity: Levels of identical designation never cross. For some configurations ($d^2$, $d^3$, $d^4$, and $d^5$) the crossovers lead to a change in the ground state. For $d^1$, for example, the lowest energy term for the free ion is a $2s$, which splits in a weak octahedral field to give $2A_u$ as the ground state. At an intermediate field, however, the $2T_u$ state drops to lower energy than $2A_u$ and becomes the ground state. The change in spin multiplicity from six to two here corresponds to a decrease in the number of unpaired electrons from five to one; there is a transition from high to low spin. In contrast, the ground states of octahedral $d^1$, $d^2$, $d^3$, and $d^{10}$ complexes remain the same under all field strengths. For example, the ground term of a [TiL$_2$]$^{2+}$ ($d^3$) complex is $2T_u$ at all values of $A''$, which means that all such complexes will have two unpaired electrons regardless of the nature of the ligand L. All of this is consistent, of course, with the bonding models that have been previously discussed in this chapter.

In order to use the correlation diagrams shown in Fig. 11.37 or simplifications of them, it is necessary to know the selection rules that govern electronic transitions.
Table 8.1

Atomic radii and multiple bonding parameters (pm)

| Element | Ionic radii (pm) | Radii from VdW | Covalent radii
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>120–145</td>
<td>37</td>
<td>104 (+3)</td>
</tr>
<tr>
<td>He</td>
<td>100</td>
<td>40</td>
<td>Zr</td>
</tr>
<tr>
<td>Li</td>
<td>90 (–1)</td>
<td>134</td>
<td>Nb</td>
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<tr>
<td>Be</td>
<td>59 (–2)</td>
<td>125</td>
<td>Mg</td>
</tr>
<tr>
<td>B</td>
<td>41 (–2)</td>
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<td>Na</td>
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<td>Fe</td>
</tr>
<tr>
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<td>13</td>
<td>57</td>
<td>Ni</td>
</tr>
<tr>
<td>At</td>
<td>12</td>
<td>58</td>
<td>Cu</td>
</tr>
<tr>
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<td>11</td>
<td>59</td>
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<tr>
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<td>60</td>
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<tr>
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<td>62</td>
<td>As</td>
</tr>
<tr>
<td>Xe</td>
<td>7</td>
<td>63</td>
<td>Se</td>
</tr>
<tr>
<td>Ba</td>
<td>6</td>
<td>64</td>
<td>Br</td>
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<td>67</td>
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<tr>
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<td>70</td>
<td>Rn</td>
</tr>
</tbody>
</table>

*a Values of van der Waals radii from Bondi, A. J. Phys. Chem. 1964, 68, 441, unless otherwise noted.
*b Ionic radii (CN = 6) are from Table 4.4 and are listed for comparative purposes only. For additional values, see that table.
*c Covalent radii estimated from homonuclear bond lengths where available and from selected heteronuclear bonds otherwise.

Fig. 8.2 Illustration of the difference between van der Waals and covalent radii in the F2 molecule.

Fig. 8.3 (a) Hypothetical F—F+ ion-pair molecule illustrating repulsion between the inner He core and the lone pair of the F+ ion. (b) More realistic representation of repulsions between inner core and valence shell electrons. (The He core is not drawn to scale in either sketch.)
Thus far in this chapter we have seen electronic spectra of four complexes: 
[Fe(phen)$_2$(CN)$_2$]+ (Fig. 11.8), and [Cr(en)$_3$]$_3^+$, [Cr(ox)$_3$]$_3^-$, and [CrF$_6$]$_3^0$ (Fig. 11.13). Causal inspection of these examples reveals that the number of absorptions varies. At the heart of the interpretation of electronic spectra is the question of how many absorptions are expected for a given complex. Answering this question requires an accurate energy level diagram for the complex of interest as well as familiarity with the selection rules governing electronic transitions.

The energy level diagrams that have been presented thus far for transition metal complexes are based on the so-called one-electron model even if the central metal ion has more than one $d$ electron. In other words, the effects of electron-electron repulsions have been ignored. Because these repulsions will make a significant contribution to electron energies in any complex that has more than one $d$ electron or more than one $d$ level vacancy, they must be taken into account in interpreting spectra. The approach that is usually followed in developing an energy level diagram for a complex is to begin with the $d^0$ configuration of the free ion and then to add, in turn, the effects of interelectronic repulsions and the effects of surrounding ligands. Our discussion will be mainly qualitative and will use the concept of fields produced by ligands, as introduced in the treatment of crystal field theory (page 294). However, from here on we will use ligand field terminology to emphasize that the discussion applies quite broadly to bonding models that range from the pure crystal field theory through the qualitative molecular orbital approach described in the foregoing section of this chapter (page 413).

As we saw in Chapter 2, electron-electron repulsions cause a given electron configuration to be split into terms. However, for the simplest case, $d^3$, there will be no such splitting of the free ion levels because there is only one electron. Thus we have only one term, the ground state $2D$, because the three orbitals are degenerate and the electron has an equal probability of being in any one of them. As we have also seen previously, these five $d$ orbitals will, under the influence of an octahedral field (either weak or strong), be split into $e_g$ and $t_{2g}$ orbitals. The $2D$ term likewise will be split into $^2T_{2g}$ and $^2E_g$ terms in an octahedral complex.

For the $d^0$ configuration, electron-electron interactions come into play, giving rise to not only a ground state free-ion term ($^2F$) but a number of excited states ($^2P$, $^2G$, $^2D$, and $^2S$) as well. Now we must be concerned with how each of these terms is affected by the ligand field. If the separation between terms is large compared to the perturbation produced by the ligands, we have the weak field case. If, on the other hand, the ligand field splitting is large in comparison to the energy difference between terms, we have the strong field condition. Figure 11.35 shows the free ion terms of a $d^0$ configuration and how they are split in the presence of a weak octahedral field (left side of the diagram). The right side of the diagram shows the effects of a strong octahedral field. The lines connecting the weak and strong field extremes allow one to estimate the relative energies of states resulting from intermediate fields. Construction of the strong field side of a correlation diagram such as this one for $d^0$ is beyond the scope of this text, but development of the weak field portion is more easily accomplished.

The wave functions for $S$, $P$, $D$, $F$, etc. terms have the same symmetry as the wave functions for the corresponding sets of $s$, $p$, $d$, $f$, etc. orbitals. This means that a $D$ term is split by an octahedral field in exactly the same manner as a set of $d$ orbitals.

**The excited state terms may be obtained by methods described in Appendix C.**

![Fig. 11.35](image_url)
Comparison of additive and experimental bond distances (pm)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Bond</th>
<th>( r_A + r_B )</th>
<th>( r_{exp} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>HF</td>
<td>98</td>
<td>92</td>
</tr>
<tr>
<td>HCI</td>
<td>HCI</td>
<td>136</td>
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</tr>
<tr>
<td>HBr</td>
<td>HBr</td>
<td>131</td>
<td>142</td>
</tr>
<tr>
<td>HI</td>
<td>HI</td>
<td>170</td>
<td>161</td>
</tr>
<tr>
<td>CIF</td>
<td>CIF</td>
<td>170</td>
<td>161</td>
</tr>
<tr>
<td>BrF</td>
<td>BrF</td>
<td>185</td>
<td>176</td>
</tr>
<tr>
<td>BrCl</td>
<td>BrCl</td>
<td>213</td>
<td>214</td>
</tr>
<tr>
<td>ICI</td>
<td>ICI</td>
<td>232</td>
<td>222</td>
</tr>
<tr>
<td>CHF</td>
<td>CHF</td>
<td>114</td>
<td>109</td>
</tr>
<tr>
<td>CIF</td>
<td>CIF</td>
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<td>136</td>
</tr>
<tr>
<td>CClF</td>
<td>CClF</td>
<td>176</td>
<td>176</td>
</tr>
<tr>
<td>CBrF</td>
<td>CBrF</td>
<td>191</td>
<td>194</td>
</tr>
<tr>
<td>ClF</td>
<td>ClF</td>
<td>280</td>
<td>215</td>
</tr>
</tbody>
</table>

The experimental bond distance in \( F_2 \) is 142 pm, about halfway between the two admittedly crude estimates. Corresponding values for the other halogens are 210 (Cl), 220 (Br), 250 (I), 199 (F), and 228 (Cl) pm for F. This is not meant to imply that the covalent bond in \( F_2 \) is either an ionic \( F^+ \cdot F^- \) or a van der Waals \( (\text{He} + \text{He}) \); it is a mixture of bonding, called a van der Waals bond, with some ionic character.

The chief factor in determining the covalent radii of atoms is the size of the core electron cloud beneath the valence shell. This might be loosely termed the "van der Waals radius of the core."

Table 8.1 lists covalent radii obtained by dividing homonuclear bond distances by two. In many cases the appropriate homonuclear single bond has not been measured and the assigned covalent radius is obtained indirectly by subtracting the covalent radius of element B in a heteronuclear bond AB to obtain the radius of atom A.

The values in Table 8.1 are reasonably additive, that is, the covalent bond distance in a molecule AB can be estimated reasonably well from \( r_A + r_B \). Some typical values are listed in Table 8.2. The agreement is fairly good. In the case of molecules with several large substituent atoms around a small central atom such as \( C \), \( Cl \), and \( Br \), the crowding apparently causes some shortening of the bond. There are other cases in which the additivity of the radii is rather poor. For example, the \( H-H \) and \( F-F \) bond distances are 74 and 142, respectively, yielding covalent radii of 37 and 71 pm. However, the bond length in the HF molecule is not 108 pm, but 92 pm. If we assume that the size of the fluorine atom is constant, then the radius of hydrogen in HF is 21. Alternatively, we could assume that the fluorine atom is somewhat smaller in the HF molecule than in the \( F_2 \) molecule, an extremely unlikely situation. Or, more realistically, we can admit that the hydrogen atom is unique, that it has no inner repulsive core to determine its covalent radius but that in bonding the proton often partially penetrates the electron cloud of the other atom and that the bond distance is determined by a delicate balance of electron-nucleus attractions and nucleus-nucleus repulsions. However, this does not really solve our problem, for a widespread deviation from additivity results from the effect of differences in electronegativity between the bonding atoms. It is usually observed that the bond length between an electropositive atom and an electronegative atom is somewhat shorter than expected on the basis of their assigned covalent radii. Over fifty years ago Schomaker and Stevenson suggested the relation

\[
r_{AB} = r_A + r_B - 7\Delta \varepsilon
\]

where \( r \) is in pm, and \( \Delta \varepsilon \) is the difference in electronegativity between atoms A and B in Pauling units. Several workers have suggested modifications to improve the accuracy, but only one will be mentioned here. Porterfield has found that Eq. 8.2 is somewhat more accurate and has a better theoretical foundation:

\[
r_{AB} = r_A + r_B - 7\Delta \varepsilon^2
\]

The significance of the bond shortening in highly polar molecules is reasonably clear. Heteropolar bonds are almost always stronger than expected on the basis of the corresponding homopolar bonds (see discussion of ionic resonance energy, Chapter 5). The atoms in the molecule AB are therefore held together more tightly and compressed somewhat relative to their situation in the molecules AA and BB, which are the basis of the covalent radii. It is helpful to analyze the source of this stabilization somewhat more closely than merely labeling it "ionic resonance energy." To a first approximation, it is caused by the extra bonding energy ("ionic" or Madelung energy) resulting from the partial charges on the atoms:

\[
\Delta H = \frac{8\, \alpha^2 \, \varepsilon}{4\pi \varepsilon_0}
\]

The difference in electronegativity between fluoride and hydrogen is about 1.8 Pauling units, predicting a shortening of about 16 pm (Eq. 8.1). The exact fit with the experimental data (108 - 92 = 16 pm) is fortuitous (Eq. 8.2 yields \( \Delta \varepsilon = 33 \) pm), and the importance of these equations lies in the predicted shortening and strengthening of heteropolar bonds. This is an important aspect of covalent bonding.

For a polyvalent atom the partial charge builds up every time another highly electronegative substituent is added. Thus the partial charge on the carbon atom in carbon tetrafluoride is considerably larger than it is in the methyl fluoride molecule, and so all of the C—F bonds shrink, though the effect is not as great for the last fluoride as for the first.
band in the photoelectron spectrum is examined under very high resolution and its first derivative is taken (Fig. 11.33), one observes a vibrational progression that has frequency spacings corresponding to M—C stretching. The vibrational fine structure results because the [Cr(CO)₆]⁺ ions that form may be in a vibrational ground state or in one of several vibrational excited states (Fig. 11.34). The value of ρ_MC for [Cr(CO)₆]⁺ obtained from the fine structure is 325 cm⁻¹, compared to 379 cm⁻¹ for the neutral molecule, the reduction being consistent with involvement of the t₂g electron in π bonding. It is estimated that this frequency shift corresponds to a 14-pm increase in the M—C bond length upon ionization. Further support that such a structural change occurs is provided by intensity data in the spectrum. If the most intense transition that is observed is to the ground vibrational state, it is an indication that there is little alteration of structure when ionization occurs (by the Franck-Condon principle). However, if the most intense transition involves a vibrational excited state, it can be concluded that a substantial perturbation in geometry has taken place in going from the neutral molecule to its positive ion. In the case of Cr(CO)₆, the latter was observed, substantiating the conclusion drawn from the frequency shift, namely, that the t₂g orbital is a π-bonding orbital.

**Electronic Spectra of Complexes**

The variety of colors among transition metal complexes has long fascinated the observer. For example, aqueous solutions of octahedral [Co(H₂O)₆]²⁺ are pink but those of tetrahedral [CoCl]²⁻ are blue. The green color of aqueous [Ni(H₂O)₆]²⁺ turns blue when ammonia is added to the solution to give [Ni(NH₃)₆]²⁺. The reduction of violet [Cr(H₂O)₆]³⁺ gives bright blue [Cr(H₂O)₆]²⁺. As with all colors, these arise from electronic transitions between levels whose spacings correspond to the wavelengths available in visible light. (Of course, when a photon of visible light is absorbed, it is its complementary color that we actually see.) In complexes, these transitions are frequently referred to as d-d transitions because they involve the molecular orbitals that are mainly metal 3d in character (the e_g and t₁g or e and t₂g orbitals in octahedral and tetrahedral complexes, respectively). Obviously, the colors produced are intimately related to the magnitude of the spacing between these levels. Since this spacing depends on factors such as the geometry of the complex, the nature of the ligands present, and the oxidation state of the central metal atom, electronic spectra of complexes can provide valuable information related to bonding and structure.

---

**Fig. 11.32** (a) UV photoelectron spectrum of Cr(CO)₆. Peak positions correspond to relative energies of molecular orbitals in the complex. [From Higgenson, B. R.; Lloyd, D. R.; Brereton, P.; Gibson, D. M.; Orchard, A. P. J. Chem. Soc., Faraday Trans. 2 1973, 69, 1659-1668. Used with permission.]

**Fig. 11.33** Expanded view of the peak labeled B in the PES spectrum shown in Fig. 11.32 along with its first derivative. [From Hubbard, J. L.; Lichtenberger, D. L. J. Am. Chem. Soc. 1982, 104, 2132-2138. Reproduced with permission.]

**Fig. 11.34** Potential well representations for M(CO)₆ and M(CO)₅⁺ showing origins of vibrational fine structure in PES spectrum. [Modified from Hubbard, J. L.; Lichtenberger, D. L. J. Am. Chem. Soc. 1982, 104, 2132-2138. Used with permission.]
where $r_1$ and $r_2$ are single bond covalent radii, and $C_1$ and $C_2$ are unitless multiple-bond parameters for each element (Table 8.1). With a few notable exceptions, Eq. 8.4 gives reasonable estimates of bond lengths over a wide range of bond order and electronegativity differences.

### Types of Chemical Forces

#### Ionic Bonding

This topic has been discussed extensively in Chapters 3 and 6, so only those aspects pertinent to comparison with other forces will be reviewed here. In general, the covalent bond is strongly directional as a result of the overlap criterion for maximum bond strength. We have seen previously the implications that this has for determining molecular structures. In addition, the covalent bond is very strong. Some typical values for purely covalent bonds are $P-P = 200 \text{ kJ mol}^{-1}$, $C-C = 346 \text{ kJ mol}^{-1}$, and $C-H = 437 \text{ kJ mol}^{-1}$. The smaller atoms can affect better overlap and hence have stronger bonds. Bond polarity can increase bond strength (cf. Pauling's electronegativity calculations, Chapter 5), and so we find a few much stronger bonds such as $S=O$ (which probably includes some $\pi$ bonding as well), 565 $\text{ kJ mol}^{-1}$. Homopolar bonds between small atoms with repulsive lone-pairs tend to be somewhat weaker than averages, for example, $N=N$, 167 $\text{ kJ mol}^{-1}$, and $F=\text{F}$, 155 $\text{ kJ mol}^{-1}$. Nevertheless, a good rule of thumb is that a typical covalent bond will have a strength of about 250-400 $\text{ kJ mol}^{-1}$. As we shall see, this is stronger than all other chemical interactions with the exception of ionic bonds.

Because of the complexity of the forces operating in the covalent bond, it is not possible to write a simple potential energy function as for the electrostatic forces such as ionic, ion-atom, and dipole-dipole interactions. Nevertheless, it is possible to describe the covalent energy qualitatively as a fairly short-range force (as the atoms are forced apart, the overlap decreases).

The strength of a purely ionic bond between two ions can be obtained quite accurately by means of the Born-Landé equation (Chapter 4). Neglecting repulsive forces, van der Waals forces, and other small contributions, we can estimate the energy of an ion pair simply as

$$E = \frac{Z^+Z^-e^4}{4\pi\varepsilon_0 r} \quad \text{(8.5)}$$

For a pair of very small ions, such as $\text{Li}^+$ and $\text{F}^-$, we can estimate a bond energy of about 665 $\text{ kJ mol}^{-1}$. The experimental values are 753 $\text{ kJ mol}^{-1}$ (Appendix E) for dissociation to atoms and 783 $\text{ kJ mol}^{-1}$ (Chapter 3) for dissociation to ions. For a pair of larger ions, such as $\text{Cs}^+$ and $\text{F}^-$, the energy is correspondingly smaller or about half as much. It is evident that the strength of ionic bonds is of the same order of magnitude as covalent bonds. The common notion that ionic bonds are considerably stronger than covalent bonds probably results from mistaken interpretations of melting-point and boiling-point phenomena, which will be discussed later.

### Ion-Dipole Forces

The various factors affecting the magnitude of the dipole moment in a polar molecule were discussed in previous chapters. The potential energy of an ion-dipole interaction is given as

$$E = \frac{Z^+Z^-e^4}{4\pi\varepsilon_0 r^3} \quad \text{(8.7)}$$

where $Z^+$ is the charge on the ion and $r$ is the distance between the ion and the molecular dipole:

$$\mu = q'$$

Ion-dipole interactions are similar to ion-ion interactions, except that they are more sensitive to distance ($1/r^3$ instead of $1/r$) and tend to be somewhat weaker since the charges ($q^+$, $q^-$) comprising the dipole are usually considerably less than a full electronic charge.

Ion-dipole forces are important in solutions of ionic compounds in polar solvents where solvated species such as $\text{NaOH}^+$ and $\text{H}_2\text{O}^-$. For solutions of $\text{NaF}$ in $\text{H}_2\text{O}$ exist. In the case of some metal ions these solvated species can be sufficiently stable to be considered as discrete species, such as $[\text{Co(NH}_3)_6]^{3+}$. Complex ions such as the latter may thus be considered as electrostatic ion-dipole interactions, but this oversimplification (Crystal Field Theory; see Chapter 11) is less accurate than are alternative viewpoints.
Infrared carbonyl stretching frequencies (cm\(^{-1}\)) for some W(CO)L complexes:

<table>
<thead>
<tr>
<th>L</th>
<th>A(^{1})</th>
<th>E</th>
<th>A(^{2})</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me(_3)CNHO</td>
<td>1847</td>
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<td>2667</td>
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<td>2671</td>
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<td>2103</td>
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<td>1945</td>
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</tr>
<tr>
<td>C(_6)H(_6)Se</td>
<td>2073</td>
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<td>2088</td>
<td></td>
</tr>
</tbody>
</table>

\( A^1 \) and \( A^2 \) are the forbidden \( B_2 \) and \( A_1 \) modes, respectively.

\( \nu^{\text{obs}} \) Infrared frequencies are generally solvent dependent. Small differences should not be taken as significant. The forbidden \( B_2 \) mode, frequently present in these spectra as a weak absorption.

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**Fig. 11.31** Vibrational stretching modes and their symmetries for W(CO)\(_6\) complexes.

NO > CO, RNC, PF\(_3\) > PCl\(_3\), CH\(_2\) = CHOH, (PO\(_3\)P\(_2\)) > PO\(_3\)H\(_2\) > CIORG(k = C\(_2\)H\(_5\), P(SR)\(_3\), PPh\(_3\), PR\(_3\), R\(_2\)SP > Ph\(_3\) > RCN > aniline > alkylamines > ethers > alcohols

This series shows many of the trends that might have been expected on the basis of electronegativity, especially for the phosphorus-bearing ligands: PF\(_3\) > PCl\(_3\) > PO\(_3\)H\(_2\) > PR\(_3\). The similarity of phosphites and phosphines is more than might have been predicted from electronegativity arguments indicating that there may be significant O-P σ bonding in the phosphites and competition for the phosphorus d orbitals. Alkylamines, ethers, and alcohols have no empty low-lying orbitals and hence form the weak end of the μ-acceptor scale.

Care must be taken in applying a μ-acidity scale such as the one just presented. In using it to interpret IR data for carbonyl complexes, one should keep in mind that factors other than inherent ligand μ-acidity can also influence \( \nu^{\text{CO}} \) values. Given that \( \sigma \) bonding is much more important than μ bonding in these systems, differences in σ-donating capacity among ligands may outweigh trends in μ-accepting ability. For example, replacing the phenyl groups on phosphorus with methyl groups has little effect upon the carbonyl stretching frequencies of W(PR\(_3\))\(_6\) complexes even though the μ-acidity series would predict that this substitution should cause an increase in \( \nu^{\text{CO}} \). It is possible that the expected increase is not observed because, in addition to being a better μ acid, Ph\(_3\)P is a better σ donor compared to Me\(_3\)P, making the total amount of electron density that is available on the metal greater in the Ph\(_3\)P complex. It is also possible that the change in ligand substituents introduces a steric perturbation that is substantial enough to have a greater effect than electronic factors (see Chapter 15).

**Photoelectron spectroscopy**. Photoelectron spectroscopy (see Chapter 5) has been used to obtain metal-carbon stretching frequencies for Group VIA (6) carbonyl complexes.\(^{13,37}\) The full spectrum for Cr(CO)\(_6\) is shown in Fig. 11.32. The signal labeled \( \beta \) corresponds to the ionization of an electron from a \( \beta_2 \) orbital, which of course is the orbital having appropriate symmetry to interact with the \( \pi^* \) orbital of carbon monoxide. In fact the interaction here, removal of the electron should weaken the metal-carbon bond and decrease its stretching frequency. If, on the other hand, there is no interaction, one would expect to see little change in \( \nu^{\text{CO}} \) upon ionization since the electron would be coming from a nonbonding orbital. When the \( \beta \) orbital is antibonding in nature, ionization will result in an increase in \( \nu^{\text{CO}} \).


Induced Dipole Interactions

The energy of interaction of two dipoles may be expressed as

\[ E = -\frac{2|\mu_1\mu_2|}{9\varepsilon_0 r^3} \]  

(8.8)

This energy corresponds to the “head-to-tail” arrangement shown in Fig. 8.4a. An alternative arrangement is the antiparallel arrangement in Fig. 8.4b. The second arrangement will be the more stable if the molecules are not too “fat.” It can be shown that the energies of the two arrangements are equal if the long axis is 1.12 times as long as the short axis. Both arrangements can exist in situations in which the attractive energy is larger than thermal energies (RT = 2.5 kJ mol\(^{-1}\) at room temperature). In the solids and liquids in which we shall be interested, this will generally be true. At higher temperatures and in the gas phase there will be a tendency for thermal motion to randomize the orientation of the dipoles and the energy of interaction will be considerably reduced.

Dipole–dipole interactions tend to be even weaker than ion–dipole interactions and to fall off more rapidly with distance (1/r). Like ion–dipole forces, they are directional in the sense that there are certain preferred orientations and they are responsible for the association and structure of polar liquids.

If a charged particle, such as an ion, is introduced into the neighborhood of an uncharged, nonpolar molecule (e.g., an atom of a noble gas such as xenon), it will distort the electron cloud of the atom or molecule in much the same way that a charged sphere can distort the electron cloud of a large, soft anion (Fajans’ rules, Chapter 4). The polarization of the neutral species will depend upon its inherent polarizability (“softness”), \( \alpha \), and on the polarizing field afforded by the charged ion, \( Z^- \). The energy of such an interaction is

\[ E = -\frac{Z^2\alpha e^2}{2r^3} \]  

(8.9)

In a similar manner, a dipole can induce another dipole in an otherwise uncharged, nonpolar species. The energy of such an interaction is

\[ E = -\frac{\mu_1 \mu_2}{r^6} \]  

(8.10)

where \( \mu \) is the moment of the inducing dipole.

Both of these interactions tend to be very weak since the polarizabilities of most species are not large. Because the energies vary inversely with high powers of \( r \), they are effective only at very short distances. Their importance in chemistry is limited to situations such as solutions of ionic or polar compounds in nonpolar solvents.

**Fig. 8.4** (a) Head-to-tail arrangement of dipoles; (b) antiparallel arrangement of dipoles.

Instantaneous Dipole–Induced Dipole Interactions

Even in atoms in molecules which have no permanent dipole, instantaneous dipoles will arise as a result of momentary imbalances in electron distribution. Consider the helium atom, for example. It is extremely improbable that the two electrons in the is orbital of helium will be diametrically opposite each other at all times. Hence there will be instantaneous dipoles capable of inducing dipoles in adjacent atoms or molecules. Another way of looking at this phenomenon is to consider the electrons in two or more “nonpolar” molecules as synchronizing their movements (at least partially) to minimize electron–electron repulsion and maximize electron–nucleus attraction. Such attractions are extremely short ranged and weak, as are dipole–induced dipole forces. The energy of such interactions may be expressed as

\[ E = -\frac{24\alpha a}{r^5} \]  

where \( \alpha \) is the mean instantaneous dipole, or more conveniently as

\[ E = -\frac{18\alpha^2}{4r^6} \]  

(8.12)

where \( \alpha \) is the polarizability and \( I \) is the ionization energy of the species.

London forces are extremely short range in action (depending upon \( 1/r^6 \)) and the weakest of all attractive forces of interest to the chemist. As a result of the small term, London forces increase rapidly with molecular weight, or more properly, with the molecular volume and the number of polarizable electrons.

It can readily be seen that molecular weight per se is not important in determining the magnitude of London forces as reflected by the boiling points of \( H_2, MW = 2, bp = 20 \) \( K \); \( D_2, MW = 4 \) (a factor of two different), \( bp = 25 \) \( K \); \( T_2, MW = 6, bp = 29 \) \( K \) — as well as similar compounds, such as hydrocarbons containing different isotopes of hydrogen. Fluorocarbons have unusually low boiling points because tightly held electrons in the fluorine atoms have a small polarizability.

All of the interactions discussed thus far are inherently attractive and would become infinitely large if \( r = 0 \). Countering these attractive forces are repulsive forces resulting from nucleus–nucleus repulsion (important in the \( H_2 \) molecule) and, more important, the repulsion of inner or core electrons. At extremely short interatomic distances the inner electron clouds of the interacting atoms begin to overlap and Pauli repulsion becomes extremely large. The repulsive energy is given by

\[ E = \frac{-4k}{r^6} \]  

(8.13)

where \( k \) is a constant and \( a \) may have various values, comparatively large. For ionic compounds, values of \( a \) ranging from 5 to 12 prove useful (Chapter 4), and the Lennard–Jones function, often used to describe the behavior of molecules, is sometimes referred to as the 6–12 function because it employs \( r^6 \) for the attractive energies.
Infrared absorptions of some metal carbonyl complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Frequency (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mn(CO)₄]⁺</td>
<td>2090</td>
</tr>
<tr>
<td>[Cr(CO)₆]⁺</td>
<td>2000</td>
</tr>
<tr>
<td>[V(CO)₆]⁻</td>
<td>2000</td>
</tr>
<tr>
<td>[Ti(CO)₆]⁻</td>
<td>1890</td>
</tr>
<tr>
<td>[Ni(CO)₂]⁺</td>
<td>1700</td>
</tr>
<tr>
<td>[Fe(CO)₄]⁻</td>
<td>1700</td>
</tr>
</tbody>
</table>

Metal-carbonyl bonds from structural data because other factors can influence bond lengths.

The most widely used experimental method for analyzing metal carbonyl complexes is infrared (IR) spectroscopy. The frequency of the IR absorption (or more properly, the force constant, k), associated with a C—O stretching vibration, is a measure of the resistance of the bond to displacement of its atoms. Hence the stretching frequency provides a qualitative measure of bond strength, with strongly bonded sets in general giving rise to IR absorptions at higher frequencies. Consider Table 11.13, which lists IR data for two isoelectronic series of metal carbonyls. On the basis of the absorption maxima, we can say that the C—O bond strengths in these two series decrease in the order, [Mn(CO)₄]⁺ > [Cr(CO)₆]⁺ > [V(CO)₆]⁻ > [Ti(CO)₆]⁻ and [Ni(CO)₂]⁺ > [Cr(CO)₂]⁻ > [Fe(CO)₄]⁻. These qualitative results are consistent with the σ-bonding model described earlier. As M—C σ bonding increases, the C—O bond becomes stronger. As one increases the metal, the strength of the metal—carbon bond increases, with the result that the C—O bond becomes weaker. The greater the positive charge on the central metal atom, the less readily the metal can donate electron density into the σ orbitals of the carbon monoxide ligands to weaken the C—O bond. In contrast, in the carbonyl anion the metal has a greater electron density to be dispersed, with the result that M—C σ bonding is enhanced and the C—O bond is diminished in strength.

In the isolated carbon monoxide ligand, the lone electron pair on carbon resides in the 3σ orbital, which is the HOMO (highest occupied molecular orbital) for this molecule (Fig. 5.20). Promotion of one of these electrons in gaseous CO to a σ* level to give the 5σ² 3σ² excited state causes the C—O stretching frequency to drop from 2143 to 1499 cm⁻¹. This dramatic change is a strong indication that even a small amount of electron shift from a central metal into the σ orbital of a bound CO can be easily detected via IR measurements.31

As has already been stated, the lone pair on carbon in the carbon monoxide ligand resides in a molecular orbital that is slightly antibonding. Support for this assertion is also provided by IR data. When one of the lone pair (HOMO) electrons is removed from CO to form CO⁺, the C—O stretching frequency increases from 2143 to 2184 cm⁻¹, showing that the C—O bond order also increases. Protonation of the molecule, which can be considered as a coordination of CO to H⁺, also leads to an increase in the stretching frequency. It would be expected that, upon donation of the CO lone pair to a metal atom, a similar increase in ν_CO should occur, provided there is no other concomitant electron shift. When this is actually observed, however, that ν_CO almost always decreases upon complex formation, an indication that electron density flows from the metal into the σ orbital of the ligand more than can make up for the increase in C—O bond order that would accrue from the ligand-to-metal σ donation.32

In a preceding section we saw crystallographic evidence that substitution of phosphorus ligands for carbon monoxide in Cr(CO)₆ leads to a strengthening of Cr—C bonds, particularly those trans to the phosphorus groups, and this was interpreted in terms of competition of the ligands for available π electron density. Changes in the CO infrared absorptions also occur and can be evaluated in the same vein. In general, substitution of CO with a ligand L will alter the CO stretching frequencies of the remaining carbonyl ligands in a manner that reflects the net electron density transmitted by L to the central metal atom. This in turn will depend both on the π-donating capacity and the σ acidity of L.

It is instructive to look at a set of W(CO)₆ complexes to see how a variety of ligands (L) perturb the C—O stretching frequencies. These complexes all have Cₓ symmetry, at least ideally, and give rise to three allowed IR absorptions (two nondegenerate and one doubly degenerate), having the symmetry labels A₁g, B₁g, and E. In Chapter 15 the procedure for obtaining symmetry assignments for vibrational modes from the appropriate character table will be illustrated, but for now we will simply use the results (Table 11.14). The particular vibrational stretching modes involved are shown in Fig. 11.31. The important one to focus on is A₁g, which corresponds to the symmetrical stretching motion of the CO group lying opposite the ligand L. It is this CO that competes most directly with L for available π electron density and therefore is in a position to best reflect the π acidity of L.

For ligands in Table 11.14 having little or no π acidity (e.g., those in which oxygen or nitrogen is the donor atom), the CO in a trans position can absorb significant electron density into its antibonding orbital, and relatively low C—O stretching frequencies are observed. In the case of the phosphorus ligands, the π acidity increases as the electronegativity of any substituent on P increases. As these ligands become more and more competitive for π electrons, CO receives less and less electron density and the C—O stretching frequency increases accordingly. The very high C—O stretching frequency of the PF₃ complex indicates that this ligand is comparable in its π acidity to carbon monoxide itself. Groups in Table 11.14 having carbon as the ligating atom, which will be discussed in Chapter 15, are quite effective π acceptors, as shown by the relatively high A₁g stretching frequencies of their complexes.

Although IR frequencies provide a useful measure of the extent of π bonding in carbonyl complexes, a better quantitative picture can be obtained from C—O force constants. These values are commonly derived from IR data by means of the Cotton-Kraihanzel force-field technique. This procedure makes certain simplifying assumptions in order to provide a practical solution to a problem that would be extremely difficult to solve rigorously. Among the important assumptions are that the C—O vibrations are not coupled to any other vibrational modes of the molecule and that the observed frequencies can be used without correction for anharmonic effects. The results of force constant calculations of this type provide a means of setting up a π-acceptor series.34

33. There is not universal agreement on the ordering of this series because many of the ligands have competing tendencies which are variously insusceptible. Arsenic and stibine compounds fall into the series alongside the corresponding phosphorus compounds. Although there are some uncertainties in the case of these compounds, it is generally believed that as the order P > As > Sb is correct. In the above series R can represent phenyl or alkyl groups with the phenyl ligands usually exhibiting weaker acceptor ability.
Chemical forces and interactions

Hydrogen Bonding

Summary of chemical forces and interactions

<table>
<thead>
<tr>
<th>Type of interaction</th>
<th>Strength</th>
<th>Energy-distance function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Covalent bond</td>
<td>Very strong</td>
<td>Complex, but comparatively long range</td>
</tr>
<tr>
<td>Ionic bond</td>
<td>Very strong</td>
<td>$1/r^3$, short range</td>
</tr>
<tr>
<td>Dipole-dipole</td>
<td>Strong</td>
<td>$1/r^6$, extremely short range</td>
</tr>
<tr>
<td>Ion-induced dipole</td>
<td>Weak</td>
<td>Extremely short range</td>
</tr>
<tr>
<td>Dipole induced dipole</td>
<td>Very weak</td>
<td>1/r, comparatively long range</td>
</tr>
<tr>
<td>London dispersion forces</td>
<td>Very weak</td>
<td>1/r, extremely short range</td>
</tr>
</tbody>
</table>

* Since London forces increase with increasing size and there is no limit to the size of molecules, these forces can become rather large. In general, however, they are very weak.

Various forces acting on chemical species are summarized in Table 8.3. The forces are listed in order of decreasing strength from the ionic and covalent bonds to the very weak London forces. The application of a knowledge of these forces to the interpretation of chemical phenomena requires a certain amount of practice and chemical intuition. In general, the importance of a particular force in affecting chemical and physical properties is related to its position in Table 8.3. For example, the boiling points of the noble gases are determined by London forces because no other forces are in operation. In a crystal of an ionic compound, however, although the London forces are still present they are dwarfed in comparison to the very strong ionic interactions and may be neglected to a first approximation (as was done in Chapter 4).

Hydrogen Bonding

Although some would contend that hydrogen bonding is merely an extreme manifestation of dipole-dipole interactions, it appears to be sufficiently different to warrant a short, separate discussion. In addition, there is no universal agreement on the best definition of the nature of the forces in the hydrogen bond.

We shall adopt an operational definition of the hydrogen bond: A hydrogen bond exists when a hydrogen atom is bonded to two or more other atoms. This definition implies that the hydrogen bond cannot be an ordinary covalent bond since the hydrogen atom has only one orbital ($1s$) at sufficiently low energy to engage in covalent bonding.

Macroscopically the effects of hydrogen bonding are seen indirectly in the greatly increased melting and boiling points of such species as NH$_3$, H$_2$O, and HF. This phenomenon is well documented in introductory texts and need not be discussed further here. On the molecular level we can observe hydrogen bonding in the greatly reduced distances between atoms, distances that fall below that expected from van der Waals radii. Indeed this is a practical method of distinguishing between a true bonding situation and one in which a hydrogen atom is close to two atoms but bonded to only one. Table 8.4 lists some distances in hydrogen bonded A--H--B systems compared with the sum of the van der Waals radii for the species involved. In many hydrogen bonds, the atoms A and B are closer together than the sum of the van der Waals radii. Even more characteristic is that the hydrogen atom is considerably closer to atom B than predicted from the sum of the van der Waals radii, indicating penetration (or compression) of atom B's electron cloud by the hydrogen.

In the typical hydrogen bonding situation the hydrogen atom is attached to two very electronegative atoms. The system is usually nearly linear and the hydrogen atom is nearer one nucleus than the other. Thus, for most of the systems in Table 8.4, the hydrogen atom is assumed to be attached to atom A by a short, normal covalent bond and attached to atom B by a longer, weaker hydrogen bond of about 50 kJ mol$^{-1}$ or less. This situation usually obtains even if both A and B are the same element as in the hydrogen bonding between oxygen atoms in water. There are important exceptions, however. These include salts of the type M$^+$HA$_2^-$, where A$^-$ may be the fluoride ion (less frequently another halide) or the anions of certain monoprotic organic acids such as acetic or benzoic acid. Alternatively, HAAH may be a diprotic acid such as malic or phthalic acid.

<table>
<thead>
<tr>
<th>Van der Waals distance</th>
<th>and observed distances (pm) for some common hydrogen bonds$^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond type</td>
<td>A</td>
</tr>
<tr>
<td>F--H--F</td>
<td>270</td>
</tr>
<tr>
<td>O--H--O</td>
<td>280</td>
</tr>
<tr>
<td>O--H--F</td>
<td>280</td>
</tr>
<tr>
<td>O--H--N</td>
<td>290</td>
</tr>
<tr>
<td>O--H--Cl</td>
<td>320</td>
</tr>
<tr>
<td>N--H--O</td>
<td>290</td>
</tr>
<tr>
<td>N--H--F</td>
<td>290</td>
</tr>
<tr>
<td>N--H--Cl</td>
<td>330</td>
</tr>
<tr>
<td>N--H--N</td>
<td>300</td>
</tr>
<tr>
<td>N--H--S</td>
<td>340</td>
</tr>
<tr>
<td>C--H--O</td>
<td>360</td>
</tr>
</tbody>
</table>

The metal-carbon bond length in carbonyl complexes provides a better measure of double bond character because these lengths are more sensitive to changes in bond order. If the covalent radii of an sp carbon atom and of the metal atom to which it is bound are known, summation of the two should give the length expected for a metal-carbonyl single bond, that is, one with no σ bonding. This value could then be compared with the measured bond length to determine the extent of σ bonding present. A factor that can cause problems with this strategy is that the covalent radius of the metal atom may not be known with certainty. However, this difficulty can be circumvented by choosing a complex that contains both carbonyl and alkyl ligands. In such a complex the covalent radius of the metal atom will be the same for both ligands in the absence of σ bonding, and can be derived from the measured M—C (alkyl) bond length and the known covalent radius for an sp carbon. This value can in turn be used to calculate an expected metal-carbonyl single bond length. The methyl derivative of a rhodium carbonyl complex, Rh(CH$_3$)(CO)$_5$, may be used to illustrate the procedure:\[29\]

\[
\text{Re—C single bond length in ReCH$_3$} = 231 \text{ pm}
\]

- (Cova-lent radius for sp$^3$ C) = 77 pm

Covalent radius for Re = 154 pm

Covalent radius for Re = 154 pm

+ (Covalent radius for sp$^3$ C) = 70 pm

Re—C single bond length for ReCO = 224 pm

The experimentally determined Re—CO bond distance for this complex is 200.4 ± 0.4 pm, about 24 pm shorter than that predicted for a σ-only bond. When this type of analysis is applied to other complexes, similar decreases in metal-carbon lengths are observed, substantiating the view that the M—CO bond has considerable double bond character.

Further crystallographic evidence for metal-carbonyl π bonding is found in phosphine and phosphite derivatives of hexacarbonylchromium. Substitution of P(Ph)$_3$ for CO in Cr(CO)$_5$ creates a complex of C$_6$ symmetry in which one CO group lies trans to the phosphorus ligand (Fig. 11.29). The two trans ligands will compete for the same σ electron density in the phosphine complex than in the phosphite complex, which would lead to a shorter metal-carbon bond for the phosphine derivative, and that is observed as well.

The P(CH$_2$CH$_2$CN)$_3$ ligand appears to be inconsistent with the model; however, its Cr—P bond distance suggests that it is a poorer σ bonding ligand than P(Ph)$_3$, whereas the Cr—C bond lengths suggest that it is a better π acceptor. Some of the ambiguity may arise because of the different steric requirements of the phosphorus ligands. Steric interaction with equatorial carbonyl ligands could lead to a Cr—P bond lengthening which obscures the intrinsic electronic effect.\[30\] It should be apparent from this discussion that it is not a simple matter to sort out σ and π contributions.

### Table 11.12

<table>
<thead>
<tr>
<th>L</th>
<th>Cr—P</th>
<th>Cr—C</th>
<th>C—O</th>
<th>C—O</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>—</td>
<td>91.5(2) av</td>
<td>—</td>
<td>114.0(2) av</td>
</tr>
<tr>
<td>P(Ph)$_3$</td>
<td>230.5(1)</td>
<td>186.1(4)</td>
<td>189.5(4) av</td>
<td>113.6(6) av</td>
</tr>
<tr>
<td>P(CH$_2$CH$_2$CN)$_3$</td>
<td>230.4(1)</td>
<td>187.6(4)</td>
<td>189.5(4) av</td>
<td>113.6(6) av</td>
</tr>
<tr>
<td>PPh$_3$</td>
<td>242.0(1)</td>
<td>184.4(4)</td>
<td>188.5(4) av</td>
<td>115.4(5) av</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>L</th>
<th>Cr—P</th>
<th>Cr—C</th>
<th>C—O</th>
<th>C—O</th>
</tr>
</thead>
<tbody>
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<td>—</td>
<td>91.5(2) av</td>
<td>—</td>
<td>114.0(2) av</td>
</tr>
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<td>188.5(4) av</td>
<td>115.4(5) av</td>
</tr>
</tbody>
</table>


** Table 11.12 Bond lengths (pm) in chromium-carbonyl complexes, Cr(CO)$_5$.**

---

Fig. 11.29 Structure of the phosphine and phosphite derivatives of hexacarbonylchromium.
This type of hydrogen bonding is termed symmetric in contrast to the more common unsymmetric form. Symmetrical hydrogen bonds form in only the strongest bonded systems. These are frequently anionic like FHF and the carboxylates mentioned above. An example of a strong, symmetric hydrogen bond in a cation is the bis(N-nitrosopyrrolidine)hydrogen cation (Fig. 8.5).12

Although the subject of symmetric versus unsymmetric hydrogen bonding has received considerable attention, there is yet little understanding of the factors involved. Certain, for the long, weak hydrogen bond we can approximate the situation by assuming the hydrogen atom to be covalently bonded to one atom and to be attracting the other. Obviously, it will be closer to the covalently bound atom than to the dipole-attracted atom. It is not so easy to see when or why the bond will become symmetrical, although if a resonance or delocalized molecular orbital model is invoked, an analogy with the equivalent bond lengths in benzene can be appealed to. The situation is more complicated than that, however, for unsymmetrical FHF ions are known in some crystals.13 In the same way the hydrogen maleate and hydrogen phthalate anions, found to be symmetrical in the crystal, appear to be unsymmetrical in the less ordered aqueous solution.14 Whether symmetrical hydrogen bonds are forced by a symmetrical environment or whether unsymmetrical bonding is induced by crystals and solutions of lower symmetry, is perhaps, a moot point.

Since hydrogen bonding generally occurs only when the hydrogen atom is bound to a highly electronegative atom,15 the first suggestion concerning the nature of the hydrogen bond was that it consists of a dipole-ion or dipole-dipole interaction of the sort 

\[
\text{A}^{-} - \text{H}^{+} \cdots \text{B}^{-} \quad \text{or} \quad \text{A}^{+} - \text{H}^{-} \cdots \text{B}^{+} - \text{R}^{+},
\]

where R is simply the remainder of a molecule containing the electronegative atom B. Support for this viewpoint comes from the fact that the strongest hydrogen bonds are formed in systems in which the hydrogen is bonded to the most electronegative elements:

\[
\begin{align*}
\text{F}^{+} + \text{HF} \rightarrow & \ FHF^{+} \\
(\text{CH}_{3})_{2}\text{CO} + \text{HF} \rightarrow & \ (\text{CH}_{3})_{2}\text{CO} \cdots \text{HF} \\
\text{H}_{2}\text{O} + \text{HON} \rightarrow & \ H_{2}\text{O} \cdots \text{HON} \quad \text{(ice)} \\
\text{HCN} + \text{HCON} \rightarrow & \ HCN \cdots \text{HCON} \\
\end{align*}
\]

\[
\Delta H = -161 \pm 8 \text{kJ mol}^{-1} \quad (8.14)^{15}
\]

\[
\begin{align*}
\Delta H = & \ -46 \text{kJ mol}^{-1} \quad (8.15) \\
\Delta H = & \ -25 \text{kJ mol}^{-1} \quad (8.16) \\
\Delta H = & \ -12 \text{kJ mol}^{-1} \quad (8.17)
\end{align*}
\]

15 Even rather electronegative elements such as carbon can cause attached hydrogen atoms to form hydrogen bonds. In HCN, for example, the effective electronegativity of the carbon is still comparable high, the hydrogen atom is positively charged, and it would be expected to hydrogen bond to the negative nitrogen atom of an adjacent molecule. It has a boiling point of 26°C compared to 20°C for HF and 100°C for H2O. Even in the methyl group of CH3CN some hydrogen bonding can apparently take place since the boiling point of acetonitrile is higher (82°C) than expected on the basis of its molecular weight (London forces) alone: 

\[
\text{HCN} + \text{HCN} \rightarrow \text{HCN} \cdots \text{HCN}
\]


The simplistic electrostatic model qualitatively accounts for relative bond energies and the geometry (i.e., linear arrangement minimizes the attractive forces and minimizes the repulsions). Nevertheless, there are reasons to believe that more is involved in hydrogen bonding than simply an exaggerated dipole-dipole or ion-dipole interaction. First, the shortness of hydrogen bonds indicates considerable overlap of van der Waals radii, and this should lead to considerable repulsive forces unless otherwise compensated. Secondly, symmetrical hydrogen bonds of the type F—H—F would not be expected if the hydrogen atom were covalently bound to one fluorine atom but weakly attracted by an ion-dipole force to the other. Of course, one can invoke resonance in this situation to account for the observed properties:

\[
\text{F} - \text{H} - \text{F} \quad \text{F} - \text{H} - \text{F}
\]

\[
\text{F} - \cdots \text{F} - \text{H} - \cdots \text{F}
\]

This implies delocalization of the covalent bond over both sides of the hydrogen atom. One might then ask whether a simpler molecular orbital treatment of the delocalization would be more straightforward. The answer is yes. The mechanism will not be given here (see Chapter 17, the three-center-four-electron bond), but the results are that the covalent bond is "smeared" over all three atoms. In symmetric hydrogen bonds it is equal on both sides; in unsymmetric hydrogen bonds more electron density is concentrated in the shorter link. Several workers have calculated and analyzed hydrogen bond energies.17 The interpretations are not identical, but all indicate strong contributions from both electrostatic (ion-dipole, dipole-dipole) and covalent (delocalization, resonance) interactions.

Systematic analyses of crystallographic data for hydrogen bonds have revealed a range of geometries and have led to proposals for rules to rationalize or predict hydrogen bonding patterns.18 An energetic preference for linear or near-linear.
including π interactions, for an octahedral M(CO)₆ complex is shown in Fig. 11.28. The increase in Δσ caused by σ bonding is substantial enough in most cases that the absorption maximum for the $\tau_p$-to-$\tau_p^*$ electronic transition is blue-shifted out of the visible region into the ultraviolet portion of the electromagnetic spectrum, with the result that the complexes are colorless. This is the case for the metal carbonyls, for example.

Halide ions such as CF₃, Br⁻, and I⁻ present a different situation. Like the fluoride ion, they have filled π orbitals, but unlike fluoride, their empty σ orbitals may participate in π bonding. It is difficult to predict which set of $\tau_p$ LGOs for these ions (those constructed from filled π or from empty σ orbitals) will interact more strongly with the $\tau_p$ orbitals of the metal. Empirically, we observe that all of the halide ions lie at the weak-field end of the spectrochemical series, indicating that the π interaction is more important than that of the σ orbitals.

The potential for $\sigma^*$ orbitals to serve as π accepters has become apparent in recent times. Phosphines, instead of using empty pure σ orbitals as π acceptors, may accept π donation into low-lying $\sigma^*$ orbitals or into hybrids involving $\sigma^*$ and 3d

![Fig. 11.28 MO diagram for an octahedral M(CO)₆ complex: both σ and π interactions are included. Correlation lines are drawn only to those molecular orbitals to which the metal d electrons contribute.](image)

**Experimental Evidence for Pi Bonding**

Crystallography. The M—CO bonding model described above suggests that the greater the extent of π bonding, the more the C—O bond will be lengthened and the M—C bond shortened. The σ interaction, on the other hand, should have the opposite effect on the C—O bond length because the lone pair on carbon that is utilized in forming the π bond as in a slightly antibonding MO of the carbon monoxide ligand (the $\pi$ orbital) in Fig. 5.20). Donation of this pair of electrons to a Lewis acid would be expected to make the C—O bond stronger and shorter relative to that of carbon monoxide. It would seem from this analysis that one could merely compare the C—O bond distance in carbon monoxide (112.8 pm) with that in a carbonyl complex and, if the latter is found to be longer, this could be taken as evidence for π bonding. A problem arises with this approach because the C—O bond length (and that of multiple bonds in general) is relatively insensitive to bond order: The difference in length between the triple bond in CO (113 pm) and typical C=O double bonds in organic molecules (~123 pm) is small. Moreover, observed C=O bond lengths among metal carbonyls fall within a very short range—about 114 to 115 pm. Unless the measurement is made with exceptional accuracy, any bond length difference within this range cannot be regarded as statistically significant, let alone as a meaningful indication of bond order.

In addition, the coordination of dihydrogen (see Chapter 15) is thought to involve π electron donation to the metal from the H—H σ bond and back donation from the metal into the $\H_2\sigma^*$ orbitals.

Few topics in coordination chemistry have received more attention than π bonding. We have seen in the preceding section that it provides a reasonable rationale for much of the spectrochemical series. In Chapter 13 we shall find that π bonding is important in determining patterns of ligand substitution reactions. It is also central in understanding reactivity and stability in organometallic complexes (Chapter 15). In this section various experimental methods of evaluating π bonding in metal carbonyl complexes and their derivatives will be examined.

There is strong agreement among inorganic chemists, theoreticians and experimentalists alike, that the stability of metal carbonyl complexes depends on the ability of carbon monoxide to accept metal electron density into its $\sigma^*$ orbitals. Although carbon monoxide is a weak base toward hydrogen ion or BH₄⁻, it has a significant affinity for electron-rich metals (see Chapter 15). For example, it reacts with metallic nickel at modest temperatures to form gaseous Ni(CO)₄. This is especially impressive when one considers that the metal-metal bonds in nickel, which must be broken for the complex to form, are quite strong. Observations such as these cannot be easily explained by σ bonding alone. The currently accepted bonding model views carbon monoxide as a $\sigma$ donor (OC—$\rightarrow$ M) and a $\pi$ acceptor (OC—<$\rightarrow$ M), with the two interactions synergistically enhancing each other to yield a strong bond:

\[
M + \text{CO} \rightarrow M = \text{CO} \rightarrow M = \text{CO} \quad \text{(11.16)}
\]


A—H • • • B configurations, at least in the crystalline state, is confirmed by the experimental data. The stereochemical requirements of hydrogen bonds determine the structure of ice and lead to the well-known fact that solid water is less dense than liquid water at the melting point. This is because the structure of ice is rather open as a result of an extensive network of hydrogen bonds (Fig. 8.6). Hydrogen bond energetics and stereochemistry have wide-ranging implications in the areas of catalysis, molecular recognition, and design of new materials.

Finally, there are other systems such as W—H—W and B—H—B (Chapter 16) which formally meet the operational definition of hydrogen bonding given above. They differ, however, in having electronegative atoms bonded to the hydrogen atom. To distinguish them from the electronegative hydrogen bonded systems, they are often termed hydrogen-bridged systems.

Hydrates and Cloathrates

The hydration of ions upon solution in water has been mentioned previously and its importance to solution chemistry discussed. In the solid crystalline hydrates, hydrogen bonding becomes important in addition to the ion-dipole attractions. Often the water molecules serve to fill in the interstices and bind together a structure which would otherwise be unstable because of disproportionate sizes of the cation and anion. For example, both FeSiF₆·6H₂O and Na₄XeO₆·8H₂O are well-defined, crystalline solids. The anhydrous materials are unknown. The large, highly charged anions presumably repel each other too much to form a stable lattice unless there are water molecules present. In general, some water molecules will be found coordinated directly to the cation and some will not. All the water molecules will be hydrogen bonded, either to the anion or to another water molecule.

A specific example of these types of hydrates is CuSO₄·5H₂O. Although there are five molecules of water for every Cu²⁺ ion, only four are coordinated to the cation, its six-coordination being completed by coordination from SO₄ (Fig. 8.8a). The fifth water molecule is held in place by hydrogen bonds, O—H • • • O, between it and two coordinated water molecules and the coordinated sulfate anion (Fig. 8.7b). Dehydration to CuSO₄·3H₂O, CuSO₄·H₂O, and eventually anhydrous CuSO₄ results in the water molecules coordinated to the copper being gradually replaced by oxygen atoms from the surface. An interesting hydrate is that of the hydronium ion in the gas phase. It consists of a dodecahedral cage of water molecules enclosing the hydronium ion: H₃O⁺(H₂O)₂₀. Each water molecule is bonded to three others in the dodecahedron (Fig. 8.8a). Of the various possible hydrates of H₃O⁺ in the gas phase, H₃O⁺(H₂O)₂₀ is by far the most stable. The dodecahedral structure may carry over into the solid phase. Note that half of the oxygen atoms in Fig. 8.8a have their fourth coordination position occupied by a hydrogen atom that can bond to adjacent polyhedra (Fig. 8.8b), and the other half have a lone pair at the fourth position which can donate a pair of electrons to form an external hydrogen bond (Fig. 8.8c). Thus in the solid, these dodecahedra can pack together to form larger structures with relatively large voids in the centers of the dodecahedra. Guest molecules such as Ar, Kr, Xe, CH₄, etc., may occupy these spaces. These gas hydrates in which the guest molecules are not bound chemically but are retained by the structure of the host are called clathrates. Since the structure can exist with incomplete filling of holes, the formulas of these clathrates are variable.

![Fig. 8.6](image)

Fig. 8.6 The open structure of normal ice that results from the directionality of the hydrogen bonding. [From Dickerson, R. E.; Geis, I. Chemistry, Matter, and the Universe: W. A. Benjamin: Menlo Park, 1976.]

![Fig. 8.7](image)

Fig. 8.7 Structure of copper(II) sulfate pentahydrate. (a) Coordination sphere of Cu²⁺, four water molecules and two sulfate ions; (b) Position of fifth water molecule (oxygen shown by heavy circle). Normal covalent bonds depicted by solid lines; O—H • • • O hydrogen bonds depicted by dashed lines.

422
11 Coordination Chemistry: Bonding, Spectra, and Magnetism

enough in energy that they can receive electron density from the metal. These orbitals
3d complex and will not be discussed here.

hybrid sp
NH₃, the ligating atom can π-bond to the metal through an approximately "ligands can be treated as above, but
bonding between metal and 0
principle this
2
, and FeO
4
~ probably contain appreciable
states such as CrO
2
energy is that derived from the slightly different populations of the two sets of orbitals.
Finally, it should be mentioned that oxyanions of transition metals in high oxidation
orbitals are raised an equal amount. Thus the only net stabilizing
nearly filled
t
orbitals are lowered in energy somewhat, but the
t
2l!
t
bonding is slight: The filled
t
tt
ligands). In the same way, the weaker field of OH
the weak field extreme in the spectrochemical series (weaker than most cr-only
bonding. It is felt that this is the source of the position of fluoride (and other halides) at
the e* orbitals is unaffected by the
bonding had not taken place. Since the level of
higher energy than they would be if π bonding had not taken place. Since the level of the
t
orbitals of the cobalt are therefore in
2g
system in [CoF
p
the metal orbitals (see Chapter 5). The molecular orbital energy diagram for the π
system in [CoF
p
will resemble the fluorine orbitals
MOs with a metal π
orbitals. There are two
additional sets
perpendicular to the
one shown.

the fluorine 2p orbitals lie at a lower energy than the corresponding metal 3d orbitals.
Under these circumstances, the bonding π MOs will resemble the fluorine orbitals more than the metal orbitals, and conversely the σ* MOs will more closely resemble the metal orbitals (see Chapter 5). The molecular orbital energy diagram for the π system in [CoF
p
is shown in Fig. 11.26. Since the 2p orbitals on the fluoride ligands are filled, these electrons will fill the resultant molecular π
π orbitals. The electrons from the 3d (t
2g
) orbitals of the cobalt are therefore in π antibonding orbitals (σ
*) at a higher energy than they would be if π bonding had not taken place. Since the level of the σ
σ* orbitals is unaffected by the π interaction, Δσ is reduced as a result of the π bonding. It is felt that this is the source of the position of fluoride (and other halides) at
the weak field extreme in the spectrochemical series (weaker than most cr-only
ligands). In the same way, the weaker field of OH
the weak field extreme in the spectrochemical series (weaker than most cr-only
bonding. This will not be particularly desirable in a complex
containing a metal in a high formal oxidation state since the metal will already carry a
partial positive charge. In low oxidation states, on the other hand, electron density that tends to be built up via the σ system can be dispersed through the π system; that is, a synergistic effect can cause the two systems to help each other. The more electron density that the σ system can transfer from the metal to the ligand, the more the metal is able to accept via the σ system. In turn, the more electron density the σ system removes from the ligand, the more readily the ligand can accept electron density through the π system. Up to a certain point, then, each system can augment the bonding possibilities of the other.

Pi bonding between metal and ligands provides a simple raison d'être for strong field ligands, an issue that crystal field theory could not resolve. If we examine the strong field end of the spectrochemical series (page 405), we find ligands such as nitrite, cyanide ion, carbon monoxide, phosphites, and phosphines. The latter two owe their positions in the series to their ability to serve as π acceptors, as described above, which increases the value of Δσ, relative to what it would be in a σ-only system (Fig. 11.27). The other three ligands π bond in a very similar fashion except that the acceptor orbital is a π* orbital as shown in Fig. 11.25c. The net result is the same as for ligands in which either d or σ* orbitals or both serve as π acceptors: The bonding of this type thus can stabilize a complex by increasing the bond energy. In
addition, the resulting σ
π orbital is delocalized over both metal and ligand as opposed to being a nonbonding σ
orbital localized on the metal, which would have been the case in the absence of π bonding. Electron density is thus removed from the metal as a result of π bonding. This will not be particularly desirable in a complex
containing a metal in a high formal oxidation state since the metal will already carry a
partial positive charge. In low oxidation states, on the other hand, electron density that tends to be built up via the σ system can be dispersed through the π system; that is, a synergistic effect can cause the two systems to help each other. The more electron density that the σ system can transfer from the metal to the ligand, the more the metal is able to accept via the σ system. In turn, the more electron density the σ system removes from the ligand, the more readily the ligand can accept electron density through the π system. Up to a certain point, then, each system can augment the bonding possibilities of the other.

Ligands such as R,P may also participate in π bonding. In these molecules, as in
NH₃, the ligating atom can π-bond to the metal through an approximately σ
hybrid orbital. Unlike nitrogen, however, phosphorus has empty 3d and σ
orbitals lying low enough in energy that they can receive electron density from the metal. These orbitals

Fig. 11.25 MO overlap of t2g
LGOs with a metal t2g (d
) orbital. There are two
additional sets
perpendicular to the
one shown.

Fig. 11.26 MO diagram for the σ system of [CoF
p
Left: MOs for the σ system of the complex; right:
MOs of t2g
symmetry; center: MOs after σ interaction. Note that Δσ is diminished by the σ interaction.

Fig. 11.27 MO diagram for the π system of an octahedral complex with acceptor ligands such as CO, PR₃, or SK₂. Note that the π interaction in this case increases Δσ.

In recent years many complexes of early transition metals in relatively high oxidation states have been prepared which contain neutral phosphorus donor ligands. Although the metal atom may prefer a harder Lewis base, in the absence of one, bonding to a phosphine may occur. 

Hydrate clathrates of organic compounds are thought to be responsible for the behavior of "ice" in the heads of comets and in wet methane under pressure.22 Unless methane is carefully dried, high-pressure lines may become clogged with the ice-like gas hydrate. There may be large deposits of methane hydrates, "the ice that burns," beneath the ocean floor.

Not all clathrates are hydrates. Other well-known examples have host lattices formed from hydrogen bonded aggregates of hydroquinone, phenol, and similar organic compounds. Non-hydrogen bonded host structures are also known. One example is cyclotriphosphazene, \( \text{C}_3\text{H}_2\text{PN}_3 \), that traps molecules such as benzene in tunnels in the crystal.23 In addition, coordination polymers are formed by ambidentate ligands, such as \( \text{CN}^- \) and \( \text{SCN}^- \), which coordinate to metal ions at both ends (Chapter 12). Perhaps the best known of this type of compound is the series of \( \text{Ni(CN)}_5\text{NH}_4 \) M compounds, where M may be benzene, thiophene, furan, pyrrole, naphthalene, or phenol.

Current interest in clathrate structures focuses on molecular recognition, a broad topic that includes resolution of enantiomers (Chapter 12), macrocyclic chelates (Chapter 12), and key-and-lock enzyme activity (Chapter 19). In terms of clathrates, the challenge is to structure the vacancy in such a way that particular molecules will be incorporated as guests.24

---

of square planar d^5 complexes: All of the bonding molecular orbitals are filled and all antibonding orbitals remain unoccupied. Adding additional electrons would destabilize a complex because the electrons would occupy antibonding levels. Fewer than sixteen electrons would also lead to lower stability, all other things being equal, because the bonding interaction would be diminished.

It should be apparent from the molecular orbital diagrams in Figs. 11.20, 11.21, and 11.22 that there are strong resemblances between the molecular orbital and crystal field descriptions for transition metal complexes. The energy levels that appear in the central portion of each MO diagram match the splitting pattern derived for a crystal field environment of the same symmetry. In the molecular orbital description some of these levels are antibonding, a concept that of course has no place in the crystal field model. From our qualitative development here, it may appear that the two models are quite similar. However, it is important to recognize that the common ground between them is limited to the symmetry aspects of the bonding description. The two theories differ fundamentally in how they describe the metal-ligand bond, with the MO view being more realistic and leading to far better quantitative predictions of properties.

In addition to forming σ bonds, many ligands are capable of π bonding interaction with a metal. There are no disputes over which ligand orbitals have the correct symmetry to participate in π bonding, but as we shall see in later sections, the extent to which this actually occurs for some ligands is vigorously debated. Even when ligand and metal orbitals have the proper symmetry for π bond formation, an energy or size mismatch may lead to insignificant interaction.

Recall (Chapter 5) that a σ bond has a nodal surface that includes the bond axis and that a π bond orbital will have lobes of opposite sign on each side of this nodal surface. From the standpoint of orbital symmetry, an octahedral complex could have up to twelve such bonds—two between the metal and each of the six ligands, although this number is never realized in an actual complex. Metal and ligand orbitals participating in π bonds will lie perpendicular to the internuclear axes. Consider four potential metal-ligand π interactions: (1) d_y-p_y, (2) d_z^*-p_z, (3) d_x^*-p_x, and (4) d_x^*-p_x (Fig. 11.23). Examples of ligands capable of each type are shown in Table 11.11. In principle, either the ligand or the metal can function as the electron donor. Filled metal d orbitals can donate electron density to an empty orbital on the ligand, or an empty d orbital on the metal can receive electron density from a filled orbital of the ligand.

The ligand group orbitals capable of π interactions in an octahedral complex fall into four symmetry categories (Fig. 11.24): t_2g, d_π, d_π^*, and t_1g. Of these, a transition metal will possess orbitals of only two of the types: t_2g(d_π^*) and d_π. Concordantly, the metal could use all of these orbitals for π bonds. However, the members of the t_1g set are directed towards the ligands and therefore participate in strong σ bonds. Formation of π bonds using these orbitals would tend to weaken the σ system and hence will not be favored. The t_2g orbitals, on the other hand, are directed between the ligands which, as we saw earlier, restricts them to a nonbonding σ system with Cr-only orbitals (Fig. 11.17b). They can, however, readily participate in bonding with LGOs of matching symmetry (Fig. 11.22). The t_2g and t_1g ligand group orbitals must remain nonbonding for the simple reason that there are no orbitals of matching symmetry on the metal. π Bonding in an octahedral complex is thus limited to the orbitals of t_2g symmetry.

One of the simplest cases of π bonding in octahedral complexes is found in [CrF_6]^{3-}. Its σ system will be similar to that in Fig. 11.20. The t_2g orbitals of the metal will interact with t_2g LGOs constructed from the fluorine 2p orbitals to form σ-bonding and antibonding molecular orbitals. Since fluorine is more electronegative than cobalt,迼

### Table 11.11

<table>
<thead>
<tr>
<th>Type</th>
<th>Description</th>
<th>Ligand examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>d_y^*</td>
<td>Donation of electrons from filled d orbitals of metal to empty π orbitals of ligand</td>
<td>R^3, R^2F, R^2O, F, I^+</td>
</tr>
<tr>
<td>d_z^*</td>
<td>Donation of electrons from filled π orbitals of metal to empty d orbitals of ligand</td>
<td>R^3, R^2Ar, R^2S</td>
</tr>
<tr>
<td>d_x^*</td>
<td>Donation of electrons from filled σ orbitals of metal to empty π antibonding orbitals of ligand</td>
<td>CO, RNC, pyridine, CN^-</td>
</tr>
<tr>
<td>d_y^+</td>
<td>Donation of electrons from filled π orbitals of metal to empty π antibonding orbitals of ligand</td>
<td>N_2, NO, ethylene</td>
</tr>
</tbody>
</table>

---

In addition to forming σ bonds, many ligands are capable of π bonding interaction with a metal. There are no disputes over which ligand orbitals have the correct symmetry to participate in π bonding, but as we shall see in later sections, the extent to which this actually occurs for some ligands is vigorously debated. Even when ligand and metal orbitals have the proper symmetry for π bond formation, an energy or size mismatch may lead to insignificant interaction.

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Ionic compounds are characterized by very strong electrostatic forces holding the ions together. Vaporization results in ion pairs and other small clusters in the vapor phase. Although the stabilizing energies of these species are large, they are considerably less than those of the crystals. Assuming a hard-sphere model as a first approximation, the difference in electrostatic energies of an ion pair in the gas and the solid lattice would lie in their Madelung constants. For NaF, A = 1.00 torr for an ion pair, 1.75 for the lattice. We should thus expect that if crystalline sodium fluoride vaporized to form ion pairs, the bond energy would be slightly more than half (1.00/1.75 = 0.57) of the lattice energy. There are several factors that help stabilize the species in the gas phase and make their formation somewhat less costly. Polarization can occur more readily in a single ion pair than in the lattice. This results in a somewhat greater covalent contribution and shorter bond distances in the gas phase. Secondly, in addition to ion pairs there are small clusters of ions with a greater number of interactions and more attractive energy. It is not surprising to learn, therefore, that vaporization costs only about one-fourth of the lattice energy, not almost one-half (Table 8.5). Nevertheless, since lattice energies are large, the energy necessary to vaporize an ionic compound is large and responsible for the high boiling points of ionic compounds.

### Table 8.5

<table>
<thead>
<tr>
<th>Compound</th>
<th>MX(g)</th>
<th>M⁺(g) + X⁻(g)</th>
<th>MX(s)</th>
<th>M⁺(s) + X⁻(s)</th>
<th>EN</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>766</td>
<td>1033</td>
<td>268</td>
<td>0.26</td>
<td></td>
<td></td>
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<tr>
<td>LiCl</td>
<td>636</td>
<td>845</td>
<td>299</td>
<td>0.22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiBr</td>
<td>615</td>
<td>799</td>
<td>184</td>
<td>0.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiF</td>
<td>573</td>
<td>741</td>
<td>167</td>
<td>0.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaF</td>
<td>644</td>
<td>916</td>
<td>272</td>
<td>0.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>556</td>
<td>778</td>
<td>222</td>
<td>0.38</td>
<td></td>
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</tr>
<tr>
<td>NaBr</td>
<td>536</td>
<td>741</td>
<td>205</td>
<td>0.28</td>
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</tr>
<tr>
<td>KF</td>
<td>542</td>
<td>812</td>
<td>230</td>
<td>0.29</td>
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<td></td>
</tr>
<tr>
<td>KCl</td>
<td>494</td>
<td>707</td>
<td>213</td>
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<td></td>
</tr>
<tr>
<td>KBr</td>
<td>477</td>
<td>678</td>
<td>201</td>
<td>0.30</td>
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<tr>
<td>RbF</td>
<td>418</td>
<td>640</td>
<td>192</td>
<td>0.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RbCl</td>
<td>565</td>
<td>778</td>
<td>213</td>
<td>0.27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RbBr</td>
<td>498</td>
<td>685</td>
<td>188</td>
<td>0.27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CsF</td>
<td>439</td>
<td>623</td>
<td>184</td>
<td>0.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CsCl</td>
<td>464</td>
<td>633</td>
<td>197</td>
<td>0.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CsBr</td>
<td>448</td>
<td>632</td>
<td>184</td>
<td>0.29</td>
<td></td>
<td></td>
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<tr>
<td>AgF</td>
<td>414</td>
<td>602</td>
<td>189</td>
<td>0.31</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Gas-phase data are from the bond energies in Appendix E corrected to the ionic case by addition of the ionization energy and electron affinity. Lattice energies are from the best values in Table 4.3. Energies of sublimation (assuming ion pairs) are the difference between the energy of the lattice and that of the ion pairs. The ratio is that of EN/subl which yields the fraction of the energy "lost" on sublimation.

Increasing the ionic charges will certainly increase the lattice energy of a crystal. For compounds which are predominantly ionic, increased ionic charges will result in increased melting and boiling points. Examples are NaF, mp = 997 °C, and MgO, mp = 2800 °C.

The situation is not always so simple as in the comparison of sodium fluoride and magnesium oxide. According to Fajans' rules, increasing charge results in increasing covalency, especially for small cations and large anions. Covalency per se does not necessarily favor either high or low melting and boiling points. For species which are strongly covalently bonded in the solid, but have weaker or fewer covalent bonds in the gas phase, melting and boiling points can be extremely high. Examples are carbon in the diamond and graphite forms (sublimes about 3000 °C) and silicon dioxide (melts at 1710 °C, boils above 2200 °C). For example, in the latter compound the transition consists of changing four strong tetrahedral ν bonds in the solid polymer to two ν and two relatively weak σ bonds in the isolated gas molecules.

On the other hand, if the covalent bonds are almost as stable and as numerous in the gas-phase molecules as in the solid, vaporization takes place readily. Examples are the depolymerization reactions that take place at a few hundred degrees. For example, red phosphorus sublimes and recondenses as white phosphorus. ¹²

### Table 8.6

<table>
<thead>
<tr>
<th>Compound</th>
<th>KF</th>
<th>AgF</th>
<th>NaF</th>
</tr>
</thead>
<tbody>
<tr>
<td>mp</td>
<td>858 °C</td>
<td>435 °C</td>
<td>993 °C</td>
</tr>
<tr>
<td>mp</td>
<td>770 °C</td>
<td>455 °C</td>
<td>801 °C</td>
</tr>
<tr>
<td>mp</td>
<td>714 °C</td>
<td>452 °C</td>
<td>747 °C</td>
</tr>
</tbody>
</table>

¹²The exact structure of red phosphorus is unknown, but this structure has been suggested. The argument here is not dependent on knowledge of the exact structure.
Tetrahedral and Square Planar Complexes

The procedures used in the preceding section may also be applied to the generation of MO diagrams for complexes of other geometries. The metal atom or ion in each case will have the same nine valence orbitals available for bonding, but their symmetry properties will vary from one geometry to another. For a tetrahedral ML₄ complex (T₄ symmetry), the metal s and p orbitals have aₒ and aₚ symmetries, respectively (see the T₄ character table in Appendix D). The five d orbitals are split into two sets: e (dₓ, y) and t₂ (dₓz, dᵧz, dₓ₋ᵧ). The four LGOs constructed from ligand lone-pair orbitals will consist of a set of a₄ orbitals and one orbital of a₁ symmetry. The a₂ LGOs interact with both sets of metal d orbitals (p and d) to give three sets of σ MOs—one bonding, one slightly antibonding, and one clearly antibonding.

A MO diagram for a tetrahedral complex is shown in Fig. 11.21. Note that in contrast to the octahedral case, the metal e orbitals are now nonbonding. The separation between the e and the next highest t₂ orbitals is labeled Δₑ as in crystal field theory. For a complex such as [CoCl₄]²⁻, the ligands provide two electrons each for a total of eight, and the d⁷ Co⁺ ion furnishes seven, giving an overall total of fifteen. Twelve electrons will fill the six lowest energy molecular orbitals (through the e set) with the final three electrons remaining unpaired and occupying the slightly antibonding t₂ molecular orbitals.

A number of four-coordinate complexes adopt a square planar geometry, which for four identical ligands, leads to D₄h symmetry. In this environment, the metal d level is split into t₂g (dₓ²₋ᵧ², dₓz, dᵧz) and e_g (dₓ, y) orbitals. The p level also loses its degeneracy, appearing as a₁ (pₓ, pᵧ) and e (pₓ, pᵧ, pᵢ). The four ligands, which will be oriented along the x and y axes, will give rise to ligand group orbitals of øₓ, øᵧ, øᵢ, and ø symmetry. They will interact with metal orbitals of the same symmetry leading to the σ MO diagram shown in Fig. 11.22. Note that the øₓ LGO overlaps with both t₂g metal orbitals, producing three MOs of this symmetry. Several metal orbitals, the øₓ and øᵧ and the b₂g remain nonbonding because they engage in no overlap with the ligand orbitals.

The square planar geometry is particularly common for complexes of d⁸ metal ions. For such a complex, there will be sixteen electrons: eight from the metal and eight more from the four ligands, to be assigned to the molecular orbitals in Fig. 11.22. These electrons will occupy the twelve lowest energy MOs and the complex will be diamagnetic. The MO description provides a clear rationale for the observed stabilities.
Solubility

Solubility and the behavior of solutes is a complicated subject, and only a brief outline will be given here. A further discussion of solutions will be found in Chapter 10.

Solutions of nonpolar solutes in nonpolar solvents represent the simplest type. The forces involved in solute-solvent and solvent-solvent interactions are all London dispersion forces and relatively weak. The presence of these forces resulting in a condensed phase is the only difference from the mixing of ideal gases. As in the latter case, the only driving force is the entropy (randomness) of mixing. In an ideal solution the change in entropy for the formation of a solution of this type is

$$\Delta S = R \left( \frac{\sum n_i}{N} \right)$$

where \( n_i \) and \( N \) are the mole fractions and total number of particles, respectively. The change in entropy is

$$\Delta S = \int \left( \frac{dH}{T} \right)_S = \int \left( \frac{\Delta H}{T} \right)_S$$

In extreme cases dissolution involves the attractive forces to become so strong as to define discrete molecules even in the solid (e.g., \( \text{AIBr}_3 \), mp = 97°C, bp = 263°C). At this point we have come full circle and are back at the SF and Cl situations.

Solubility

Table 8.7

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting point (°C)</th>
<th>Boiling point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KBr</td>
<td>734</td>
<td>1435</td>
</tr>
<tr>
<td>CsF</td>
<td>682</td>
<td>1335</td>
</tr>
<tr>
<td>BaF_2</td>
<td>1221</td>
<td>2177</td>
</tr>
</tbody>
</table>

predominantly ionic species CaF and BaF_2 and the more covalent species KBr and CsF (Table 8.7). The change from 1:1 to 1:2 composition in the highly ionic CaF produces the expected increase in lattice energy and corresponding increase in the transition temperature. For the more covalent bromides, however, the molecular species \( \text{KBr}_2 \) (in the gas phase and possibly to some extent in the liquid) has sufficient stability to allow the solute ion to be dissolved to form a solution of this type. Then the enthalpy of solution is negative and the entropy of solution is positive, the free energy of solution becomes more important. For many salts the enthalpy contribution to the free energy change for dissolution is comparable in magnitude to the entropy change and both terms must be considered.

Chapter 10.

Effects of Chemical Forces

At the other extreme from the ideal solutions of nonpolar substances are solutions of ionic compounds in a very polar solvent such as water. The entropy change for such a process may be positive or negative unlike in the ideal solute-solvent interaction described above. In addition to the increased disorder expected as ions go from solid to solution, there will also be an ordering of solvent molecules as the ions become solvated. The positive term will be dominant for large ions of low charge, but for ions that interact strongly with water (small size and high charge), the negative term becomes more important. For many salts the entropy contribution to the free energy change for dissolution is comparable in magnitude to the entropy change and both terms must be considered.

In order for an ionic compound to dissolve, the Madelung energy or electrostatic attraction between the ions in the lattice must be overcome. In a solution in which the ions are separated by molecules of a solvent with a high dielectric constant \( (\varepsilon_{\text{H}_{2}O} = 81.7) \) the attractive force will be considerably less. The process of solution of an ionic compound in water may be considered by a Born-Haber cycle of type.

The overall enthalpy of the process is the sum of two terms, the enthalpy of dissociating the ions from the lattice (the lattice energy), and the enthalpy of introducing the dissociated ions into the solvent (the solution energy):

$$\Delta H = \Delta H_{\text{solid}} + \Delta H_{\text{solution}}$$

(8.23)

Two factors will contribute to the magnitude of the enthalpy of solution. One is the inherent ability of the solvent to coordinate strongly to the ions involved. Polar solvents are able to coordinate well through the attraction of the solvent dipole to the ionic lattice. The other factor is the type of ion involved, particularly its size. The strength and number of interactions between solvent molecules and an ion will depend upon how large the latter is. The lattice energy of the solute also depends upon ion size. The forces in the lattice are inherently stronger (ion-ion) than those holding the solute molecules to the ion (ion-dipole), but there are several of the latter interactions for each ion. As a result, the enthalpy of solvation is roughly of the same order of magnitude as the lattice enthalpy, and so the total enthalpy of solution can be either positive or negative depending upon the particular compound. When the enthalpy of solution is negative and the entropy of solution is positive, the free energy of solution is especially favorable since then the enthalpy and entropy of solution reinforce each other.

In many cases the entropy of solution for ionic compounds in water is positive. In these cases we find the solution cooling as the solute dissolves. The mixing tendency of entropy is forcing the solution to do work to pull the ions apart, and since in an adiabatic process such work can be done only at the expense of internal energy, the solution cools. If the entropy of solution is sufficiently positive, favorable entropy may not be able to overcome it and the compound will be insoluble. Thus some ionic compounds, such as \( \text{KClO}_4 \), are essentially insoluble in water at room temperature.

The fact that the solubility of a salt depends critically upon the entropy of solution raises an interesting question concerning the magnitude of this quantity.


Fig. 11.18 Identification of the symmetries of ligand group orbitals and metal orbitals involved in the σ bonds (represented as vectors) of an octahedral ML₆ complex. The characters of the reducible representation, \( \Gamma'_a \), are derived by counting the number of vectors that remain unmoved under each symmetry operation of the O₆ point group. The irreducible components of \( \Gamma'_a \) are obtained by application of Eq. 3.1.

\[
\begin{align*}
\Gamma'_a & = 6 \ 6C_3 \ 6C_2 \ 6C_1 \ \frac{3C_4 + C_2}{2} \\
\Gamma'_a & = a_1 + e' + t_2
\end{align*}
\]

Fig. 11.19 Ligand group orbitals (LGOs) and symmetry-matched metal atomic orbitals appropriate for σ bonding in an octahedral ML₆ complex.

same, which is taken to be positive. The six ligands can interact equally with this orbital, and each contributing orbital must also have a positive sign. Thus the \( n_a \) LGO can be constructed from an additive combination of the six ligand orbitals:

\[
\Sigma_\nu \sigma = \sum \left( \sigma_x + \sigma_y + \sigma_z + \sigma_{x'y'} + \sigma_{y'z'} + \sigma_{x'z'} \right)
\]

where \( \Sigma \) and \( \sigma \) represent the wave functions for the ligand group orbital and the contributing ligand orbitals, respectively, and \( 1/\sqrt{6} \) is a normalization constant. The LGO that can interact with the \( d_{x'y'} \) orbital will have components only along the \( x \) and \( y \) axes:

\[
\Sigma_\nu \sigma_{x'y'} = (\sigma_x + \sigma_y - \sigma_z - \sigma_{x'y'})
\]  \hspace{1cm} (11.14)

The LGO that matches the \( d_z^2 \) metal orbital is

\[
\Sigma_\nu \sigma_{d_z^2} = \frac{1}{\sqrt{3}} (2\sigma_x + 2\sigma_y - \sigma_z - \sigma_{x'y'})
\]  \hspace{1cm} (11.15)

The three LGOs of \( t_{2g} \) symmetry that will overlap with the metal \( p \) orbitals are constructed in a similar manner, as shown in Fig. 11.19. Since the metal \( t_{2g} \) orbitals cannot participate in \( \sigma \) overlap, they are considered nonbonding molecular orbitals in complexes where there is no possibility for \( \sigma \) bonding. In cases where there are ligand orbitals of appropriate symmetry available, the \( t_{2g} \) orbitals will be involved in \( \pi \) bonds.

A molecular orbital energy diagram for the \( \sigma \) bonds in an octahedral complex such as [Co(NH₃)₆]³⁺ is shown in Fig. 11.20. There are several approximations involved and the diagram shown is only qualitatively accurate; even the ordering of the energy levels is somewhat uncertain. However, this does not detract from the usefulness of the diagram. It is certain that the overlap of the metal \( 4s \) and \( 4p \) orbitals with ligand group orbitals is considerably better than that of the \( 3d \) orbitals. Consequently, the

---

25 In general, \( d \) orbitals tend to be large and diffuse and, as a result, overlap of \( d \) orbitals with others may be quantitatively poor even when qualitatively favorable. This problem is discussed in Chapter 18.
Obviously, a large solvation enthalpy contributes toward a favorable enthalpy of solution. However, we find that the solvation enthalpy alone provides us with little predictive usefulness. Water soluble salts are known with both large (CaF$_2$, -2180 kJ mol$^{-1}$) and small (K$_2$SO$_4$, -611 kJ mol$^{-1}$) hydration energies; insoluble salts are also known with large (CaF$_2$, -782 kJ mol$^{-1}$) or small (LiF, -1004 kJ mol$^{-1}$) hydration energies. It is apparent that the hydration energies alone do not determine the solubility. Countering the hydration energies in these cases is the lattice energy. Both lattice energy and hydration energy (Fig. 4.20) are favored by large charge (Z) and small size (r). The difference lies in the nature of the dependence upon distance. The Born-Landé equation for the lattice energy (Eq. 4.13) may be written as a function of distance:

$$U = f_1 \left( \frac{1}{r} + \frac{1}{r_c} \right)$$  \hspace{1cm} (8.24)

The simplest equation for the enthalpies of hydration of the cation and anion (Eq. 4.27) may be rewritten as:

$$\Delta H_{\text{hyd}} = f_2 \left( \frac{1}{r} \right) + f_3 \left( \frac{1}{r_+} \right)$$  \hspace{1cm} (8.25)

Now the lattice energy is inversely proportional to the sum of the radii, whereas the hydration enthalpy is the sum of two quantities inversely proportional to the individual radii. Clearly the two functions will respond differently to variation in r and r$_c$. Without delving into the details of the calculations, we may note that Eq. 8.24 is favored relative to Eq. 8.25 when r$_c = r$, and the reverse is true for r$_c < r$ or r$_c > r$. To express it in terms of a physical picture, the lattice energy is favored when the ions are similar in size—the presence of either a much larger cation or a much larger anion can effectively reduce it. In contrast, the hydration enthalpy is the sum of the two individual ion enthalpies, and if just one of these is very large (from a single, small ion), the total may still be sizable even if the counterion is unfavorable (because it is large). The effects of this principle may be seen from the solubility of the alkali halides in water. Lithium fluoride is simultaneously the least soluble lithium halide and the least soluble alkali fluoride. Cesium iodide is the least soluble cesium halide and the least soluble alkali iodide. The most soluble salts in the series are those with the most disparate sizes, cesium fluoride and lithium iodide.\(^{29}\)

The enthalpy of solution has been discussed somewhat more quantitatively by Morris.\(^{29}\) He has pointed out the relation between the enthalpy of solution and the difference between the hydration enthalpies of the cation and that of the anion. This difference will be largest when the cation and anion differ most in size (Fig. 8.9). In these cases the enthalpy of solution tends to be large and negative and favors solvation. When the hydration enthalpies (and the sizes) are more nearly alike, the crystal is favored. When entropy effects are added, a very nice correlation with the solubility and the free energy solution is found (Fig. 8.10).\(^{30}\)

There is a very practical consequence of the relation of solubility to size. It is often possible to make a large, complex ion from a metal and several ligands that is stable in solution but difficult to isolate without decomposition. Isolation of such large complex ions is facilitated by attempting to precipitate them as salts of equally large counterners. This favors the stability of the crystalline state relative to solution and makes it easier to obtain crystals of the desired complex. For example, the [Ni(NCN)$_3$]$^{2-}$ ion was known to exist in solution but was isolated as the [Ni(NCN)$_3$][KCN] and [Ni(NCN)$_3$][Ni(NCN)$_2$]$^{2-}$ complexes. Even the [Cr(NH$_3$)$_5$]$^{2+}$ ion could be isolated as [Cr(NH$_3$)$_5$NO]Cl$_3$. However, addition of large complex ions of chromium such as hexaamminechromium(III), [Cr(NH$_3$)$_5$]$^{2+}$ and tris(ethylenediamine)chromium(III), [Cr(NH$_3$)$_3$($C_2$H$_5$NH)$_2$]$^{2+}$, allows the isolation of [Cr(NH$_3$)$_5$][Ni(NCN)$_3$]·2H$_2$O and


Additional evidence for covalency in metal-ligand bonds is provided by electron paramagnetic resonance (EPR). As a result of their spins, unpaired electrons behave like magnets and align themselves either parallel or antiparallel to an applied magnetic field. These two alignments will have slightly different energies, and transitions from one level to the other can be induced and detected by applying resonant energy in the form of electromagnetic radiation. An unpaired electron that is not subject to interactions with other unpaired electrons or with magnetic nuclei will show a single absorption for this transition. The EPR spectra of many complexes, however, show hyperfine splitting patterns that arise from the interaction of the unpaired metal electron with magnetic nuclei on the ligands (Fig. 11.16). This clearly indicates that the electron is at least partially delocalized over the ligands.

Octahedral Complexes

The construction of molecular orbitals for an octahedral complex involves the same general approach that was used in Chapter 5 for simpler molecules and ions. In the case of the complex, there will merely be more overlapping orbitals and electrons to consider. For a complex ion such as [Cu(NH₃)₆]²⁺, the valence orbitals available on the central metal will be the 3d, 4s, and 4p. The ligand orbitals involved in σ bonds to the metal will be the six approximately σ⁰ hybrid lone pair orbitals on the ammonia molecules. (For π-bonding ligands, additional orbitals would have to be considered.) Although it may at first appear that finding the proper linear combinations of nine metal orbitals and six ligand orbitals would be a formidable task, we can draw on our previous experience, which has shown that using the symmetry properties of the orbitals greatly expedites the procedure.

Since the molecular orbitals we are seeking will be linear combinations of metal and ligand atomic orbitals having the same symmetry, it is appropriate to begin by constructing linear combinations of the ligand orbitals, or ligand group orbitals (LGOs), that will overlap with metal orbitals along the octahedral bonding axes. (Recall that this approach was used previously for BF₃ and N₂O_5 in Chapter 5.) These LGOs must match the symmetries of the metal orbitals available for bonding. As has already been stated, the metal valence orbitals of interest are the 3s, 3p, and 3d. Their symmetry properties in an octahedral complex can be determined by reference to an O₆ point group (Appendix D), which reveals that the 3d and one set of p orbitals transform as t₂g, whereas the other set of p orbitals loses their degeneracy and transform as e_g. The sign of the wave function for the metal orbital is everywhere the same as that of the ligand orbital.

Overlap of ligand orbitals in the σ plane with metal (a) and π orbitals (b). (From Owen, J. Faraday Disc. Chem. Soc. 1955, 19, 127-134. Reproduced with permission.)

Fig. 11.17 Overlap of ligand orbitals in the σ plane with metal d(π) (a) and π (b) orbitals. Note that an appropriate choice of sign for the ligand orbitals provides positive overlap with the d(π) orbital, but there is no single sign choice for the ligand orbital wave function that produces positive overlap with the π orbital.

Within a group-theoretical analysis, this is normally accomplished with projection operators. For a discussion of this method, see the group theory texts listed in Footnote 3 of Chapter 3.
The solvation energies are limited to those from ion-induced dipole forces, which are considerably weaker than ion-dipole forces and not large enough to overcome the very strong ion-ion forces of the lattice.

The reason for the insolvability of nonpolar solutes in some polar solvents such as water is less apparent. The forces holding the solute molecules to each other (i.e., the forces tending to keep the crystal from dissolving) are very weak, London forces. The interactions between water and the solute (dipole-induced dipole) are also weak but expected to be somewhat stronger than London forces. It might be supposed that this small solvation energy plus the entropy of mixing would be sufficient to cause a nonpolar solute to dissolve. In fact, it does not because any entropy resulting from the disordering of the hydrogen bonded structure of the solvent water is more than offset by the loss of energy from the breaking of hydrogen bonds. Anthropomorphically we might say that the solute would willingly dissolve but that the water would rather associate with itself.

We can summarize the energetics of solution as follows. There will usually be an entropy driving force favoring solution. In cases where the entropy is negative, zero, or slightly positive, solution will take place. If the entropy change accompanying solution is too positive, solution will not occur. In qualitatively estimating the entropy effect, solute-solute, solvent-solvent, and solute-solvent interactions must be considered:

\[
\Delta H_{\text{solution}} = \Delta H_{\text{solute-solute}} + \Delta H_{\text{solute-solvent}} + \Delta H_{\text{solvent-solvent}} (8.26)
\]

where the various energies result from ion-ion, ion-dipole, ion-induced dipole, dipole-dipole, and London forces.

8.1 From Fig. 8.1 describe the crystal structure of solid argon.

8.2 Confirm the statement made on page 290 that the van der Waals radius of argon is 190 pm.

8.3 Predict the internuclear distances in the following molecules and lattices by use of the dipole-dipole, and London forces.

8.4 At one time the melting points of (be) fluorides of the third-row elements were taken to indicate the discontinuity between ionic bonding (AlF) and covalent bonding (SiF). Explore the observed trend assuming that the bond polarity decreases uniformly from NaF to SiF

- NaF = 993 °C
- AlF = 1291 °C
- SiF = 83 °C

8.5 List the following in order of increasing boiling point:

- H₂O
- Xe
- LiF
- H₂
- BaO
- SiCl₄
- SO₂

8.6 The majority of ionic compounds involve hydrogen bonding in the host cages. Discuss how the intermolecular nature of the hydrogen bond (i.e., stronger than van der Waals forces, weaker than ionic forces) is related to the prevalence of hydrogen bonded clathrates.

8.7 Two forms of boron nitride are known. The ordinary form is a slippery white material. The second, formed artificially at high pressures, is the second hardest substance known. Both remain as solids at temperatures approaching 3000 °C. Suggest structures.

8.8 Predict bond lengths in the following: FLO, HCl, NF

8.9 The Schomaker-Stevenson relationship states that homopolar bonds are always stronger than hypothetical, purely covalent bonds between the same atoms. In an ionic crystal, would you expect some covalency to shorten or lengthen the bond? Explain.

8.10 Find the melting points and boiling points of the elements or compounds listed. For each series, tabulate the data and explain the trends you observe in terms of the forces involved:

- a. He, Ne, Ar, Kr, Xe
- b. H₂O, H₂S, H₂Se, H₂Te
- c. CH₄, CH₂Cl₂, CH₂ClCH₃, CH₃Cl, CCl₄
- d. Carbon, nitrogen, oxygen, fluorine, neon

8.11 Consider the sizes of the isoelectronic species N⁺, O₂⁻, F⁻, and Ne. Discuss the forces operating. Careful! Be careful in choosing which numbers to use in your discussion.

8.12 The stability of noble gas configurations was discussed in Chapter 4, where it was pointed out that many ions are not stable, that is, they are endothermic with respect to the corresponding atoms, but they are stabilized by the ionic lattice. However, some chemists argue that these ions are stable because they exist in solution as well as in lattices. Discuss.

8.13 Consider the ions [Ph₃P=N—PPh₃]+ and [Ph₃P=N—PPh₃]²⁻. Work out the electronic structure of these ions in detail including assigning formal charges.

8.14 Water is well known to have an unusually high heat capacity. Not so well known is the liquid XeF₄ also has a high heat capacity compared to "normal" liquids such as argon, carbon tetrachloride, or sulfur dioxide. From your knowledge of the structures of these solids and the gaseous molecules of these materials (most of them are sketched in this text), explain the "anomalous" heat capacity of XeF₄.

8.15 Find the solubilities in water of the alkali halides. Calculate the osmotic pressure (more convenient) of a saturated solution for each and plot them in matrix form with columns headed F, Cl, Br, I, and horizontal rows labeled Li, Na, K, Rb, and Cs. Observe any trends you notice.

8.16 In these first eight chapters you have encountered many tables of atomic and molecular
Several factors undoubtedly play a role in determining whether an oxide adopts the normal or inverse spinel structure, one of which is $d$ orbital splitting energy. Although the CFSE contribution to the total bonding energy of a system is only about 5-10%, it may be the deciding factor when other contributions are reasonably constant. The crystal field contribution for spinors can be assessed by considering the difference in crystal field stabilization energies for octahedral compared to tetrahedral coordination for the metal ions involved. For purposes of estimating this difference, it can be assumed that the oxide ions will provide a moderately weak crystal field similar to that for water, for which a number of $A_e$ values have been measured. Values of $A_e$ for the four-coordinate sites can be approximated by the relationship $A_e = \beta (A_e)_w$.

Octahedral site preference energies determined in this manner for $d^0$ and $d^1$ ions of the first transition series are given in Table 11.9. Table 11.8 reveals that most spinels involving $Fe^{3+}$ (APFeO$_4$) have the inverse structure. The $d^0 Fe^{3+}$ ion will have a CFSE of zero for both tetrahedral and octahedral coordination, so if there is to be a site preference it will be due to the $A(I)$ ion. This is clearly the case for Ni$_2$Fe$_3$O$_4$, for example, the $Ni^{2+}$ ion having an octahedral site preference energy of 86 kJ mol$^{-1}$. In magnetite, Fe$_3$O$_4$, both A and B ions are iron, with some in the $+2$ oxidation state and others in $+3$. Fe$_6$Fe$^{3+}$O$_8$. For the $d^0 Fe^{3+}$, octahedral coordination is more favorable than tetrahedral by about 15 kJ mol$^{-1}$, which, although only a modest amount, is apparently sufficient to invert the structure. In contrast, the similar oxide Mn$_3$O$_4$ has the normal structure. In this instance, the $d^5$ Mn$^{2+}$ has no CFSE in either octahedral or tetrahedral fields, i.e., $d^5$ Mn$^{2+}$ shows a preference of 106 kJ mol$^{-1}$ for octahedral sites. For Co$_2$O$_3$, another mixed-valence oxide, there is an additional factor to take into account---Co$^{2+}$ is low spin in the field produced by six oxide ions. This makes for complications in estimating an octahedral site preference energy for Co$^{2+}$ because in a tetrahedral site it would be high spin. However, the low spin $d^6$ configuration imparts additional stabilization to Co$^{3+}$ in an octahedral hole. Thus the octahedral preference for Co$^{3+}$ will clearly outweigh that for Co$^{2+}$ (29.3 kJ mol$^{-1}$), favoring the normal arrangement.

Although crystal field theory quite successfully rationalizes observed structures of the spinels of the first transition series, it must be applied with care to other examples. In comparing structures in which other factors (ionic radii, covalency, etc.) are more dissimilar, $d$ orbital splittings alone generally do not explain the observations. In these cases, a broader analysis is required.

### Table 11.9

<table>
<thead>
<tr>
<th>No. of $d$ electrons</th>
<th>Ion</th>
<th>Free ion ground state</th>
<th>Octahedral field configuration</th>
<th>Tetrahedral field configuration</th>
<th>CFSE (kJ mol$^{-1}$)</th>
<th>Octahedral site preference energy (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ti$^{4+}$</td>
<td>$d^0$</td>
<td>$t^1_2$</td>
<td>$e^1$</td>
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<td>$t^1_2$</td>
<td>$e^2$</td>
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<td>8870</td>
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<td>$t^1_2$</td>
<td>$e^3$</td>
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<td>$e^4$</td>
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<tr>
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<td>$e^{13}$</td>
<td>12,000</td>
<td>5330</td>
</tr>
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</table>


* Octahedral site preference energy not calculated because [Co(H$_2$O)$_6$]$^{2+}$ is low spin.

### Table 11.10

<table>
<thead>
<tr>
<th>Ligand</th>
<th>$h$</th>
<th>Metal</th>
<th>$k$</th>
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<td>0.8</td>
<td>Mn(II)</td>
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</tr>
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<td>V(III)</td>
<td>0.1</td>
</tr>
<tr>
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<td>1.2</td>
<td>Ni(II)</td>
<td>0.12</td>
</tr>
<tr>
<td>$H_2$N$_2$</td>
<td>1.4</td>
<td>Mn(III)</td>
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<tr>
<td>$H_2$O</td>
<td>1.5</td>
<td>Co(III)</td>
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</tr>
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<td>ox</td>
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<td>Fe(III)</td>
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</tr>
<tr>
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<td>Cu(II)</td>
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<td>Au(III)</td>
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* The total nephelauxetic effect in a complex MX$_2$ is proportional to the product $h(k + 1)$. For ligand abbreviations, see Table 11.7. Jørgensen, C. K. Oxidation Numbers and Oxidation States; Springer: New York; 1969; p 100. Used with permission.
properties. They may be classified into two groups: (1) radial wave functions, ionization energies, electron affinities, etc.; (2) ionic radii, covalent radii, electronegativities, etc.

a. What distinguishes and separates these two groups?

b. Lee Allen (pers. comm.) has suggested that it is the problems associated with the second group that make chemistry a distinct and interesting science, not just a sub-branch of chemical physics. Discuss.

8.17 Predict which of the following bonding interactions will be the stronger:

a. O=O or O—O
b. C—C or Si—Si
c. Ne—Ne or Xe—Xe
d. LiF⁺ or MgO⁺ (ion pair)
e. LiF⁺ or BaCl⁺ (ion pair)
f. LiF⁺ or C—C (in diamond)

8.18 Predict the following bond lengths:

C—O (ketone) C—O (carbon monoxide)
C—N (ammonia) P—O (single vs. double in H₃PO₃)
N—O (nitric oxide) N—O (nitrogen dioxide)

Compare your answers with the values given in Table E.1, Appendix E.

8.19 Reconsider Problem 4.15. Extend your explanation: Suggest a means of stabilizing hexafluoroplatinate(V) salts.

8.20 How will the IR and Raman spectra of FH⁻ and CH⁻ differ?

8.21 On page 302 it was stated that although the FH⁻ ion was usually symmetrical, occasionally it was found to be unsymmetrical in the solid. What physical methods could you use to detect unsymmetrical F⁻ ions in a solid?

8.22 If you did not do Problems 4.37 and 4.38 when you read Chapter 4, do them now.

8.23 In the preparation of the bis(N-nitrosopyrrolidine)hydrogen cation with the short hydrogen bond (Fig. 8.5), the complex was made by evaporating a solution of N-nitrosopyrrolidine and hexafluorophosphoric acid in ether to obtain crystals. Why hexafluorophosphoric acid? Why not hydrofluoric acid?

8.24 If you did not do Problem 6.15 when you read Chapter 6, do it now.

8.25 How would you characterize the hydrogen bond described in Problem 3.42?

8.26 The ammonium ion is about the same size (r₁ = 121 pm) as the potassium ion (r₂ = 152 pm) and this is a useful fact to remember when explaining the resemblance in properties between these two ions. For example, the solubilities of ammonium salts are similar to those of potassium salts. Explain the relation between ionic radii and solubility. On the other hand, all of the potassium halides crystallize in the NaCl structure with C.N. = 6 (see Chapter 4), but none of the ammonium halides do so. The coordination numbers of the ammonium halides are either four or eight. Suggest an explanation.

8.27 Find as many data as you can (distances, energies, etc.) on hydrogen bonds and hydrogen bridges. Use this chapter, Chapters 15 and 16, and any other sources. Arrange the data and argue (however you conclude) that hydrogen bonds such as F—H—F and hydrogen bridges such as W—H—W (are, are not) merely the ends of a continuous spectrum of bonding. (See Ban, R., Teller, R. G., Körner, S. W., Köstable, T. F., Acc. Chem. Res. 1979, 12, 176-183.)

8.28 If you did not do Problem 3.34 when you read Chapter 3, do it now.

8.29 The classical qualitative analysis scheme is based on solubility rules: Acetates, nitrates, and chlorides (except for Ag⁺, Hg²⁺, and Pb²⁺) are always soluble. There are specific solubility patterns for sulfides, carbonates, and phosphates. Find a qualitative scheme and explain it in terms of your understanding of solution processes.
The crystal field model can also be used to account for the stability of particular oxidation states. In aqueous solution Co(III) is unstable with respect to reduction by an electron from the $e_g$ level, is endothermic because of the high ionization energy ($\Delta H^{\text{ion}}$), but the increase in CFSE (1.8 A$^2$ to 2.4 A$^2$) will favor ionization. It should be pointed out that CFSE is only one of a number of factors affecting the emf.

In particular, entropy effects associated with chelate rings can be important and are largely responsible for the fact that the order of ligands in Eqs. 11.6-11.12 is different from that in the spectrochemical series. In any event, the emf of a couple can be "tuned" by varying the nature of the ligands, a phenomenon that becomes exquisitely important in biological systems (see Chapter 19).

Crystal field factors may also be used to help account for observed site preferences in certain crystalline materials such as the spinels. Spinels have the formula $AB_2O_4$, where $A$ can be a Group IIA (2) metal or a transition metal in the +3 oxidation state and $B$ is a Group IIIA (3) metal or a transition metal in the +3 oxidation state. The oxide ions form a close-packed cubic lattice with eight tetrahedral holes and four octahedral holes per unit. In a so-called normal spinel such as MgAl$_2$O$_4$, the Mg$^{2+}$ ions occupy one-eighth of the tetrahedral holes and the Al$^{3+}$ ions occupy one-eighth of the octahedral holes. This is the arrangement that would be predicted to be most stable inasmuch as it yields a coordination number of 4 for the divalent ion and 6 for the trivalent ion (cf. [Be(H$_2$O)$_4$]$^{2+}$ and [Al(H$_2$O)$_6$]$^{3+}$, page 393). Very interesting, therefore, are spinels having the inverse structure in which the A(II) ions and one-half of the $B$(III) ions have exchanged places; i.e., the A(II) ions occupy octahedral holes along with one-half of the $B$(III) ions while the other one-half of the $B$(III) ions are in tetrahedral holes. Also observed are cases that are intermediate between the normal and inverse distributions. It is common to describe the structure of a spinel by the parameter $A$, defined as the fraction of $B$ ions in tetrahedral holes. The value of $A$ ranges from zero for normal spinels to 0.50 for those having the inverse composition. Cation distributions (as $A$ values) in a number of common spinels are given in Table 11.8.
Acid-Base Chemistry

Acids and bases are fundamental to inorganic chemistry. Together with the closely related subjects of redox and coordination chemistry, they form the basis of descriptive inorganic chemistry. Because they are so fundamental, there has been much work (and sometimes much disagreement) attempting to find the "best" way of treating the subject.

The first point to be made concerning acids and bases is that so-called acid-base theories are in reality definitions of what an acid or base is; they are not theories in the sense of valence bond theory or molecular orbital theory. In a very real sense, we can make an acid be anything we wish; the differences between the various acid-base concepts are not concerned with which is "right" but which is most convenient to use in a particular situation.

All of the current definitions of acid-base behavior are compatible with each other. In fact, one of the objects in the following presentation of many different definitions is to emphasize their basic parallelism and hence to direct the students toward a cosmopolitan attitude toward acids and bases which will stand them in good stead in dealing with various chemical situations, whether they be in aqueous solutions of ions, organic reactions, nonaqueous titrations, or other situations.

**Bronsted-Lowry Definition**

In 1923 J. N. Brønsted and T. M. Lowry independently suggested that acids be defined as proton donors and bases as proton acceptors. For aqueous solutions the Bronsted-Lowry definition does not differ appreciably from the Arrhenius definition of hydrogen ions (acids) and hydroxide ions (bases):

\[
2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-
\]

The usefulness of the Bronsted-Lowry definition lies in its ability to handle any protonic solvent such as liquid ammonia or sulfuric acid:

\[
\text{NH}_4^+ + \text{OH}^- \rightarrow 2\text{NH}_3 + \text{H}_2\text{O}
\]

In addition, other proton-transfer reactions that would not normally be called neutralization reactions but which are obviously acid-base in character may be treated as readily:

\[
\text{NH}_4^+ + \text{S}^2^- \rightarrow \text{NH}_3 + \text{HS}^- 
\]

Chemical species that differ from each other only in the extent of the transferred proton are termed conjugates (connected by brackets in Eq. 9.4). Reactions such as the above proceed in the direction of forming weaker species. The stronger acid and the stronger base of each conjugate pair react to form the weaker acid and base. The emphasis which the Brønsted-Lowry definition places on competition for protons is one of the assets of working in this context, but it also limits the flexibility of the concept. However, as long as one is dealing with a protonic solvent system, the Bronsted-Lowry definition is as useful as any. The acid-base definitions given below were formulated in an attempt to extend acid-base concepts to systems not containing protons.

**Lux-Flood Definition**

In contrast to the Brønsted-Lowry theory, which emphasizes the proton as the principal species in acid-base reactions, the definition proposed by Lux and extended by Flood describes acid-base behavior in terms of the oxide ion. This acid-base concept was advanced to treat nonprotonic systems which were not amenable to the Brønsted-Lowry definition. For example, in high-temperature inorganic melts, reactions such as the following take place:

\[
\text{CaO} + \text{SiO}_2 \rightarrow \text{CaSiO}_3
\]

As this book was going to press the International Union of Pure and Applied Chemistry recommended that the word proton be used only when the H\(^+\) ion was intended, and that the more general hydron be used everywhere else, as in hydron donor. See Appendix 1, Section 2. We have not attempted at the last minute to change all of these "protons" to "hydrons." Like the SI system of units, this change, if accepted by the world's chemists, will take some time, and the term "proton donor" will not soon disappear.
Among the early successes of crystal field theory was its ability to account for magnetic and spectral properties of complexes. In addition, it provided a basis for understanding and predicting a number of their structural and thermodynamic properties. Several such properties are described in this section from the crystal field point of view. Certainly other bonding models, such as molecular orbital theory, can also be used to interpret these observations. Even when they are, however, concepts from crystal field theory, such as crystal (or ligand) field stabilization energy, are often invoked within the discussion.

One of the first indications that crystal field stabilization energy might be important in transition metal chemistry, several of which are discussed in the next section.

Applications of Crystal Field Theory

The ions that do not show such discrepancies are those with (high spin), and d°, d⁰, d°, (high spin), and d⁰, d°, d°, (high spin), and d⁰, d°, d°, (high spin), and d⁰, d°, d°, (high spin). Wherever a serious difference for a six-coordinate metal ion is found, it may be attributed to the CFSE. The ions that do not show such discrepancies are those with d⁰, d°, (high spin), and d⁰, d°, (high spin), configurations, which all have in common that CFSE = 0. Consider the lattice energies of the halides from CaX₂ to ZnX₂, in which the metal ions occupy octahedral holes. Inasmuch as we might expect a gradual decrease in ionic radius from Ca²⁺ to Zn²⁺ (Chapter 22), we should also expect a gradual and smooth increase in lattice energy based on the Born-Lande equation (Chapter 4). However, as shown by Fig. 11.14, the expected smooth curve is not observed. The ions Ca²⁺, Mn²⁺, and Zn²⁺ lie on a curve that is nearly a straight line. Moreover, deviations from this approximate line are maximized in two places: in the region of V²⁺ and the region of Ni²⁺. Table 11.3 indicates that for a weak octahedral field (recall that the halide ions are on the weak end of the spectrochemical series), V²⁺ (d⁷) and Ni²⁺ (d⁸) have the greatest CFSE values (1.2A,). The d⁷, d⁶, d⁵, and d⁴ ions have somewhat less (0.6 and 0.8A,) and the d⁴, d³, and d² cases have zero CFSE, qualitatively confirming the shape of the curve within the unfortunately large experimental errors.

Ligand of g/ and Selected values of factors

<table>
<thead>
<tr>
<th>Ligand</th>
<th>f factor</th>
<th>Metal ion</th>
<th>g factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br⁻</td>
<td>0.72</td>
<td>Mn(II)</td>
<td>3.0</td>
</tr>
<tr>
<td>SCN⁻</td>
<td>0.73</td>
<td>Ni(II)</td>
<td>8.7</td>
</tr>
<tr>
<td>CI⁻</td>
<td>0.78</td>
<td>Co(II)</td>
<td>9</td>
</tr>
<tr>
<td>N₃⁻</td>
<td>0.83</td>
<td>V(II)</td>
<td>12.0</td>
</tr>
<tr>
<td>F⁻</td>
<td>0.9</td>
<td>Fe(III)</td>
<td>14.0</td>
</tr>
<tr>
<td>ox = C₃O₂⁻</td>
<td>0.99</td>
<td>Cr(III)</td>
<td>17.4</td>
</tr>
<tr>
<td>H₂O</td>
<td>1.00</td>
<td>Co(II)</td>
<td>18.2</td>
</tr>
<tr>
<td>NCS⁻</td>
<td>1.02</td>
<td>Ru(II)</td>
<td>20</td>
</tr>
<tr>
<td>gly⁻ = NH₄CH₂CO₂⁻</td>
<td>1.18</td>
<td>Mn(V)</td>
<td>21</td>
</tr>
<tr>
<td>py = C₃H₂N</td>
<td>1.23</td>
<td>Mo(II)</td>
<td>24.6</td>
</tr>
<tr>
<td>N₃⁻</td>
<td>1.25</td>
<td>Rh(III)</td>
<td>27.0</td>
</tr>
<tr>
<td>en = NH₂CH₂CH₂NH₂</td>
<td>1.28</td>
<td>Tc(V)</td>
<td>30</td>
</tr>
<tr>
<td>bpy = 2,2'-bipyridine</td>
<td>1.33</td>
<td>Ir(III)</td>
<td>32</td>
</tr>
<tr>
<td>CN⁻</td>
<td>1.7</td>
<td>Pt(IV)</td>
<td>36</td>
</tr>
</tbody>
</table>


* In units of kK (= 1000 cm⁻¹). Liganding atoms are shown in boldface type.

Modern Aspects of Ligand Field Theory

Crystal Field Theory
The base (CaO) is an oxide donor and the acid (SiO₂) is an oxide acceptor. The usefulness of the Lux-Flood definition is mostly limited to systems such as melt oxides.

This approach emphasizes the acid- and basic-anhydride aspects of acid-base chemistry, certainly useful though often neglected. The Lux-Flood base is a basic anhydride:

\[ \text{Ca}^{2+} + \text{O}^{2-} + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{OH}^- \]  

and the Lux-Flood acid is an acid anhydride:

\[ \text{SiO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SiO}_3 \]  

(This latter reaction is very slow as written and is of more importance in the reverse, dehydration reaction.) The characterization of these metal and nonmetal oxides as acids and bases is of help in rationalizing the workings, for example, of a basic Bessemer converter in steelmaking. The identification of these acids and bases will also prove useful in developing a general definition of acid-base behavior.

An acidity scale has been proposed in which the difference in the acidity parameters, \( a_b - a_a \), of a metal oxide and a nonmetal oxide is the square root of the enthalpy of reaction of the acid and base.

\[ A_a \rightarrow B_a + \text{H}_2\text{O} \]  

Thus for reaction 9.5, the enthalpy of reaction is expected to be only about \(-1.7 - 5.5\) or about \(-7.2\) kJ mol\(^{-1}\). This latter reaction is very slow as written and is of more importance in the reverse, the dehydration reaction.) The characterization of these metal and nonmetal oxides as acids and bases is of help in rationalizing the workings, for example, of a basic Bessemer converter in steelmaking. The identification of these acids and bases will also prove useful in developing a general definition of acid-base behavior.

A species that increases the characteristic cation of the solvent, and a base as a species that increases the characteristic anion of the solvent system, and a base as a species that increases the characteristic anion of the solvent system. The advantages of this approach are principally those of convenience. One may treat nonequivalent solvents by analogy with water. For example:

\[ K_a = [\text{H}_2\text{O}^+][\text{OH}^-] = 10^{-14} \]  

where \([A^+]\) and \([B^-]\) are the concentrations of the cationic and anionic species characteristic of a particular solvent. Similarly, scales analogous to the pH scale of water may be constructed with the neutral point equal to \(-1 \log K_{an}\), although, in practice, little work of this type has actually been done. Some examples of data of this type for nonequivalent solvents are listed in Table 9.2. The "levelling" effect follows quite naturally from this viewpoint. All acids and bases stronger than the characteristic cation and anion of the solvent will be "levelled" to the latter. Acids and bases weaker than those of the solvent system will remain in equilibrium with them. For example:

\[ \text{H}_2\text{O} + \text{HClO}_4 \rightarrow \text{H}_3\text{O}^+ + \text{ClO}_4^- \]  

\[ (9.15) \]
Some values of \( \Delta \) for transition metal complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Oxidation state of metal</th>
<th>Symmetry</th>
<th>( \Delta ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>VCl(_4)(^{2-})</td>
<td>4</td>
<td>( T_d )</td>
<td>15,400</td>
</tr>
<tr>
<td>VC(_4)</td>
<td>4</td>
<td>( T_d )</td>
<td>7900</td>
</tr>
<tr>
<td>CoF(_6)(^{3-})</td>
<td>3</td>
<td>( O_h )</td>
<td>22,000</td>
</tr>
<tr>
<td>[Co(H(_2)O)(_6)](^{3+})</td>
<td>6</td>
<td>( O_h )</td>
<td>17,400</td>
</tr>
<tr>
<td>[CrF(_6)(^{2-})</td>
<td>3</td>
<td>( O_6 )</td>
<td>22,500</td>
</tr>
<tr>
<td>[Cr(CN)(_6)(^{3-})</td>
<td>3</td>
<td>( O_6 )</td>
<td>26,600</td>
</tr>
<tr>
<td>[MnF(_6)(^{3-})</td>
<td>3</td>
<td>( O_6 )</td>
<td>26,600</td>
</tr>
<tr>
<td>[MnF(_6)(^{3-})</td>
<td>3</td>
<td>( O_6 )</td>
<td>21,800</td>
</tr>
<tr>
<td>[TeF(_6)(^{3-})</td>
<td>3</td>
<td>( O_6 )</td>
<td>28,300</td>
</tr>
<tr>
<td>[ReF(_6)(^{3-})</td>
<td>3</td>
<td>( O_6 )</td>
<td>32,600</td>
</tr>
<tr>
<td>[Fe(CN)(_6)(^{3-})</td>
<td>2</td>
<td>( O_6 )</td>
<td>35,500</td>
</tr>
<tr>
<td>[Rh(H(_2)O)(_6)(^{3+})</td>
<td>3</td>
<td>( O_6 )</td>
<td>28,600</td>
</tr>
<tr>
<td>[Rh(CN)(_6)(^{3-})</td>
<td>2</td>
<td>( O_6 )</td>
<td>28,700</td>
</tr>
<tr>
<td>[Ru(H(_2)O)(_6)(^{3+})</td>
<td>2</td>
<td>( O_6 )</td>
<td>19,800</td>
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<td>2</td>
<td>( O_6 )</td>
<td>33,800</td>
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<tr>
<td>[CoF(_6)(^{3-})</td>
<td>4</td>
<td>( O_6 )</td>
<td>20,300</td>
</tr>
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<td>3</td>
<td>( O_6 )</td>
<td>13,100</td>
</tr>
<tr>
<td>[Co(H(_2)O)(_6)(^{3+})</td>
<td>3</td>
<td>( O_6 )</td>
<td>20,760</td>
</tr>
<tr>
<td>[Co(NH(_3))(_6)(^{3+})</td>
<td>3</td>
<td>( O_6 )</td>
<td>22,870</td>
</tr>
<tr>
<td>[Co(en)(_3)(^{3+})</td>
<td>3</td>
<td>( O_6 )</td>
<td>23,160</td>
</tr>
<tr>
<td>[Co(H(_2)O)(_6)(^{3+})</td>
<td>2</td>
<td>( O_6 )</td>
<td>9200</td>
</tr>
<tr>
<td>[Co(NH(_3))(_6)(^{3+})</td>
<td>2</td>
<td>( O_6 )</td>
<td>10,200</td>
</tr>
<tr>
<td>[Co(NH(_3))(_6)(^{3+})</td>
<td>2</td>
<td>( T_d )</td>
<td>5900</td>
</tr>
<tr>
<td>[ReF(_6)(^{3-})</td>
<td>4</td>
<td>( O_6 )</td>
<td>20,500</td>
</tr>
<tr>
<td>[Rh(H(_2)O)(_6)(^{3+})</td>
<td>3</td>
<td>( O_6 )</td>
<td>27,200</td>
</tr>
<tr>
<td>[Ru(NH(_3))(_6)(^{3+})</td>
<td>3</td>
<td>( O_6 )</td>
<td>34,100</td>
</tr>
<tr>
<td>[IrF(_6)(^{3-})</td>
<td>4</td>
<td>( O_6 )</td>
<td>27,000</td>
</tr>
<tr>
<td>[Ir(NH(_3))(_6)(^{3+})</td>
<td>3</td>
<td>( O_6 )</td>
<td>41,200</td>
</tr>
</tbody>
</table>

Jorgensen has developed a means of estimating the value of \( \Delta \) for an octahedral complex by treating it as the product of two independent factors:

\[
\Delta = \Delta \times g
\]

(11.5)

The quantity \( g \) describes the field strength of a ligand relative to water, which is assigned a value of 1.00. Values range from about 0.7 for weak field bromide ions to about 1.7 for the very strong field cyanide ion. The \( g \) factor is characteristic of the metal ion and varies from 8000 to 36,000 cm\(^{-1}\) (Table 11.7). Equation 11.5 is useful for approximating \( \Delta \) and, in combination with pairing energies (Table 11.4), for predicting whether a new octahedral complex will be high or low spin.

Although the spectrochemical series and other trends described in this section allow one to rationalize differences in spectra and permit some predictability, they present serious difficulties in interpretation for crystal field theory. If the splitting of the \( d \) orbitals resulted simply from the effect of point charges (ions or dipoles), one should expect that anionic ligands would exert the greatest effect. To the contrary, most anionic ligands lie at the low end of the spectrochemical series. Furthermore, \( \text{OH}^- \) lies below the neutral \( \text{H}_2\text{O} \) molecule and \( \text{NH}_3 \) produces a greater splitting than \( \text{H}_2\text{O} \), although the dipole moments are in the reverse order (Table 11.7). The model is also unable to account for the fact that with certain strong field ligands (such as \( \text{CN}^- \)), \( \Delta \) varies only slightly for analogous complexes within a group. These apparent weaknesses in the theory called into question the assumption of purely electrostatic interactions between ligands and metal ions.
Substances which increase the chloride ion concentration may be considered bases.

\[
{\text{OPCl}_3} + \text{PCl}_5 \rightarrow \text{OPCl}_4^+ + \text{PCl}_4^-
\]

(9.25)

Extensive studies of reactions between chloride ion donors (bases) and chloride ion acceptors (acids) have been conducted by Gutmann, who interpreted them in terms of the above equilibria. An example is the reaction between tetramethylammonium chloride and iron(III) chloride, which may be carried out as a titration and followed conductometrically:

\[
(\text{CH}_3)N^+\text{Cl}^- + \text{FeCl}_3 \rightarrow (\text{CH}_3)N^+\text{FeCl}_4^- + \text{PCl}_4^-
\]

(9.26)

which was interpreted by Gutmann in terms of

\[
(\text{CH}_3)N^+\text{Cl}^- \text{Insoluble in} \text{OPCl}_3 \rightarrow (\text{CH}_3)N^+\text{Cl}^- + \text{Cl}^-
\]

(9.27)

\[
\text{FeCl}_3 + \text{OPCl}_3 \rightarrow \text{OPCl}_4^+ + \text{FeCl}_2^-
\]

(9.28)

\[
\text{OPCl}_4^+ + \text{Cl}^- \rightarrow \text{OPCl}_3
\]

(9.29)

Meek and Drago showed that the reaction between tetramethylammonium chloride and iron(III) chloride can take place as readily in triethyl phosphate, \(\text{OP(OEt)}_3\), as in phosphorus oxychloride, \(\text{OPCl}_3\). They suggested that the similarities in physical properties of the two solvents, principally the dielectric constant, were more important in this reaction than the difference in chemical properties, namely, the presence or absence of autoionization to form chloride ions.

One of the chief difficulties with the solvent system concept is that in the absence of data, one is tempted to push it further than can be justified. For example, the reaction of thiophenyl halides with sulfites in liquid sulfur dioxide might be supposed to occur as follows, assuming that autoionization occurs:

\[
2\text{SO}_3 \rightarrow \text{SO}_2^+ + \text{SO}_4^{2-}
\]

(9.30)

Accordingly, sulfite salts may be considered bases because they increase the sulfite ion concentration. It might then be supposed that thiophenyl halides behave as acids because of dissociation to form thiolyl and thiolate ions:

\[
\text{SOCl}_2 \rightarrow \text{SO}^+ + \text{SO}_4^{2-}
\]

(9.31)

The reaction between cesium sulfite and thionyl chloride might now be considered to be a neutralization reaction in which the thiol and sulfite ions combine to form solvent molecules:

\[
\text{SO}^+ + \text{SO}_4^{2-} \rightarrow 2\text{SO}_3
\]

(9.32)

Indeed, solutions of cesium sulfite and thionyl chloride in liquid sulfur dioxide yield the expected products:

\[
\text{Cs}_2\text{SO}_4 + \text{SOCl}_2 \rightarrow 2\text{SOCl} + 2\text{SO}_3
\]

(9.33)

---


3 See Chapter 18 for further discussion of this point.

---

### Table 9.3

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Ion product</th>
<th>pH range</th>
<th>Neutral point</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$SO$_3$</td>
<td>10$^{-3}$</td>
<td>9-13</td>
<td>6.5</td>
</tr>
<tr>
<td>CH$_3$COOH</td>
<td>10$^{-2.5}$</td>
<td>0-20</td>
<td>10</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>10$^{-7}$</td>
<td>0-20</td>
<td>8</td>
</tr>
<tr>
<td>C$_2$H$_5$OH</td>
<td>10$^{-7}$</td>
<td>0-20</td>
<td>10</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>10$^{-7}$</td>
<td>0-20</td>
<td>14.5</td>
</tr>
</tbody>
</table>


---

* Although this reaction appears to be different from the others in stoichiometry and products, the difference lies merely in the relative basicity of H$_2$O, ROH, and NH$_3$ and the stability of their conjugate acids toward dissociation: NH$_3^+$ + H$^+$ $\rightarrow$ B + H$_2$O.

Symmetries
Fields of Other
Orbital Splittings in
eral important variables and trends can be
Magnitude of
surrounding ligands are split.

There are a number of factors that affect the extent to which metal d orbitals are split by surrounding ligands. Representative values of \( \Delta \) for a variety of complexes are listed in Table 11.5 along with energies for the more common geometries. From the values in the table, energy level diagrams similar to those given previously for octahedral, tetrahedral, and square planar complexes can be constructed for any of the symmetries listed.

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Nature of the metal ion. Significant differences in \( \Delta \) also occur for analogous complexes within a given group, the trend being \( 3d < 4d < 5d \). In progressing from Cr to Mo or Co to Rh, the value of \( \Delta \) increases by as much as 50%. Likewise, the values for Ir complexes are some 25% greater than for Rh complexes. An important result of this trend in that complexes of the second and third transition series have a much greater tendency to be low spin than do complexes of the first transition series.

Number and geometry of the ligands. As we have seen, the point-charge model predicts that \( \Delta \) for a tetrahedral complex will be about 20% as large as for an octahedral complex, all other factors being equal. This approximate relationship is observed for VCl\(_4\) and YCl\(_4\)\(^{2-}\), as well as for [Co(NH\(_3\))\(_6\)Cl\(_2\)]\(^{3-}\) and [Co(NH\(_3\))\(_6\)Cl\(_4\)]\(^{-}\). Nature of the ligands. The effect of different ligands on the degree of splitting is illustrated in Fig. 11.13, which shows the absorption spectra of three CrL\(_6\) complexes. Three d-d transitions are predicted for each one, based on an analysis that includes the effects of electron-electron repulsion (see pages 433-437). The transitions labeled \( v_1 \) correspond to \( \Delta / 2 \) or \( 10 \Delta q \). Note that there is a steady increase in the frequency of this absorption as the ligating atom changes from F to O to N, corresponding to a progressive increase in the field strength. Based on similar data for a wide variety of complexes, it is possible to list ligands in order of increasing field strength in a spectrochemical series. Although it is not possible to form a complete series of all ligands with a single metal ion, it is possible to construct one from overlapping series, each constituting a portion of the series:22

\[
\begin{align*}
\Gamma^- &< \text{Br}^- < \text{I}^- < \text{SCN}^- < \text{CN}^- < \text{N}_2 < \text{F}^- < \text{O}, \quad \text{OH}^- < \text{ox}, \\
\text{O}^2- &< \text{H}_2\text{O} < \text{NCS}^- < \text{py}, \quad \text{NH}_3 < \text{en} < \text{bpy}, \quad \text{phen} < \text{NO}_2^- < \text{CH}_3\text{CN} < \text{CN}^- < \text{CO}
\end{align*}
\]

22 Abbreviations are ox = oxalate, py = pyridine, en = ethylenediamine, bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline. For SCN\(^-\) and NCS\(^-\), the bound atom is given first. See: L. G. T. and R. E. G. (Eds.), Inorganic Electronic Spectroscopy 3rd ed.; Elsevier: New York, 1986; Jergensen, C. K., Modern Aspects of Ligand Field Theory; Elsevier: New York, 1971; Chapter 18.

---

Furthermore, the amphoteric behavior of the aluminum ion can be shown in sulfur dioxide as readily as in water. Just as $\text{Al(OH)}_3$ is insoluble in water but dissolves readily in either a strong acid or basic solution, $\text{Al}_2(\text{SO}_4)_3$ is insoluble in liquid sulfur dioxide. Addition of either base ($\text{SO}_2^{-}$) or acid ($\text{SO}_2^{2-}$) causes the aluminum sulfate to dissolve, and it may be reprecipitated upon neutralization.

The application of the solvent system concept to liquid sulfur dioxide chemistry stimulated the elucidation of reactions such as those of sulfuric acid. However, there is no direct evidence at all for the formation of $\text{SO}_2^{-}$ in solutions of thionyl halides. In fact, there is evidence to the contrary. When solutions of thionyl bromide or thionyl chloride are prepared in $^{18}$-labeled ($^{18}$) sulfur dioxide, almost no exchange takes place. The half-life for the exchange is about two years or more. If ionization took place:

$$\text{SO}_2^{-} \rightarrow \text{SO}_2^{2-} + \text{e}^-$$

one would expect rapid scrambling of the tagged and untagged sulfur in the two compounds. The lack of such a rapid exchange indicates that either Eq. 9.34 or 9.35 (or both) is incorrect.

The fact that labeled thionyl bromide exchanges with thionyl chloride indicates that perhaps the ionization shown in Eq. 9.35 actually occurs as indicated in Eq. 9.36.

$$\text{SOCl}_2 \rightarrow \text{SO}^+ + \text{Cl}^-$$

In a solvent with a permittivity as low as sulfur dioxide ($\varepsilon = 15.6\varepsilon_0$ at $0 \, ^\circ\text{C}$) the formation of highly charged ions such as $\text{SO}_2^{2-}$ is energetically unfavorable. When the ionic species formed in solution are known, the solvent system approach can be useful. In solvents that are not conducive to ion formation, or for which little or nothing is known of the nature or even the existence of ions, one must appeal to the Lewis concept

Lewis Definition

In 1923 G. N. Lewis proposed a definition of acid-base behavior in terms of electron-pair donation and acceptance. The Lewis definition is perhaps the most widely used of all because of its simplicity and wide applicability, especially in the field of organic reactions. Lewis defined a base as an electron-pair donor and an acid as an electron-pair acceptor. In addition to all of the reactions discussed above, the Lewis definition includes reactions in which no ions are formed and no hydrogen ions or other ions are transferred.

$$\text{R}^+ + \text{BF}_3 \rightarrow \text{R}^+\text{BF}_3^+$$

$$\text{CO} + \text{N} \rightarrow \text{NiCO}_3$$

The Lewis definition thus encompasses all reactions involving hydrogen ion, oxide ion, or solvent interactions, as well as the formation of acid-base adducts such as $\text{H}_3\text{BF}_4$, and all coordination compounds. Usage of the Lewis concept is extensive in both inorganic and organic chemistry, and so no further examples will be given here, but many will be encountered throughout the remainder of the book. The Lewis definition includes all Lewis acid-base reactions plus redox reactions, which may consist of complete transfer of one or more electrons. Usanovich also stressed unsaturation involved in certain acid-base reactions:

$$\text{OH}^- + \text{O} = \text{C} = \text{O} \rightarrow \text{HOCO}_2^-$$

Unfortunately the Usanovich definition of acids and bases is often dismissed casually with the statement that it includes "almost all of chemistry and the term 'acid-base reaction' is no longer necessary, the term 'reaction' is sufficient." If some chemical reactions were called acid-base reactions simply to distinguish them from other, non-acid-base reactions, this might be a valid criticism. However, most workers who like to talk in terms of one or more acid-base definitions do so because of the great systematizing power which they provide. As an example, Pearson has shown that the inclusion of many species, even organic compounds not normally considered acidic or basic, in his principle of hard and soft acids and bases helps the understanding of the nature of chemical reactions (pages 344-355). It is unfortunate that a good deal of faddism and provincialism has been shown by chemists in this area.

As each new concept came along, it was opposed by those who felt ill at ease with the new definitions. For example, when the solvent system was first proposed, some chemrists refused to call the species involved acids and bases, but insisted that they were "acid analogues" and "base analogues." This is semantics, not chemistry. A similar controversy took place when the Lewis definition became widely used and later when the Usanovich concept was popularized. Because the latter included redox reactions, the criticism that it included too much was especially vehement. That the dividing line between electron-pair donation-acceptance (Lewis definition) and oxidation-reduction (Usanovich definition) is not a sharp one may be seen from the following example. The compound $\text{CH}_3\text{N}_2\text{O}_2$, pyridine oxide, can be formed by the

$$2\text{L} + \text{SnCl}_4 \rightarrow \text{SnCl}_4\text{L}_2$$

$$2\text{NH}_3 + \text{Ag}^+ \rightarrow \text{AgNH}_3\text{L}$$

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Table 11.4

<table>
<thead>
<tr>
<th>Ion</th>
<th>$P_{med}$</th>
<th>$P_{ex}$</th>
<th>$P_\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr$^{3+}$</td>
<td>71.2 (5950)</td>
<td>173.1 (14,475)</td>
<td>244.3 (20,425)</td>
</tr>
<tr>
<td>Mn$^{3+}$</td>
<td>87.9 (7350)</td>
<td>213.7 (17,865)</td>
<td>304.6 (25,215)</td>
</tr>
<tr>
<td>Mn$^{4+}$</td>
<td>67.3 (5625)</td>
<td>144.3 (12,062)</td>
<td>211.6 (17,687)</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>91.0 (7610)</td>
<td>194.0 (16,215)</td>
<td>285.0 (23,825)</td>
</tr>
<tr>
<td>Fe$^{4+}$</td>
<td>120.2 (10,400)</td>
<td>237.1 (19,625)</td>
<td>357.4 (29,875)</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>73.5 (6145)</td>
<td>106.6 (8418)</td>
<td>174.2 (14,363)</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>89.2 (7460)</td>
<td>129.8 (11,020)</td>
<td>225.1 (19,150)</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>113.0 (9950)</td>
<td>169.6 (14,175)</td>
<td>282.6 (23,625)</td>
</tr>
<tr>
<td>Co$^{3+}$</td>
<td>87.9 (7350)</td>
<td>123.6 (10,330)</td>
<td>211.5 (17,680)</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>100 (8400)</td>
<td>150 (12,400)</td>
<td>250 (20,800)</td>
</tr>
</tbody>
</table>

*Pairing energies in kJ mol$^{-1}$ (and cm$^{-1}$) calculated from formulas and data given by Orpen, L. E. J. Chem. Phys. 1965, 43, 1899, and Griffith, J. S. J. Inorg. Nucl. Chem. 1956, 2, 1. 229. The values pertain to the free ion and may be expected to be from 15% to 30% smaller for the complexed ion as a result of the nephelauxetic effect. $P_{med}$, $P_{ex}$, and $P_\gamma$ refer to the coulombic, exchange, and total energy opposing pairing of electrons.

If four ligands are removed from alternate corners of the cube in Fig. 11.10, the remaining ligands form a tetrahedron about the metal ion. Furthermore, since the center-of-gravity rule holds, the upper levels are raised by 0.4 eV and the lower ones stabilized by 0.6 eV from the barycenter, giving an energy level scheme that is exactly the inverse of that for octahedral symmetry.

If two trans ligands in an octahedral ML$_6$ complex (for example those along the $z$-axis) are moved either towards or away from the metal ion, the resulting complex is said to experience a decrease in electrostatic repulsions from the ligands and will therefore be stabilized. At the same time, the "non-z" orbitals will be raised in energy, with the barycenter remaining constant. The overall result is that the $e$ levels are split into two levels, an upper $e_u$ ($d_{z^2}$) and a lower $e_g$ ($d_{x^2}$). The $t_{2g}$ set is split into a $t_{2g}$ ($d_{xy}$, $d_{yz}$, $d_{zx}$) and a doubly degenerate $t_{2g}$ ($d_{x^2-y^2}$, $d_{z^2}$). Assignment of these symmetry labels can be confirmed by referring to the $D_4h$ character table in Appendix D. The energy spacing between the $t_{2g}$ ($d_{xy}$, $d_{yz}$, $d_{zx}$) levels is defined as $\Delta$. As in the octahedral case, this splitting is equal to 100$\Delta$. However, the full crystal field description of the orbital properties in a tetrahedral environment (see the character table for the $D_4h$ point group in Appendix D) for the $d_{xy}$, $d_{yz}$, and $d_{zx}$ orbitals, and $e$ for the $d_{x^2}$ and $d_{z^2}$ orbitals. The $g$ subscripts which were used for the octahedral and cubic fields are no longer appropriate because the tetrahedron lacks a center of inversion.

The crystal field splitting in a tetrahedral field is intrinsically smaller than that in an octahedral field because there are only two-thirds as many ligands and they have a less direct effect on the $d$ orbitals. The point-charge model predicts that for the same metal ion, ligands, and metal-ligand distances, $\Delta = 1\Delta_0$. As a result, orbital splitting energies in tetrahedral complexes generally are not large enough to force electrons to pair, and low spin configurations are rarely observed. Rather, under conditions favoring strong crystal fields, other geometries are preferred over tetrahedral structures.

If two trans ligands in an octahedral ML$_6$ complex (for example those along the $z$-axis) are moved either towards or away from the metal ion, the resulting complex is said to be tetragonally disordered. Ordinarily such distortions are not favored since they result in a net loss of bonding energy. In certain situations, however, such a distortion is favored because of a Jahn-Teller effect (page 449). A complex of general formula trans-MA$_2$B$_2$ also will have tetragonal ($D_{4h}$) symmetry. For now, we will merely consider the limiting case of tetragonal elongation, a square planar ML$_4$ complex, for the purpose of deriving its $d$ orbital splitting pattern.
Acid-Base Concept


In this case the charge on the metal ion is the same in each species, but in the BeO2^- ion it is packed into a much smaller volume, hence its effect is more pronounced. As a result, BeO is more acidic and less basic than the oxides of the larger metals. In this case, "positiveness" is a matter of the size and charge of the cation. This is closely related, of course, to the Fajans polarizing ability (Chapter 4).

2. Acidity of nonmetal oxides. With increasing covalency oxides become less basic and more acidic. Nonmetal oxides are acid anhydrides. This effect is seen in several metal and nonmetal oxides (see Table 9.1). It can be shown that these nonmetallic oxides are directly related to the electronegativities of the metals and nonmetals involved.

3. Hydration and hydrolysis reactions. We have seen (Chapters 4 and 8) that large charge-to-size ratios for cations result in an increase in hydration energies. Closely related to hydration and, in fact, inseparable from it except in degree is the phenomenon of hydrolysis. In general, we speak of hydration if no reaction beyond simple coordination of water molecules to the cation occurs:

$$Na^+ + nH_2O \rightarrow [NaH_2O]^+$$

In the case of hydrolysis reactions, the acidity (charge-to-size ratio) of the cation is so great as to cause rupture of H-O bonds with ionization of the water to yield hydronium ion:

$$Al^{3+} + 6H_2O \rightarrow [Al(H_2O)_6]^{3+} \rightarrow H_3O^+ + [Al(H_2O)_5(OH)]^2$$

Cations that hydrolyze extensively are those which are either small (e.g., Be^2+) or are highly charged (e.g., Fe^2+, Sn^4+) or both, and have a high charge-to-size density. Values of pK_a (negative log of the hydrolysis constant) are compared to the (charge)/(size) ratio\(^{11}\) in Table 9.3. The correlation is good for the main group elements and La^3+ but less so for the transition metals, especially the heavier ones. The reason for the apparently anomalous behavior of metal ions such as Hg^2+, Sn^4+, and Pb^2+ is not completely clear, but it may be related to their "softness" (see page 345).

The concept of hydrolysis may also be extended to the closely related phenomenon of the reaction of nonmetal halides with water:

$$PCl_5 + 5H_2O \rightarrow H_3PO_3 + 3H_2O^+ + 3Cl^-$$

In this case the water attacks and hydrolyzes not a cation but a small, highly charged center (the trivalent phosphorus atom) resulting from the inductive effect of the chlorine atoms.

4. Acidity of oxyacids. The strength of an oxyacid is dependent upon several factors that relate to the inductive effect of the central atom on the hydroxyl group: (a) The inherent electronegativity of the central atom. Perchloric acid, HClO_4, and nitric acid, HNO_3, are among the strongest acids known; sulfuric acid, H_2SO_4, is only slightly weaker. In contrast, phosphoric acid, H_3PO_4, and carbonic acid, H_2CO_3, are considerably weaker and basic acid, H_3BO_3, is extremely weak. (b) The inductive effect of substituents. Although acetic acid, CH_3COOH, is rather weak, successive substitution of chlorine atoms on the


\(^{14}\) Z^+/r has been used here, but any of the Z^+/r functions would give similar results. See Chapter 4.
This quantity is termed the crystal field stabilization energy (CFSE). For \( d^1 \) and \( d^3 \) metal ions, we would expect the electrons to obey Hund’s rule and thus to occupy different degenerate \( t^2 \) orbitals and to remain unpaired. The resulting configurations, \( t^2 \) and \( t^2 \), have CSFEs of 0.8 \( \Delta_e \) and 1.2 \( \Delta_e \), respectively. When one more electron is added to form the \( d^4 \) case, two possibilities arise: either the electron may enter the higher energy \( e_g \) level or it may pair with another electron in one of the \( t^2 \) orbitals. The actual configuration adopted will, of course, be the lowest energy one and will depend on the relative magnitudes of \( \Delta_e \) and \( P \), the energy necessary to cause electron pairing in a single orbital. For \( \Delta_e < P \), the weak-field or high spin condition, the fourth electron will enter one of the \( e_g \) orbitals rather than “pay the price” of pairing with one in a \( t^2 \) orbital. The configuration will be \( t^2 e_g \) and the net CFSE will be
\[
\text{CFSE} = (3 \times +0.4 \Delta_e) - (1 \times +0.6 \Delta_e) = 0.6 \Delta_e.
\]
(11.4)

The addition of a fifth electron to a weak field complex gives a configuration \( t^2 e_g \) and a CFSE of zero. The two electrons in the unfavorable \( e_g \) level exactly balance the stabilization associated with three in the \( t^2 \) level (Fig. 11.9a).

If the splitting of the \( d \) orbitals is large with respect to the pairing energy (\( \Delta_e > P \)), it is more favorable for electrons to pair in the \( t^2 \) level than to enter the strongly unfavorable \( e_g \) level. In these strong field or low spin complexes, the \( e_g \) level remains unoccupied for \( d^4 \) through \( d^9 \) ions (Fig. 11.9b). As a result, the crystal field stabilization energies of complexes having four to seven \( d \) electrons will be greater for strong field than for weak field cases. For \( d^4 \), for example, the low spin configuration will be \( t^2 e_g \), giving a CFSE of 1.6 \( \Delta_e \), compared to 0.6 \( \Delta_e \) for the high spin arrangement. A summary of configurations, crystal field stabilization energies, and numbers of unpaired electrons for \( d^4 \) through \( d^{10} \) in both strong and weak field situations is given in Table 11.3.

A comparison of total energies for strong and weak field cases, including electron-pairing energies (\( P \)), may be computed. The CFSE for a low spin \( d^4 \) configuration will be \( 2 \Delta_e - P \). The corresponding high spin configuration would have a CFSE of \( 0.4 \Delta_e - P \) for a difference between the two of \( 2.0 \Delta_e - 2P. \) Since the two configuration energies differ in the spins of two electrons, this amounts to an energy factor of \( (1.0 \Delta_e - P) \) per electron spin.

The electron-pairing energy is composed of two terms. One is the inherent electrostatic repulsion that must be overcome when forcing two electrons to occupy the same orbital. A gradual decrease in the magnitude of this contribution is observed as one proceeds from top to bottom within a given group of the periodic table. The larger, more diffuse \( 5d \) orbitals of the heavier transition metals more readily accommodate two negative charges than the smaller \( 3d \) orbitals. The second factor of importance is the loss of exchange energy (customarily taken as the basis of Hund’s rule, Chapter 2) that occurs as electrons with parallel spins are forced to have antiparallel spins. The exchange energy for a given configuration is proportional to the number of pairs of electrons having parallel spins. Within a \( d \) subshell the greatest loss of exchange energy is expected when the \( d^4 \) configuration is forced to pair. Hence \( d^3 \) complexes (e.g., \( \text{Mn}^{2+} \) and \( \text{Fe}^{2+} \)) frequently are high spin. Some typical values of pairing energies for some gaseous transition metal ions are listed in Table 11.4.

The two most common geometries for four-coordinate complexes are the tetrahedral and square planar arrangements. The square planar geometry, discussed in the next section, is a special case of the more general \( D_{4h} \) symmetry, which also includes tetragonal distortion of octahedral complexes (page 448). Tetrahedral coordination is closely related to cubic coordination. Although the latter is not common in coordination chemistry, it provides a convenient starting point for deriving the crystal field splitting pattern for a tetrahedral \( \text{ML}_4 \) complex.

Consider eight ligands aligned on the corners of a cube approaching a metal atom located in the center as shown in Fig. 11.10. A complex such as this would belong to the same point group \( (O_h) \) as an octahedral one so the \( d \) orbitals will be split into two degenerate sets, \( e_g \) and \( t_{2g} \), as for the octahedral case. In the cubic arrangement,
Acid–Base Concepts

329

Increasing tendency to hydrolyze because of charge-size function

Increasing tendency to hydrolyze because of carbon-chlorine substitution

Values of pKw from Yatsimirksii, K. B.; Vasyev, V. P. Instability Constants of Complex Compounds; Pergamon; Elmsford, NY, 1960, except for Bi, Hf, Lu, Pu, Sc, and Tl, which are from Stability Constants of Metal-Ion Complexes: Part II. Inorganic Ligands; Bjerntorp, J.; Schwarzcnbach, G.; Sillen, L. G., Eds.; The Chemical Society; London, 1958. For many elements there is considerable uncertainty in the hydrolysis constants not only as a result of experimental errors but also because some have not been corrected to infinite dilution. Z^+/z values were calculated from ionic radii in Table 4.4.

Electron-withdrawing substitution

Less basic

Electron-donating substitution

More basic

NH₃OH = 7.97 NH₂NH₂ = 5.77 Me₃SiNH = 3.36 Me₂NH = 3.29 MeNH = 3.25

CH₃NH₂ = 3.35 i-PrNH₂ = 3.28 i-Pr₂NH = 2.95

i-BuNH₂ = 3.31 i-Bu₂NH = 3.17 i-Bu₃N = 3.18

methyl group increases the dissociation of the proton until trichloroacetic acid is considerably stronger than phosphoric acid, for example.

More important for inorganic oxyacids is the number of oxygen atoms surrounding the central atom. Thus in the series of chlorine oxyacids, acid strength increases in the order HOCl < HOCIC < HOCIO₂ < HOCIO₃. The trends in acidity of oxyacids, and even reasonably accurate predictions of their pKₐ values, can be obtained from:

pKₐ = 10.5 = 5.0n - xₜ (9.46)

for acids of the formula X(OH)ₙOᵣ, and where xₜ is the electronegativity of the central atom. Both effects (a) and (b) are included in Eq. 9.46.

5. **Basicity of substituted ammonia.** In water, ammonia is a weak base, but nitrogen trifluoride shows no basicity whatsoever. In the NH₃ molecule, the nitrogen atom is partially charged negatively from the inductive effects of the hydrogen atoms, but the reverse is true in the NF₃ molecule. Replacement of a hydrogen atom in the ammonia molecule with an electron-withdrawing group such as —OH or —NH₂ also results in decreased basicity. Because alkyl groups are normally electron donating (more so than hydrogen) toward electronegative elements, we might expect that replacement of a hydrogen atom by a methyl group would increase the basicity of the nitrogen atom. This effect is readily seen in the familiar equilibrium constants for weak bases in water (Table 9.4).

As expected, substitution of an alkyl group for a hydrogen atom in the ammonia molecule results in increased electron density on the nitrogen atom and increased basicity. Substitution of a second alkyl group also increases the basicity, although less than might have been expected from the previous substitutional effect. The trialkylamines do not continue this trend and surprisingly are as weak as or weaker than the monoalkylamines. Although the explanation of this apparent anomaly is fairly simple, it does not depend upon electron density and so will be postponed to the next section.

6. **Urine acids and bases.** Familiarity with the idea that acidity and basicity are related to electron density at reacting sites and charge-to-size ratio...
three. Division into these two groups arises from the symmetry properties of the $d$ orbitals within an octahedral environment, which we can confirm by referring to the character table for the $O_6$ point group (Appendix D). We see that the $d_x^2$ and $d_y^2$ orbitals transform as the $E$ representation and the $d_{xy}$, $d_{xz}$, and $d_{yz}$ orbitals transform as the $T_2g$ representation. Our earlier conclusion that the orbitals are split into two sets, one doubly degenerate and the other triply degenerate, is thus substantiated. The labels customarily given to these two groups also denote these symmetry properties: $\epsilon_g$ for the triply degenerate set and $\epsilon_u$ for the doubly degenerate pair; the lower case being appropriate for orbitals. Of course a symmetry analysis does not tell us which of the two sets of orbitals is higher in energy. To determine relative orbital energies, the nature of the interactions giving rise to the splitting must be considered.

The extent to which the $\epsilon_g$ and $\epsilon_u$ orbitals are separated in an octahedral complex is denoted by $\Delta_e$ (the $o$ subscript signifying octahedral) or $D_q$ (Fig. 11.7). More insight into the nature of this splitting can be obtained by viewing formation of a complex as a two-step process. In the first step, the ligands approach the central metal, producing a hypothetical spherical field which repels all of the $d$ orbitals to the same extent. In the second, the ligands exert an octahedral field, which splits the orbital degeneracy. Going from the first to the second step, we find that the barycenter, or "center of gravity," of the orbitals remains constant. That is to say, the energy of all of the orbitals will be raised by the repulsion of the advancing ligands in step one, but merely rearranging the ligands from a hypothetical spherical field to an octahedral field does not alter the average energy of the five $d$ orbitals. To maintain the constant barycenter, it is necessary for the two $\epsilon_g$ orbitals to be further repelled by $0.6\Delta_e$ while the three $\epsilon_u$ orbitals are stabilized to an extent of $0.4\Delta_e$. In going from the first to the second step, we find that the barycenter of the $d$ orbitals holds for all complexes, regardless of geometry.

To gain some appreciation for the magnitude of $\Delta_e$ and how it may be measured, let us consider the $d^1$ complex, [Ti(H$_2$O)$_6$]$^{3+}$. This ion exists in aqueous solutions of $\text{Tl}^{1+}$ and gives rise to a purple color. The single $d$ electron in the complex will occupy the lowest energy orbital available to it, i.e., one of the three degenerate $\epsilon_u$ orbitals. The purple color is the result of absorption of light and promotion of the $\epsilon_u$ electron to the $\epsilon_g$ level. The transition can be represented as $\epsilon_u \rightarrow \epsilon_g$.

The absorption spectrum of [Ti(H$_2$O)$_6$]$^{3+}$ (Fig. 11.8) reveals that this transition occurs with a maximum at 20,300 cm$^{-1}$, which corresponds to 243 kJ mol$^{-1}$ of energy for $\Delta_e$.

The absorption maximum of ReF$_6$ (also a $d^1$ species) is 32,500 cm$^{-1}$ or 338 kJ mol$^{-1}$. These are typical values for $\Delta_e$, and are of the same order of magnitude as the energy of a chemical bond.

The $d^1$ case is the simplest possible because the observed spectral transition reflects the actual energy difference between the $\epsilon_u$ and $\epsilon_g$ levels. For the more general $d^n$ situation, electron-electron interactions must be taken into account and the calculation becomes somewhat more involved. The appropriate methods are discussed on pages 433 and following.

In the $d^1$ case discussed above, the electron occupies a $\epsilon_u$ orbital, which has an energy of $-0.4\Delta_e$ relative to the barycenter of the $d$ orbitals. The complex can thus be said to be stabilized to the extent of $-0.4\Delta_e$ compared to the hypothetical spherical-field case.

---

\[ D_q = 10\Delta_e \]

---

\[ \text{Fig. 11.7 Splitting of the five } d \text{ orbitals by an octahedral field. The condition represented by the degenerate levels on the left is a hypothetical spherical field.} \]

---

\[ \text{Fig. 11.8 Electronic spectrum of a } 0.1 \text{ M aqueous solution of [Ti(H}_2\text{O)}_6]^{3+}. \text{ The letters at the top indicate the colors associated with portions of the visible spectrum. [From Hartmann, H.; Schäffer, H. L.; Hansen, K. H. Z. Anorg. Allg. Chem. 1956, 294, 153-161. Reproduced with permission.]} \]

---

\[ \text{It is suggested that the reader verify this equivalence by means of appropriate conversion factors.} \]

---

\[ \text{Ref.} \]
Historically, acid-base chemistry has been strongly tied to solution chemistry, not only in water but in nonaqueous solvents as well (Chapter 10). Chemists knew that there were strong solvation effects that might be altering or obscuring inherent acid-base properties, and they tried various means of estimating these effects or eliminating them through the use of nonpolar solvents. Nevertheless, for many years the solution thermodynamics of acid-base behavior was only poorly understood. In the past 10-15 years a remarkable amount of data on solutionless, that is, gas-phase, acid-base chemistry has been collected. Since it is easiest to see inherent acid-base effects in the absence of competing solvent effects, the following discussion will proceed: gas-phase → nonpolar solvents → polar solvents, though this treats the subject in reverse chronological order.

The most fundamental measure of the inherent basicity of a species is the proton affinity. It is defined as the energy released for the reaction:

\[ B(g) + H(g) \rightarrow BH(g) \quad \Delta H^\text{gas} = -PA \]  

Note that the proton affinity (PA) has the opposite sign from the enthalpy of reaction of Eq. 9.47: Proton affinities are always listed as positive numbers despite referring to exothermic reactions (recall the same convention with electron affinities, Chapter 2). Proton affinities may be obtained in a number of ways. The simplest, and most fundamental for defining an absolute scale of proton affinities, is to use a Born-Haber cycle of the sort:

\[ \begin{align*} 
B(g) + H(g) & \rightarrow BH(g) \\
& \rightarrow \Delta H^\text{gas} = -PA \\
B(g) + H^+(g) & \rightarrow BH(g) \\
& \rightarrow \Delta H^\text{gas} = -PA 
\end{align*} \]

The molecule BH must be sufficiently stable that its bond energy (enthalpy of atomization, \( \Delta H^\text{atom} \)) and ionization potential (\( \Delta E^\text{ion} \)) can be measured. Once several proton affinities have been established in this way, many more may be obtained by a technique known as ion cyclotron resonance spectroscopy and related methods, in which measure the equilibrium concentrations of the species involved in the competition:

\[ B(g) + BH^+(g) \rightleftharpoons BH(g) + B(g) \]  

Gas-phase proton affinities (Table 9.5) confirm many of our intuitive ideas about the basicities of ions and molecules, though some of the first to be obtained contradicted our prejudices based on solution data (see page 344). The greatest proton affinity estimated to date is that of the trinuclear nitride ion, \( N_3^- \), because of the large electrostatic attraction of the \( -3 \) ion. The dissociative ion, \( NH^+ \), has a very large but somewhat lower value, followed by amide, \( NH_2^- \), and ammonia, \( NH_3 \). Inductive effects are readily observed with values ranging from nitrogen trifluoride, \( NF_3 = 604 \text{ kJ mol}^{-1} \), through ammonia, \( NH_3 = 872 \text{ kJ mol}^{-1} \), to trimethylamine, \( (CH_3)_3N = 974 \text{ kJ mol}^{-1} \). Similar effects can be seen for toluene vs. benzene, acetonitrile vs. hydrogen cyanide, ethers vs. water, and several other comparisons.

In the absence of competing solvent effects, the following discussion will proceed: gas-phase → nonpolar solvents → polar solvents, though this treats the subject in reverse chronological order.

Since the proton affinity of a cation indicates its tendency to attract and hold a proton, its value will also be the enthalpy of dissociation of its conjugate acid in the gas phase. Consider HF (PA\( _{HF} \) = 1554 \text{ kJ mol}^{-1}):

\[ HF \rightarrow H^+ + F^- \quad \Delta H = -1554 \text{ kJ mol}^{-1} \]  

The more endothermic Eq. 9.50 is, the weaker the acid will be. Therefore Table 9.5 may readily be used to compare gas-phase acid strengths, and HF is a weaker acid in the gas phase than are the other \( HX \) acids, as it is also in aqueous solution. In the same way, acetic acid (\( PA_{CH_3COOH} = +1459 \text{ kJ mol}^{-1} \)) is a weaker acid than trifluoroacetic acid (\( PA_{CF_3COOH} = +1554 \text{ kJ mol}^{-1} \)). Which is the stronger acid, methane or toluene? Does Table 9.5 confirm or contradict your memory from organic chemistry?

The Bronsted-Lowry concept was not fruitful.

Concerning the "ultimate" base, one might choose various small highly charged ions such as \( H^+, F^-, \) or \( O^2- \), all of which are indeed quite basic. However, the electron appears to be the complement of the proton. It might be objected that the isolated electron has even less justification as a chemical entity than the proton, but solutions (and even solids) are known in which "free" electrons are very basic. This topic will be discussed in further detail in the section on liquid ammonia chemistry in the next chapter.

Proton Loss

Gas-phase Acidity:

Electron Affinities

The basicity of an ion or molecule can be estimated from its proton affinity. The molecules BH must be sufficiently stable that its bond energy (enthalpy of atomization, \( \Delta H^\text{atom} \)) and ionization potential (\( \Delta E^\text{ion} \)) can be measured. Once several proton affinities have been established in this way, many more may be obtained by a technique known as ion cyclotron resonance spectroscopy and related methods, in which measure the equilibrium concentrations of the species involved in the competition:

\[ B(g) + BH^+(g) \rightleftharpoons BH(g) + B(g) \]  

Gas-phase proton affinities (Table 9.5) confirm many of our intuitive ideas about the basicities of ions and molecules, though some of the first to be obtained contradicted our prejudices based on solution data (see page 344). The greatest proton affinity estimated to date is that of the trinuclear nitride ion, \( N_3^- \), because of the large electrostatic attraction of the \( -3 \) ion. The dissociative ion, \( NH^+ \), has a very large but somewhat lower value, followed by amide, \( NH_2^- \), and ammonia, \( NH_3 \). Inductive effects are readily observed with values ranging from nitrogen trifluoride, \( NF_3 = 604 \text{ kJ mol}^{-1} \), through ammonia, \( NH_3 = 872 \text{ kJ mol}^{-1} \), to trimethylamine, \( (CH_3)_3N = 974 \text{ kJ mol}^{-1} \). Similar effects can be seen for toluene vs. benzene, acetonitrile vs. hydrogen cyanide, ethers vs. water, and several other comparisons.


21 It should be noted that the proton affinities of all of the trinuclear nitride and dissociative ions are calculated by means of a Born-Haber cycle. They are not experimentally accessible since these ions have no existence outside of a stabilizing crystal environment—they would exothermically expel an electron (see Chapter 2).

22 There is a complicating factor here in that acidity can refer to the acceptances of a single electron or an electron pair. Thus a free radical might have a high electron affinity but not have an empty, low-lying orbital to accept an electron pair. Thus, comparisons of \( SO_2 \) (EA = 107 \text{ kJ mol}^{-1} \) as a stronger acid than \( SO_3 \) (EA = 107 \text{ kJ mol}^{-1} \) is valid, but a similar comparison with the free radical OH (EA = 176 \text{ kJ mol}^{-1} \), which does not have a completely empty low-lying orbital, is not.
Crystal Field Theory

The negative field and the negative electrons in the orbitals. If the field results from the influence of real ligands (either anions or the negative ends of dipolar ligands such as NH₃ or H₂O), the symmetry of the field will be less than spherical and the degeneracy of the d orbitals will be removed. It is this splitting of d orbital energies and its consequences that are at the heart of crystal field theory.

Crystal Field Effects: Octahedral Symmetry

Let us consider first the case of six ligands forming an octahedral complex. For convenience, we may regard the ligands as being symmetrically positioned along the axes of a Cartesian coordinate system with the metal ion at the origin, as shown in Fig. 11.6. As in the case of a spherical field, all of the d orbitals will be raised in energy relative to the free ion because of negative charge repulsions. However, it should be pictorially obvious that not all of the orbitals will be affected to the same extent. The orbitals lying along the axes (the dₓz and the dₓ²₋ᵧ²) will be more strongly repelled than the orbitals with lobes directed between the axes (the dₓᵧ, dᵧz, and dᵧₓ). The d orbitals are thus split into two sets with the dₓz and dₓ²₋ᵧ² in a higher energy than the other
probably because of the fact that formerly there were few electron affinity values known for molecules (Table 2.6). Those Lewis acids having large electron affinities are apt to be strong acids. This idea is especially powerful when applied to metal cations. Recall that the electron affinity of a monopositive cation is the same as the ionization energy of the metal atom. From this point of view it is readily apparent why the alkali and alkaline earth metals are such weak Lewis acids when compared to the transition metals:

<table>
<thead>
<tr>
<th>Group</th>
<th>Data Source</th>
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<tbody>
<tr>
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</table>
Crystal Field Theory

The model that largely replaced valence bond theory for interpreting the chemistry of coordination compounds was the crystal field theory, first proposed in 1929 by Hans Bethe. As originally conceived, it was a model based on a purely electrostatic interaction between the ligands and the metal ion. Subsequent modifications, which began as early as 1935 with papers by J. H. Van Vleck, allow some covalency in the interaction. These adjusted versions of the original theory generally are called ligand field theory. It is an interesting feature of scientific history that, although the development of crystal and ligand field theories was contemporary with that of valence bond theory, they remained largely within the province of solid state physics for about 20 years. Only in the 1950s did chemists begin to apply crystal field theory to transition metal complexes.

Pure crystal field theory assumes that the only interaction between the metal ion and the ligands is an electrostatic or ionic one with the ligands being regarded as negative point charges. Despite this rather unrealistic premise, the theory is quite successful in interpreting many important properties of complexes. Moreover, the symmetry considerations involved in the crystal field approach are identical to those of the molecular orbital method. The electrostatic model thus serves as a good introduction to modern theories of coordination chemistry.

In order to understand clearly the interactions that are responsible for crystal or ligand field effects in transition metal complexes, it is necessary to have a firm grasp of the geometrical relationships of the d orbitals. There is no unique way of representing the five d orbitals, but the most convenient representations are shown in Figs. 11.3 and 11.4. In fact, there are six wave functions that can be written for orbitals having the so-called four lobed form (d_σ, d_σ*, d_σ̅, and d_σ̅*). Thus these latter two orbitals have no independent existence, but the d_σ can be thought of as having average properties of the two (Fig. 11.5). Therefore, since both have high electron density along the z axis, the d_σ orbital has a large fraction of its electron density concentrated along the same axis. Also, since one of the component wave functions (d_σ) has lobes along the 3 and the other (d_σ̅) along the 3 direction, the resultant d_σ orbital has a large fraction of its electron density in the xy plane. This xy component, which is often referred to as a “doughnut” or a “collar,” is frequently neglected in pictorial representations, especially when an attempt is being made to portray all five d orbitals simultaneously. Nevertheless, it is important to remember this xy segment of the d_σ orbital.

The five d orbitals in an isolated, gaseous metal ion are degenerate. If a spherically symmetric field of negative charges is placed around the metal, the orbitals will remain degenerate, but all of them will be raised in energy as a result of the repulsion between

14 There is some inconsistency in the use of the label “ligand field theory” among textbooks and other sources. In some instances it is taken as essentially a substitute for the label crystal field theory on the premise that the latter is misleading (see, for example, Schlüter, H. I.; Ghiggino, G. Bonding Principles of Ligand Field Theory: Wiley-Interscience, New York, 1969, p 17). At the other extreme are those who put the term to mean a molecular orbital description of bonding in complexes. It is significant that Van Vleck in his 1935 paper was seeking to reconcile Bethe’s theory with Mulliken’s molecular orbital approach. This effort has been described by Balhausen (see Footnote 13) as “incoherently the best features of both the pure crystal field theory and molecular orbital theory.” It seems appropriate, then, to view ligand field theory as a model that uses its origins to crystal field theory and shares with it a central emphasis on the perturbation of metal valence orbitals by ligands, while at the same time serving as a bridge to the full molecular orbital treatment of complexes.


---

In contrast, Al^{3+} can adequately accommodate six water molecules; however, the nitrogen donor of the ammonia ligands is not sufficiently electronegative to prevent the buildup of excess electron density on aluminum in [Al(NH₃)₆]³⁺, with the result that the complex is unstable.

In apparent contradiction to the electroneutrality principle, there are many complexes in which the metal exists in a low oxidation state and yet is bonded to an element of fairly low electronegativity. Among the most prominent examples are the transition metal carbonyls, a large class of compounds in which the ligand (CO) is bound to the central metal through carbon. The source of stability in these complexes is the capacity of the carbon monoxide ligand to accept a “back donation” of electron density from the metal atom. Within valence bond theory, this process can be described in terms of resonance:

\[
\begin{align*}
\text{Cr} & = \text{O} \rightarrow \text{Cr} \equiv \text{O} \\
(1) & \quad (II)
\end{align*}
\]

To whatever extent canonical form II contributes to the resonance hybrid, electron density will be shifted from chromium to oxygen. A more precise examination of this process indicates that the delocalization of the electron density occurs via overlap of a d orbital on the metal with an orbital of appropriate symmetry on the carbonyl ligand. In valence bond theory, the ligand orbital would be one of the p orbitals of the carbon atom (thus making it unavailable for π bond to the oxygen), whereas the molecular orbital theory would speak in terms of overlap with the π antibonding orbital of carbon monoxide (Fig. 11.2). In either representation a π bond forms between metal and ligand and provides a mechanism for a shift in electron density away from the metal toward the ligand. The formation of π bonds of this type will be discussed at greater length later in this chapter.

---

Fig. 11.2 Effect of metal-ligand π bonding; the Cr—C bond order is increased and the C—O bond order is decreased. (a) VB viewpoint: π bond between d orbital on Cr atom and p orbital on C atom. (b) MO viewpoint: π bond between d orbital on Cr atom and antibonding orbital (π *) on the CO ligand.

---

In fact, since both have high electron density along the z axis, the d_σ orbital has a large fraction of its electron density concentrated along the same axis. Also, since one of the component wave functions (d_σ) has lobes along the z axis and the other (d_σ̅) along the y axis, the resultant d_σ orbital has a large fraction of its electron density in the xy plane. This xy component, which is often referred to as a “doughnut” or a “collar,” is frequently neglected in pictorial representations, especially when an attempt is being made to portray all five d orbitals simultaneously. Nevertheless, it is important to remember this xy segment of the d_σ orbital.
This gets us back to the fundamental property of the ionization energy of a metal that determines not only its redox chemistry but also its tendency to bond to anions and other Lewis bases.23

The evaluation and correlation of strengths of Lewis acids and bases have attracted the interest of many inorganic chemists. Recently gas-phase data have become available, but before that many systems were studied in aprotic, nonpolar solvents. Even today, such solvents allow the collection of large amounts of data by various methods. Solvation effects will be small and, it is hoped, approximately equal for reactants and products such that their neglect will not cause serious errors.

It is common to equate the strength of interaction of an acid and a base with the enthalpy of reaction. In some cases this enthalpy may be measured by direct calorimetry: 

$$\Delta H = q$$

for an adiabatic process at constant pressure.

Often the enthalpy of reaction is obtained by measuring the equilibrium constant of an acid-base reaction over a range of temperatures. If $K$ is plotted versus $1/T$, the slope will be equal to $-\Delta H/\text{R}$. Thus various experimental methods have been devised to measure the equilibrium constant by spectrophotometric methods. Any absorption which differs between one of the reactants (either acid or base) and the acid-base adduct is a potential source of information on the magnitude of the equilibrium constant since it gives the concentration of two of the three species involved in the equilibrium directly and the third indirectly from a knowledge of the stoichiometry of the reaction. For example, consider the extensively studied reaction between organic carbonyl compounds and iodine. The infrared carbonyl absorption is shifted in frequency in the adduct with respect to the free carbonyl compound. Thus the equilibrium mixture exhibits two absorption bands in the carbonyl region of the spectrum (Fig. 9.1) and the relative concentrations of the free carbonyl and the adduct can be obtained.24 Alternatively, one can observe the absorption of the iodine molecule, I$_2$, in the 300-600 nm portion of the visible spectrum. Again, the adduct absorbs at a different frequency than the free iodine and the two absorption maxima provide information on the relative concentrations of the species present.25

Two complications can prevent a simple determination of the concentration of each species from a measurement of absorbance at a chosen frequency. Although most of the acid-base reactions of interest result in a one-to-one stoichiometry, one cannot assume this a priori, and two-to-one and three-to-one adducts might also be present. Fortunately, this is usually an easy point to resolve. The presence of an isosbestic point or point of constant absorbance (see Fig. 9.1) is usually a reliable criterion that only two absorbing species (the free acid or base and a single adduct) are present.26

The second problem is somewhat more troublesome. The separation between the absorption maximum of the adduct and that of the free acid (or base) is seldom large and so there is considerable overlapping of bands (see Fig. 9.1). If the absorptivities of each of the species at each frequency were known, it would be a simple matter to ascribe a proportion of the total absorbance at a given frequency to each species. It is usually a relatively simple matter to measure the absorptivity, $e$, of the free acid (or base) over the entire working range. Since it is often impossible to prepare the pure adduct (in the absence of equilibrium concentrations of free acid and base), its absorptivity cannot be measured. However, if the equilibrium is studied at two different concentrations of acid (or base), it is possible to set up two simultaneous equations in terms of the two unknowns $K$ and $e$ and solve for both.27

Alternative methods of measuring the enthalpy of acid-base reactions involve measuring some physical property which depends upon the strength of the interaction. In general, such methods must be calibrated against one of the previous types of measurement, but once this is done they may often be extended to reactions that prove difficult to measure by other means. One example is the study of phenol as a Lewis acid.28 Phenol forms strong hydrogen bonds to Lewis bases, especially those that have a donor atom with a large negative charge. The formation of the hydrogen bond alters the electron density in the O—H group of the phenol and this O—H stretching frequency in the infrared. Once the frequencies of a series of known phenol-base adducts have been used for calibration (Fig. 9.2), it is possible to estimate the enthalpy of addition formation of bases with similar functional groups directly from IR spectra.

A second method involves the relation between a character and NMR coupling constants. Drago and coworkers29 have shown that there is a good correlation between the 1950-H coupling constant in chloroethylstannane-base adducts and the strength of the base–donor bond. In the free stannane (the strongly bonding methyl groups can maximize their bond strength, a character, and thus $J_{1950}$—31]. It has been suggested that the stronger bases force the tin to rehybridize to a greater extent [32].
include pairing of electrons as well as ligand-metal-ligand bond angles of 90°. Pauling suggested this occurs via hybridization of one (n - 1)d, the a, and two sp orbitals to form four equivalent dsp hybrids directed toward the corners of a square. These orbitals then participate in covalent σ bonds with the ligands, the bonding electron pairs being furnished by the ligands. The eight electrons that were distributed among the five d orbitals in the free ion are assigned as pairs to the four unhybridized metal d orbitals (Fig. 11.1a).

With some ligands, such as Cl⁻, Ni(II) forms four-coordinate complexes that are paramagnetic and tetrahedral. For these cases, VB theory assumes the d orbital occupation of the complex to be the same as that of the free ion, which eliminates the possibility that valence-level d orbitals can accept electron pairs from the ligands. Hybrid orbitals of either the spd or spd² type (the latter involving n-level d orbitals) or a combination of the two provide the proper symmetry for the σ bonds as well as allowing for the magnetic properties (Fig. 11.1b). The examples presented here illustrate a useful rule, originally called "the magnetic criterion of bond type," which allows prediction of the geometry of a four-coordinate d⁴ complex if its magnetic properties are known: diamagnetic = square planar; paramagnetic = tetrahedral.⁹

The valence bond picture for six-coordinate octahedral complexes involves dsp₃ hybridization of the metal (Fig. 11.1c, d). The specific d orbitals that meet the symmetry requirements for the metal-ligand σ bonds are the dₓ² and dₓz, yz (page 390). As with the four-coordinate d⁴ complexes discussed above, the presence of unpaired electrons in some octahedral compounds renders the valence level (n - 1)d orbitals unavailable for bonding. This is true, for instance, for paramagnetic [CoF₄]²⁻ (Fig. 11.1c). In these cases, the VB model invokes participation of n-level d orbitals in the hybridization.

### The Electroneutrality Principle and Back Bonding

One difficulty with the VB assumption of electron donation from ligands to metal ions is the buildup of formal negative charge on the metal. Since this is a problem that arises, in one form or another, in all complete treatments of coordination compounds,保罗 suggested a useful rule, originally called "the magnetic criterion of bond type," which allows prediction of the geometry of a four-coordinate d⁴ complex if its magnetic properties are known: diamagnetic = square planar; paramagnetic = tetrahedral.⁹

Pauling has made semiquantitative calculations correlating the stability of complexes with the charges on the central metal atom. Pauling pointed out why metals would not in fact exist with such unfavorable negative charges. Because donor atoms in general are highly electronegative (e.g., N, O, and the halogens), the bonding electrons will not be shared equally between the metal and ligands. Pauling suggested that complexes would be most stable when the electronegativity of the ligand was such that the metal achieved a condition of essentially zero or low electrical charges. This tendency for zero or low electrical charges on atoms is a rule-of-thumb known as the electroneutrality principle, and it is used to make predictions regarding electronic structure in many types of compounds, not only complexes. Pauling has made semiquantitative calculations correlating the stability of complexes with the charges on the central metal atom. Six typical results are:

<table>
<thead>
<tr>
<th>Metal</th>
<th>Charge</th>
<th>Electronegativity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be²⁺</td>
<td>+2.00</td>
<td>1.12</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>+3.00</td>
<td>0.12</td>
</tr>
<tr>
<td>Si⁴⁺</td>
<td>+4.00</td>
<td>-1.12</td>
</tr>
<tr>
<td>BeOH₂⁺</td>
<td>+2.00</td>
<td>1.12</td>
</tr>
<tr>
<td>Al(OH)₃⁺</td>
<td>3.00</td>
<td>0.12</td>
</tr>
<tr>
<td>Si(OH)₄⁺</td>
<td>4.00</td>
<td>-1.12</td>
</tr>
</tbody>
</table>

Although the above values involve very rough approximations, they do indicate qualitatively how buildup of excessive negative charge on a metal can destabilize a complex. Within the group of complexes shown, [Be(H₂O)₂]⁺ and [Al(OH)₃]⁺ are stable, but the other two are not. Poisonous metals effectively neutralize the +2 ionic charge of beryllium, but toxic water molecules donate too much electron density.


In free Me,SnCl, —Sn—d in the limit of strong base adducts) than weaker ones, and thus the change in a character of the Sn—C bonds.

Systematics of Lewis Acid—Base Interactions

Drago and coworkers have proposed a number of ways of expressing enthalpies of reactions in terms of contributing parameters of acids and bases. The first was

$$
\Delta H = E_A E_B + C_A C_B 
$$

(9.56)

where $\Delta H$ is the enthalpy of formation of a Lewis acid—base adduct, $E_A$ and $E_B$ are parameters characteristic of the acid, and $C_A$ and $C_B$ are parameters characteristic of the base. The $E$ parameters are interpreted as the species to undergo electron transfer (anionic or pseudo-dipole-dipole) interactions and the $C$ parameters are the susceptibility to form covalent bonds. From this we expect those acids which bond well electrostatically ($E_A$ is large) to form the most stable adducts with bases that bond well electrostatically (since the product $E_A E_B$ will then be large). Conversely, acids that bond well covalently will tend to form their most stable adducts with bases that bond well covalently. Some typical values of $E_A$, $E_B$, $C_A$, and $C_B$ are listed in Table 9.6. The application of Eq. 9.56 may be illustrated with the reaction between pyridine ($E = 1.78, C = 3.54$) and iodine ($E = 0.50, C = 2.00$; by definition, the origin of the scale; see Footnotes 30, 36).

$$
\Delta H_{exp} = E_A E_B + C_A C_B = (0.59 \times 1.78) + (2.00 \times 3.54) = (7.97 \text{ kcal mol}^{-1}) + (33.3 \text{ kJ mol}^{-1}) = 7.8 \text{ kcal mol}^{-1} 
$$

The importance of the $E-C$ parameters is manifold. First, they enable predictions to be made of the enthalpies of reactions that have not been studied. Thus the parameters in Table 9.6 and comparable values were obtained from a few hundred

Table 9.6

<table>
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<th>Acid and base parameters</th>
<th>$E_A$</th>
<th>$C_A$</th>
<th>$E_B$</th>
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<td>NH$_3$</td>
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</tr>
<tr>
<td>CH$_3$CN</td>
<td>2.16</td>
<td>1.32</td>
<td>0.39</td>
<td>1.44</td>
<td>0.90</td>
</tr>
<tr>
<td>(CH$_3$)$_2$CN</td>
<td>1.80</td>
<td>4.21</td>
<td>1.84</td>
<td>1.59</td>
<td>1.07</td>
</tr>
<tr>
<td>(CH$_3$)$_3$CN</td>
<td>1.21</td>
<td>3.61</td>
<td>0.75</td>
<td>0.25</td>
<td>1.37</td>
</tr>
<tr>
<td>CH$_2$=CHN</td>
<td>2.35</td>
<td>3.03</td>
<td>0.54</td>
<td>1.06</td>
<td>1.20</td>
</tr>
<tr>
<td>(CH$_3$)$_2$N</td>
<td>1.49</td>
<td>3.37</td>
<td>0.76</td>
<td>1.85</td>
<td>0.90</td>
</tr>
<tr>
<td>HCCl$_2$N$_2$</td>
<td>0.80</td>
<td>6.72</td>
<td>0.82</td>
<td>0.70</td>
<td>0.81</td>
</tr>
<tr>
<td>CH$_2$CN</td>
<td>1.78</td>
<td>3.54</td>
<td>0.73</td>
<td>0.06</td>
<td>1.13</td>
</tr>
<tr>
<td>4-C$_6$H$_5$CN</td>
<td>1.74</td>
<td>3.93</td>
<td>0.73</td>
<td>1.19</td>
<td>0.90</td>
</tr>
<tr>
<td>3-C$_6$H$_5$CN</td>
<td>1.76</td>
<td>3.72</td>
<td>0.74</td>
<td>1.56</td>
<td>0.70</td>
</tr>
<tr>
<td>3-C$_6$H$_5$OH</td>
<td>1.74</td>
<td>3.72</td>
<td>0.74</td>
<td>1.56</td>
<td>0.70</td>
</tr>
<tr>
<td>OCH$_2$Cl$_2$</td>
<td>1.64</td>
<td>0.71</td>
<td>0.83</td>
<td>0.24</td>
<td>1.03</td>
</tr>
<tr>
<td>OCH$_2$COOH</td>
<td>1.74</td>
<td>1.67</td>
<td>0.80</td>
<td>2.78</td>
<td>0.30</td>
</tr>
<tr>
<td>OCH$_2$COOH$_2$</td>
<td>1.62</td>
<td>0.98</td>
<td>0.89</td>
<td>1.92</td>
<td>0.71</td>
</tr>
<tr>
<td>HCOOHCOOH$_2$</td>
<td>2.15</td>
<td>3.41</td>
<td>0.74</td>
<td>9.73</td>
<td>4.28</td>
</tr>
<tr>
<td>(CH$_3$)$_2$O</td>
<td>1.80</td>
<td>1.63</td>
<td>0.76</td>
<td>5.70</td>
<td>12.30</td>
</tr>
<tr>
<td>CH$_3$COOH$^+$</td>
<td>1.64</td>
<td>0.29</td>
<td>0.75</td>
<td>6.74</td>
<td>5.86</td>
</tr>
<tr>
<td>CH$_3$COO$^-$</td>
<td>1.20</td>
<td>2.02</td>
<td>0.74</td>
<td>7.32</td>
<td>4.62</td>
</tr>
<tr>
<td>HCOH$_2$SO</td>
<td>0.24</td>
<td>0.35</td>
<td>1.06</td>
<td>0.43</td>
<td>4.60</td>
</tr>
<tr>
<td>4-C$_6$H$_5$COOH</td>
<td>1.20</td>
<td>4.42</td>
<td>0.77</td>
<td>10.03</td>
<td>9.73</td>
</tr>
</tbody>
</table>


Tentative parameters from limited enthalpy data.

If not indicated otherwise, the bases in this table have $E_B$ and $C_B$ determined from the fit of neutral acid—neutral base adducts (Footnote 39).

The $E_A$ and $C_A$ for these bases are well determined. The $T_B$ values are tentative for these have been determined from limited data. See the original papers for methods and accuracy of the values.
A second important contribution that Werner made to the study of coordination chemistry was the postulate that the bonds to the ligands were fixed in space and therefore could be treated by application of structural principles. By means of the numbers and properties of the isomers obtained, Werner was able to assign the correct geometric structures to many coordination compounds long before any direct experimental method was available for structure determination. Werner's method was that used previously by organic chemists to elucidate the structures of substituted benzenes, namely isomer counting. Werner postulated that the six ligands in a complex such as \(\text{Co(NH}_3\text{)}_6^{2+}\) were situated in some symmetrical fashion with each NH group equidistant from the central cobalt atom. Three such arrangements come to mind: a planar hexagon—similar to the benzene ring—and two polyhedra, the trigonal prism and the octahedron. The trigonal prism is closely related to the octahedron, being formed by a 60° rotation of one of the trigonal faces of the octahedron (in fact, the octahedron can be considered a trigonal antiprism). For a "disubstituted" complex, \(\text{MA}_2\text{B}_4\), the planar arrangement gives three isomers, the familiar ortho, meta, and para arrangements of organic chemistry. The trigonal prism yields three isomers also, but there are only two octahedral arrangements for this formulation. The total number of isomers expected for each geometrical arrangement together with the experimental results for various compositions are listed in Table 11.2.

In every case Werner investigated, the number of isomers found was equal to that expected for an octahedral complex. For \(\text{Co(NH}_3\text{)}_6\text{Cl}_3\text{Cl}\), for example, two isomers (one violet and one green) were observed. Although the correlation here was perfect, it must be borne in mind that the observation of two instead of three isomers for this compound and others constitutes negative evidence concerning the structure of these complexes. Even though Werner worked carefully and examined many systems, there was always the possibility, admittedly small, that the third isomer had escaped his detection. The failure to synthesize a compound, to observe a particular property, or to effect a particular reaction can never be positive proof of the nonexistence of that compound, property, or reaction. It may simply reflect some failure in technique on the part of the chemist. One well-known example of the fallacy of negative evidence involves the overthrow of the dogmatic belief in the chemical inertness of the noble gases (see Chapter 17).

Werner was correct, however, in his conclusions concerning the octahedral geometry of coordination number 6 for cobalt(III) and platinum(IV). He was also correct, and on a firmer logical footing, in his assignment of square planar geometries to the four-coordinate complexes of palladium and platinum from the fact that two isomers had been isolated for compounds of formula \(\text{MA}_2\text{B}_4\). The most likely alternative structure, the tetrahedron, would produce only one isomer for this compound. The ability of Werner and others to assign the correct structures from indirect data and logic was hailed by Henry Eyring:

"The ingenuity and effective logic that enabled chemists to determine complex molecular structures from the number of isomers, the reactivity of the molecule and of its fragments, the freezing point, the empirical formula, the molecular weight, etc., is one of the outstanding triumphs of the human mind."

There has been much work done in attempting to formulate theories to describe the bonding in coordination compounds and to rationalize and predict their properties. The first success along these lines was the valence bond (VB) theory applied by Linus Pauling and others in the 1930s and following years. In the 1950s and 1960s the crystal field (CF) theory and its modifications, generally known under the label ligand field theory, gained preeminence and in turn gradually gave way to the molecular orbital (MO) theory. Although both the valence bond and crystal field theories have been largely displaced as working models for the practicing inorganic chemist, they continue to contribute to current discussions of coordination compounds. Because they shaped the thinking about these compounds in the very recent past, the earlier models still serve as the background against which newer ones are evaluated. Moreover, certain of their features remain part of the conceptual framework and vocabulary used by current chemists. Hence they must be appreciated in order to have a full understanding of modern constructs.

From the valence bond point of view, formation of a complex involves reaction between Lewis bases (ligands) and a Lewis acid (metal or metal ion) with the formation of coordinate covalent (or dative) bonds between them. The model utilizes hybridization of metal s, p, and d valence orbitals to account for the observed structures and magnetic properties of complexes. For example, complexes of Ni(II) and Pt(II) are usually four-coordinate, square planar, and diamagnetic, and this arrangement is often found for Ni(II) complexes as well. Inasmuch as the free ion in the ground state in each case is paramagnetic \((s^2 \Perp P)\), the bonding picture has to

---

Table 11.2 Numbers of isomers expected and found for C.N. = 6

<table>
<thead>
<tr>
<th>Formula</th>
<th>Planar</th>
<th>Trigonal prismatic</th>
<th>Octahedral</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA₂B₂</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>MA₂B₃</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>MA₃B₃</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

---

6 The first crystallographic confirmation of Werner's assignment of octahedral geometry to Pt(IV) complexes was not until 1921, some twenty years after his theories were completed (Wyckoff, R. W. G.; Pemmaraju, S. J. Am. Chem. Soc. 1921, 43, 2292-2300; [NIJ]₃PtCl₃). The square planar structure of Pt(II) complexes was confirmed the next year (Dickinson, R. G. J. Am. Chem. Soc. 1922, 44, 2404-2411; [NH₃]₂PtCl₄). The square planar structure of Pt(II) complexes was not published until 1921, some twenty years after his theories were completed (Wyckoff, R. W. G.; Pemmaraju, S. J. Am. Chem. Soc. 1921, 43, 2292-2300; [NIJ]₃PtCl₃). The square planar structure of Pt(II) complexes was confirmed the next year (Dickinson, R. G. J. Am. Chem. Soc. 1922, 44, 2404-2411; [NH₃]₂PtCl₄). Interestingly, neither major revision of Werner's work is immediately clear. Eyring, H. Chem. Eng. News 1963, 4(11), 5.

338 9-Acid-Base Chemistry

reactions of acids and bases, but they can be used to predict the enthalpies of thousands of reactions. For example, accurate values can be obtained for reactions such as:

\[(\text{CH}_3)_2N + \text{SO}_2 \rightarrow (\text{CH}_3)_2\text{NSO}\_2\]  \hspace{1cm} (9.58)

\[\Delta H_{\text{aco}} = 38.5 \text{ kJ mol}^{-1} (9.2 \text{ kcal mol}^{-1})\]

\[\Delta H_{\text{exp}} = 40.2 \text{ kJ mol}^{-1} (9.6 \text{ kcal mol}^{-1})\]

\[(\text{CH}_2)_2\text{C} \_\text{O} + \text{HOC}_2H_5 \rightarrow \left[\begin{array}{c}
\text{O} \\
\text{CH}_2CH_3 \\
\text{O} \\
\text{CH}_2CH_3 \\
\text{O} \\
\text{HOC}_2H_5 \\
\text{CH}_2CH_3 \\
\text{O} \\
\text{CH}_2CH_3 \\
\text{O} \\
\text{HOC}_2H_5
\end{array}\right]\]  \hspace{1cm} (9.59)

\[\Delta H_{\text{aco}} = 23.4 \text{ kJ mol}^{-1} (5.6 \text{ kcal mol}^{-1})\]

\[\Delta H_{\text{exp}} = 23.4 \text{ kJ mol}^{-1} (5.6 \text{ kcal mol}^{-1})\]

The second item of importance with respect to parameters of this sort is that they enable us to obtain some insight into the nature of the bonding in various systems. Thus, if we compare the \(E_P\) and \(E_B\) parameters of iodine and phenol, we find that \(E_B\) is twice as good a "covalent-bonder" as phenol, but that the latter is about five times as effective through electrostatic attractions. This is not unexpected inasmuch as phenol, \(\text{C}_5\text{H}_4\text{OH}\), is a very strong hydrogen bonding species. In contrast, iodine has no dipole moment but must react with a Lewis base by expanding its octet and accepting electrons to form a covalent bond.

A similar effect can be observed in the bases. The \(E_B\) value of dimethylsulfoxide, \((\text{CH}_3)_2\text{SO}\), is much larger than that of diethylsulfoxide, \((\text{CH}_2)_2\text{S}\), corresponding to the large dipole moment of \((\text{CH}_3)_2\text{SO}\) (\(\mu = 13.2 \times 10^{-30} \text{ C m} = 3.96 \text{ D}\)) compared with that of the latter (\(\mu = 5.14 \times 10^{-30} \text{ C m} = 1.56 \text{ D}\)). On the other hand, the \(E_P\) values are reversed, corresponding to the enhanced ability of the sulfur atom to bond covalently to the acid.

Drago and coworkers have modified Eq. 9.56 by adding a constant specified by the acid (acceptor).

\[-\Delta H = E_P E_B + C_P C_B - W\]  \hspace{1cm} (9.60)

Eq. 9.56 deals with a simplified situation: the approach of \(A\) and \(B\) to the bond distance with a resultant \(E_P E_B\) electrostatic energy based on the inherent electrostatic bonding capabilities (dipole-dipole interactions, etc.) and a resultant \(C_P C_B\) term based on the inherent covalent bonding capabilities (related to overlap, etc.). This approximation is quite good for neutral species, and small discrepancies (such as the increase in covalency through electrostatic polarization) could be (and have been) accommodated by incorporating them into the \(E_P\) and \(C_B\) parameters.

34 One must be careful in making comparisons using these numbers. A comparison of \(E_P\) to \(E_{\text{trans}}\) is valid, but one cannot compare the \(E\) and \(C\) parameters directly against each other for a single species because of the necessary, arbitrary assignments: \(E_P = 0.50\); \(C_B = 2.00\).

35 Drago, R. S.; Wong, N.; Blgurin, C.; Vogel, G.-G. Am. Chem. Soc. 1977, 78, 9-14. The constant \(W\) is for an energy always associated with a particular reaction, such as the endlability of dissociation of a dimer allowing it to react as a monomer.

36 By adjusting \(E\) and \(C\) to give the best fit of the experimental data, some of the neglect of transfer energy can be alleviated.

If the amount of charge transfer from base to acid is large, however, as it must be if either species, or both, is an ion, this energy must be explicitly accounted for. Fundamentally, it is the energy change as an atom (ion) runs along the energy-change curve of Fig. 5.32. Thus, this transfer energy term parallels ionization energies and, to a lesser extent, also involves electron affinities.36 It can be treated by adding a term composed of two additional parameters: \(K_R\) (acceptance, energy) and \(T_E\) (transmission, base).36

\[-\Delta H = E_P E_B + C_P C_B + R_k T_E\]  \hspace{1cm} (9.61)

Two processes illustrate the application of Eq. 9.61:

\[\text{H}_2\text{O} + \text{H}^+ \rightarrow \text{H}_3\text{O}^+\]

\[\Delta H_{\text{aco}} = 695 \text{ kJ mol}^{-1} (166 \text{ kcal mol}^{-1})\]  \hspace{1cm} (9.62)

\[\Delta H_{\text{exp}} = 696 \text{ kJ mol}^{-1} (159.9 \text{ kcal mol}^{-1})\]  \hspace{1cm} (9.63)

\[\text{CH}_3\text{O} + \text{H}^+ \rightarrow (\text{CH}_3)\text{O}^+\]

\[\Delta H_{\text{aco}} = 803 \text{ kJ mol}^{-1} (192 \text{ kcal mol}^{-1})\]  \hspace{1cm} (9.64)

\[\Delta H_{\text{exp}} = 795 \text{ kJ mol}^{-1} (191.1 \text{ kcal mol}^{-1})\]  \hspace{1cm} (9.65)

The last term represents the energy accompanying the transfer of electron density from an electron-rich base to an electron-poor acid. The details need not concern us, but the results certainly are of interest:

1. To obtain a complete picture of bonding in acid-base interactions, three separate factors must be taken into account: a) the electrostatic energy associated with the acid-base interaction; b) the covalent energy of the acid-base interaction; c) the energy involved when electron transfer takes place. These results were anticipated in principle on the basis of Mulliken-Jaffe electronegativity.37

2. In the gas phase the proton is a tremendous acceptor of electron density, and the transfer energy is very large. This transfer energy has already been largely "spent" for the solvated proton (e.g., hydronium ion) in solution where the reactions are of a displacement type:

\[\text{H}_3\text{O}^+ + \text{NH}_3 \rightarrow \text{H}_2\text{O} + \text{NH}_4^+\]  \hspace{1cm} (9.66)

37 The neglect of the electron affinity in electronegativity can often be justified because in \(\chi_M = \Delta H_{\text{aco}} + E_A\), the value of \(E_A\) may be an order of magnitude larger than that of EA. Thus a two-parameter system may be approximated by a one-parameter equation. However, the recent development in acid-base theory reported from here to the end of the chapter reflects the realization that acid-base interactions are more subtle than one-parameter equations predict. For a direct comparison, note how well a one-parameter electronegativity system (Pauling's) works, in general, even though electronegativity is obviously a two-parameter function (Mulliken-Jaffe). See also discussion on page 361.


39 Evans, R. S.; Huber, L. J. J. Inorg. Nucl. Chem. 1970, JJ, 777-793. The approach here involved the reverse process: First electronegativity equilibration was assumed (equally optimizing the electron transfer energy) and then modifications for ionic and covalent contributions were added. This worked best on ion-ion interactions (Li\(^+\) + F\(^-\) \(\rightarrow\) Li\(^+\)F\(^-\)) and more poorly on neutral molecules (H\(_2\)O and HF, unpublished). See page 351.
and to none, and had not been prejudiced by some of the theories of valence current in his day, he might well have achieved the same results and fame as Werner. Werner, in formulating his ideas about the structure of coordination compounds, had before his facts such as the following. Four complexes of cobalt(III) chloride with ammonia had been discovered and named according to their colors:

<table>
<thead>
<tr>
<th>Complex</th>
<th>Color</th>
<th>Early name</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoCl₂ 6NH₃</td>
<td>Yellow</td>
<td>Laito complex</td>
</tr>
<tr>
<td>CoCl₂ 5NH₃</td>
<td>Purple</td>
<td>Purpur complex</td>
</tr>
<tr>
<td>CoCl₂ 4NH₃</td>
<td>Green</td>
<td>Praseo complex</td>
</tr>
<tr>
<td>CoCl₂ 4NH₃</td>
<td>Violet</td>
<td>Violeo complex</td>
</tr>
</tbody>
</table>

One of the more interesting facts about this series is that two compounds have identical empirical formulas, CoCl₂ 4NH₃, but distinct properties, the most noticeable being a difference in color. Furthermore, Werner noted that the reactivities of the chloride ions in these four compounds differed considerably. Addition of silver nitrate resulted in different amounts of precipitated silver chloride:

\[
\begin{align*}
\text{CoCl}_2 \cdot 6\text{NH}_3 + \text{excess Ag}^+ & \rightarrow 3\text{AgCl}(s) \quad (11.1) \\
\text{CoCl}_2 \cdot 5\text{NH}_3 + \text{excess Ag}^+ & \rightarrow 2\text{AgCl}(s) \quad (11.2) \\
\text{CoCl}_2 \cdot 4\text{NH}_3 + \text{excess Ag}^+ & \rightarrow 1\text{AgCl}(s) \quad (11.3)
\end{align*}
\]

Reaction 11.1 occurs for both the praseo and violeo complexes.

The correlation between the number of ammonia molecules present and the number of equivalents of silver chloride precipitated led Werner to the following conclusion:

"We can thus make the general statement: Compounds M(NH₃)ₓXₜ [M = Cr, Co; X = Cl, Br, etc.] are derived from compounds M(NH₃)ₓXₜ by loss of one ammonia molecule. With this loss of an ammonia molecule, however, a simultaneous change in function of one acid residue X [= chloride ion] occurs...[In Co(NH₃)₄Cl₂]...two chlorine atoms behave as ions and are precipitated by silver nitrate at room temperature, while the third behaves completely analogously to chlorine in chloroform, that is, it no longer acts as an ion."

From this conclusion Werner postulated perhaps the most important part of his theory, that in this series of complexes cobalt exhibits a constant coordination number of 6, and as ammonia molecules are removed, they are replaced by chloride ions which then act as though they are covalently bound to the cobalt rather than as free chloride ions. To describe the complex chemistry of cobalt, one must therefore consider not only the oxidation state of the metal but also its coordination number.

Werner thus formulated these four salts as [Co(NH₃)₄Cl₂], [Co(NH₃)₃Br₂], and [Co(NH₃)₃Cl₃].

Realizing that these formulations implied a precise statement of the number of ions formed in solution, Werner chose as one of his first experimental studies measurement of the conductivities of a large number of coordination compounds. Some of the results of this work are listed in Table 11.1 together with values for simple ionic compounds for comparison.

### Table 11.1

<table>
<thead>
<tr>
<th>Complex</th>
<th>Conductivity</th>
<th>Werner formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>123.7</td>
<td>[Pt(NH₃)₄Cl₂]</td>
</tr>
<tr>
<td>PCl₅ 2NH₃</td>
<td>96.8</td>
<td>[Pt(NH₃)₄Cl₂]</td>
</tr>
<tr>
<td>PCl₅ 2NH₃</td>
<td>106.8</td>
<td>[Pt(NH₃)₄Cl₂]</td>
</tr>
<tr>
<td>PCl₅ 2NH₃</td>
<td>260.8</td>
<td>[Pt(NH₃)₄Cl₂]</td>
</tr>
<tr>
<td>CoCl₂ 3NH₃</td>
<td>261.3</td>
<td>[Co(NH₃)₃Cl₃]</td>
</tr>
<tr>
<td>CoCr₂ 3NH₃</td>
<td>267.6</td>
<td>[Co(NH₃)₃Br₂]</td>
</tr>
<tr>
<td>CoCl₂ 3NH₃</td>
<td>260.2</td>
<td>[Co(NH₃)₃Cl₃]</td>
</tr>
<tr>
<td>CrBr₂ 3NH₃</td>
<td>268.1</td>
<td>[Co(NH₃)₃Br₂]</td>
</tr>
<tr>
<td>PCl₅ 2NH₃</td>
<td>228.9</td>
<td>[Pt(NH₃)₄Cl₂]</td>
</tr>
<tr>
<td>PCl₅ 2NH₃</td>
<td>256.8</td>
<td>[Pt(NH₃)₄Cl₂]</td>
</tr>
<tr>
<td>LaCl₃</td>
<td>393.5</td>
<td>[La(NH₃)₃Cl₃]</td>
</tr>
<tr>
<td>CoCl₂ 6NH₃</td>
<td>413.6</td>
<td>[Co(NH₃)₄Cl₂]</td>
</tr>
<tr>
<td>CoBr₂ 6NH₃</td>
<td>425.9</td>
<td>[Co(NH₃)₄Br₂]</td>
</tr>
<tr>
<td>CrCl₃ 6NH₃</td>
<td>441.7</td>
<td>[Co(NH₃)₄Cl₂]</td>
</tr>
<tr>
<td>PCl₅ 2NH₃</td>
<td>404</td>
<td>[Pt(NH₃)₄Cl₂]</td>
</tr>
<tr>
<td>PCl₅ 4NH₃</td>
<td>522.9</td>
<td>[Pt(NH₃)₄Cl₂]</td>
</tr>
</tbody>
</table>

*This is the molar conductivity measured at a concentration of 0.001 M. Values are from Werner and Mischel, except for [Pt(NH₃)₄Cl₂], which is from Vodopjev, N.; Chaube, L. A. *Compt. rend.* 1925, 160, 840.

*The theoretical value is, of course, zero, but impurities or a reaction with the solvent water could produce a small concentration of ions.*

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3 Werner, A. *Z. Anorg. Chem.* 1959, 267-268. For a translation see the second reference in Footnote 2. All bracketed material and ellipses are ours.

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For Werner's terminology and symbolism differed in small, relatively unimportant ways from that used today. For example, Werner referred to oxidation state as "primary valency" (Hauptvalenz) and coordination number as "secondary valency" (Nachvalenz). Also, he wrote formulas as [Co(NH₃)₄Cl₂], instead of [Co(NH₃)₄Cl₂].
3. The nearest anionic analogue of $H^+$ is the $F^-$ ion. Some of the calculations for it are at first surprising, but parallel those of the proton and are acceptable under closer scrutiny: (a) $F^-$ forms a stronger covalent bond than $Cl^-$ ($\text{Br}^+ > \text{I}^-$)28. (b) $F^-$ is a very strong base with a large transfer of electron density to the acid. This is a result of the low charge capacity (low electron affinity) of fluorine.

4. As with any successful model, exceptions call attention to themselves and signal the existence of unusual effects: repulsions, $\pi$-bonding, or adduct geometry variation.

**Bond Energies**

There are two ways to approach the formation of a polar bond $X^+ - Y^-$. We have already encountered both. One is to consider the formation of a nonpolar molecule, $X-Y$, followed by an electronegativity-controlled shift of electron density from $X$ towards $Y$. Alternatively, one can form the ions $X^+$ and $Y^-$, followed by their interaction. We can view the latter as the Fajans polarization of $Y$ by $X^+$, or basic towards $Y$. Ultimately, inherent in the bond $A-B$ is the covalent energy term arising from the overlap of orbitals, whether it be from the covalent bond picture or polarization of ionic species.

We can now examine in further detail the $E$, $C$, $R$, and $T$ parameters of Drago's system. We have seen that $E_xE_y$ and $C_xC_y$ terms indicate tendencies to form electrostatic ($E_x$) or covalent ($E_y$) acid-base interactions. Finally, the $R_xR_y$ term provides a measure of $E_x$ which can be clearly shown to be related to $15-E_A$ energy (see page 339). Note, however, that in contrast to the ion-pair example given above, where $E_x-E_A$ ($E_y$) was destabilizing, in covalent acid-base reactions of ionic species, the $E_y$ term will be strongly stabilizing. This is especially true of species such as $H^+$ and $F^-$, in accordance with the electronegativity argument given above, and the $R_xR_y$ term will be a major contributor to the stabilization of the donor-acceptor bond.

An example of the importance of the energy associated with this transfer of electron density is found in covalent acid-base reactions of ionic species. Because of the very large value of electron transference energy (resulting from the high ionization energy of hydrogen), the energy associated with the gas-phase attachment of $H^+$ to bases (proton affinity) is unique; other acids, including the aurochloridion ion, are different. This is because the bare proton has an extremely high charge/size ratio and releases an extremely large amount of $E_x$ upon addition formation ($E_x = 130.21$) compared to all other acids that have several atoms over which to delocalize the cationic charge. This is analogous to the $b$ parameter of Mulliken-Laidlaw electronegativity (see Chapter 5), which measures the capacity of a group to "soak up" charge and stabilize it. Thus methyl groups can stabilize charge on a cation (have a low electronegativity $b$ term) for exactly the same reason that as ions they have lower $R_x$ values than the proton ($R_x = 55.09$).

In reactions between Lewis acids and bases such as amines and boranes or boron halides, bulky substituents on one or both species can affect the stability of the acid-base adducts. Perhaps the most straightforward type of effect is simple steric hindrance between substituents on the nitrogen atom and similar large substituents on the boron atom. Figure 9.3 is a diagrammatic sketch of the adduct between molecules of tripropylamine and triethylborane. This phenomenon is known as front or "F-

---

28 This is merely the consequence of smaller ions having better overlap. The usual prejudice that fluorine cannot bond covalently arises from the unfortunate tendency to overemphasize the difference between covalent and ionic bonding. Bonding is too often characterized as covalent or ionic, rather than possibly covalent and ionic.

10.10 Consider each of the following solvents individually: (1) ammonia, (2) acetic acid, (3) sulfuric acid.
a. Give equations for autoionization of the pure solvent.
b. Discuss what will happen if CH₃COONH₄ is dissolved in each of the solvents, that is, what ions will form. Give appropriate equations. Will the solution be acidic or basic with respect to the pure solvent? Will the solute act as a weak or strong acid (base)?
c. Give an example of a strong base, a strong acid, and a neutralization reaction.

10.11 As a working hypothesis, assume that you accept the solvent system picture of OPCI₇ and a value of 5 x 10⁻¹⁴ mol L⁻¹ for the ion product. Set up a pH scale for OPCI₇, draw the equivalent of Fig. 10.1 for it, and discuss how you would go about obtaining data for compounds to complete your diagram.

10.12 The stability constant, K, for Au(CN)₃⁻ is defined as 

\[ K = \frac{[Au(CN)_3]^-}{[Au^3+][CN^-]} \]

a. From the E° of +0.60 V for Eq. 10.131 estimate K.
b. Qualitatively describe why this complex is so stable.

c. When solutions (a) or (b) are evaporated carefully in vacuo.
d. When (a) is treated with Fe₃O₄.

How can (d) he considered a leveling reaction?

10.13 Single-crystal "cesium electride" is almost entirely diamagnetic. Reconcile this with the formulation [Cs(ligand)]e⁺. Is there a paradox here?

10.14 Correlate the behavior of various solutes in "superacids" with their gas-phase proton affinities. What factors besides proton affinities affect their solution chemistry? Predict what species will be present when XH₃ (Group VA, 15), H₂X (Group VIA, 16) and HX (Group VIIA, 17) are dissolved in "superacids."²²

10.15 On page 372, HgCl₂ is mentioned as an exception to the obviously intuitive rule that "good acceptors should not be good donors, and vice versa." Can you suggest a reason why Hg(II) might be paradoxical?

10.16 Suggest equilibria for the redox chemistry at an aluminum electrode and show how the potential can be related to the (Cl⁻)²⁻.

10.17 On page 376 it was stated that one of the difficulties with the cell described there was diffusion of CuCN. Explain.

10.18 In the diffusion discussed on page 376 and in Problem 10.17 a fatal flaw? (Hint: Recall what you know from general chemistry about a simple aqueous cell: Zn | Zn²⁺ || Cu | Cu²⁺.)

"Proton Sponges" and can have a considerable influence on the stability of the adduct since the alkyl groups tend to sweep out large volumes as they rotate randomly.

A second, similar effect is known as "back strain." It results from the structural necessity for the nitrogen atom in amines to be approximately tetrahedral, in order to bond effectively through its lone pair. If the alkyl groups on the nitrogen atom are sufficiently bulky, presumably they can force the bond angles of the amine to open up, causing more s character to be used in these bonds and more p character to be left in the lone pair. The extreme result of this would be the formation of a planar, trigonal molecule with a lone pair in a pure p orbital, poorly suited for donation to an acid (Figure 9.4).

Related to B-strain, but less well understood, is "I-strain" (see internal strain). In cyclic amines and ethers, such as (CH$_3$)$_2$O, the basicity varies with ring size. In such compounds the hybridization (and hence the overlapping ability and electronegativity) of not only the basic center (N, O, etc.), but also of the carbon atoms in the ring will vary with ring size, and there are no simple rules for predicting the results.

When the basic center is exocyclic, as in lactams, lactones, etc., the results can be interpreted in a straightforward way analogous to the argument given previously (Chapter 5) for biphenylene. Consider the series of lactams:

As the ring size is reduced, the internal bond angles must reduce, and the hybridization of the cyclic atoms must have less s character and lower electronegativity. Toward the exocyclic oxygen atom, the basic center, the cyclic carbon atom must in turn exhibit greater s character and a higher electronegativity. The carbonyl groups in small ring compounds are therefore less basic.

Although steric effects and strain always work against basicity in simple molecules and monocyte compounds, there are a few compounds in which the steric and strain effects stabilize the H$^+$ adduct, increasing the basicity. An example is the 1,8-bis(dimethylamino)napthalene molecule in which steric hindrance of the methyl groups and repulsions of lone pairs on the nitrogen destabilize the free base:

![Diagram of a molecule](image)

Fig. 9.4 B-strain in substituted amines: (a) small substituents, no strain, good base; (b) moderate strain from intermediate-sized substituents, some rehybridization; (c) extreme bulkiness of substituents, nitrogen atom forced into planar, ap + p hybridization, weak base.

For a review of steric effects and basicity, including cyclic compounds and proton sponges, see Alder, R. W. Chem. Rev. 1989, 89, 1215-1221. Note that many proton sponges have low solubilities in pure water.

Such compounds are very basic (pK$_b$ = 1.9; cf. NH$_3$, pK$_b$ = 4.74; 1-dimethylaminoanthelene, pK$_b$ = 4.57), and have been nicknamed "proton sponges" from their avidity for hydrogen ions. The strong, symmetric N-H-N hydrogen bond (see Chapter 8) stabilizes the conjugate base. Note, however, that a second proton cannot be added without incurring the original steric problem: Diprotonation is only half complete in 80% sulfuric acid!
Table 10.6

<table>
<thead>
<tr>
<th>Pyrometallurgy</th>
<th>Hydrometallurgy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy</td>
<td>Because high temperatures are involved in dissolution processes, they require little energy; although reaction rates are slow. However, a requirement for electrowinning or for cleaning effluents may more than offset this energy advantage.</td>
</tr>
<tr>
<td>consumption</td>
<td>Because low temperatures are involved in dissolution processes, they require little energy; although reaction rates are slow. However, a requirement for electrowinning or for cleaning effluents may more than offset this energy advantage.</td>
</tr>
<tr>
<td>Dust</td>
<td>Most processes emit large amounts of dust, which must be recovered to abate pollution or because the dust itself contains valuable metals; equipment for dust recovery is bulky and expensive.</td>
</tr>
<tr>
<td>Toxic gases</td>
<td>Many processes generate toxic gases, so that reactors must be gas-tight and the gases removed by scrubbers or other systems; this is expensive, especially when the gases are hot and corrosive.</td>
</tr>
<tr>
<td>Solid residues</td>
<td>Many residues, such as slags, are coarse and harmless, so that they can be stored in exposed piles without danger of dissolution, although the piles may be esthetically unappealing.</td>
</tr>
<tr>
<td>Treatment of sulfide ores</td>
<td>Sulfur dioxide is generated, which in high concentrations must be converted to sulfuric acid (for which a market must be found) and in low concentrations must be disposed in other ways (available but expensive).</td>
</tr>
<tr>
<td>Treatment of complex ores</td>
<td>Unsuitable because separation is difficult.</td>
</tr>
<tr>
<td>Treatment of low-grade ores</td>
<td>Unsuitable because large amounts of energy are required to melt gangue materials.</td>
</tr>
<tr>
<td>Economics</td>
<td>Best suited for large-scale operations requiring a large capital investment.</td>
</tr>
</tbody>
</table>

Problems

10.1 Suggest the specific chemical and physical interactions responsible for the reversal of Eqs. 10.3 and 10.4 in water and ammonia solutions.

10.2 Using a Born-Haber cycle employing the various energies contributing to the formation of $\text{NH}_3$, $\text{CH}_4$, $\text{H}_2$, and $\text{O}_2$, explain why such solutions form only with the most active metals.

10.3 When 1 mol of $\text{N}_2\text{O}_4$ is dissolved in sulfuric acid, 2 equivalents of base are produced. Conductivity studies indicate that $\eta = 6$ for $\text{N}_2\text{O}_4$. Propose an equation representing the solvolysis of $\text{N}_2\text{O}_4$ by sulfuric acid.

10.4 What is the strongest acid listed in Fig. 10.1? The strongest base?

10.5 From Fig. 10.1 determine how the following solutes will react with the solvents, and how the equilibria will lie, that is, will the solute be completely leveled or in equilibrium? State whether the solvent formed in each case will be more acidic or more basic than the pure solvent.

<table>
<thead>
<tr>
<th>Solute</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{SO}_4$</td>
<td>Acetic acid</td>
</tr>
<tr>
<td>$\text{H}_2\text{SO}_4$</td>
<td>Water</td>
</tr>
<tr>
<td>$\text{H}_2\text{SO}_4$</td>
<td>Ammonia</td>
</tr>
<tr>
<td>$\text{CH}_3\text{COOH}$</td>
<td>Ammonia</td>
</tr>
<tr>
<td>$\text{CH}_3\text{COOH}$</td>
<td>Water</td>
</tr>
<tr>
<td>$\text{PhNH}_2$</td>
<td>Ammonia</td>
</tr>
<tr>
<td>$\text{PhNH}_2$</td>
<td>Water</td>
</tr>
<tr>
<td>$\text{PhNH}_2$</td>
<td>Acetic acid</td>
</tr>
<tr>
<td>$\text{PhNH}_2$</td>
<td>Sulfuric acid</td>
</tr>
</tbody>
</table>

10.6 Construct the Latimer diagram for manganese in basic solution (from values in Table F.1), and predict which oxidation states will be stable. Explain the source of instability for each unstable species.

10.7 Calculate the potential for the oxidation of $\text{UO}_2^+$ to $\text{UO}_2^{2+}$ in acid solution from the following information.

- $\text{UO}_2^+ + e^- \rightarrow \text{UO}_2^{2+}$, $E^\circ = 0.16$ V
- $\text{UO}_2^{2+} + e^- \rightarrow \text{UO}_2^{3+}$, $E^\circ = 0.16$ V

10.8 Use the Latimer diagram for plutonium in acid solution below to answer the following questions.

$$\left(\text{PuO}_2^{2+}\right) \rightleftharpoons \text{PuO}_2^{3+} + \text{H}_2\text{O}$$

a. Would you expect plutonium metal to react with water?
b. $\text{Pu}^{4+}$ is stable in concentrated acid but disproportionate to $\text{PuO}_2^{2+}$ and $\text{Pu}^{3+}$ at low acidities. Explain.
c. $\text{PuO}_2^{3+}$ leads to disproportionation to $\text{Pu}^{4+}$ and $\text{Pu}^{3+}$. Under what pH conditions would this reaction be least likely to occur?

10.9 With equations and words describe what happens when metallic potassium is dissolved in ammonia to form a dilute solution.
b. When more potassium is added to form concentrated solutions.
Hence the basicity of the amines is enhanced in proportion to the extent of solvation of the conjugate ammonium ion, and the energies of solvation are $\text{RNH}_3^+ > \text{RNH}_2OH > \text{R}^2\text{OH} > \text{R}^3\text{OH}$ with the "explaining" being that the electron-releasing alkyl groups force electron density onto the oxygen of the conjugate base making it more basic. But note that the electronegativities of branched and unbranched alkyl groups are practically identical, and if there is any trend, those groups having more carbon atoms are slightly more electronegative: Me $= 2.36$, Et $= 2.32$, $f$/Pr $= 2.34$, $i$/Bu $= 2.36$ (see Table 5.7). However, these groups differ significantly in their charge capacity (Chapter 5). Thus highly branched groups are both better donors (when attached to electronegative centers) and better acceptors (when attached to electropositive centers). Seemingly paradoxical (but refer again to Figs. 2.13 and 5.34) $O^\ominus$ is electropositive; the oxygen atom will be stabilized if the anionic charge is delocalized. This can best be accomplished by groups with larger charge capacities.

Relative to the hydrogen atom (1.0), the charge capacities of groups are Me $= 2.8$, Et $= 3.4$, $f$/Pr $= 3.9$, and $i$/Bu $= 4.2$. The net result is that in gas-phase reactions with no complicating solvation energies, the order of basicity is $\text{OH}^\ominus > \text{R}(1°)\text{OH} > \text{R}(2°)\text{OH} > \text{R}(3°)\text{OH}$ with the "explanation" being that the electron donating alkyl group adds to the charge capacity of the conjugate basic group.

For example, the basicities of various metal ions can be classified as hard or soft. Pearson suggested the terms "hard" and "soft" to describe the members of class (a) and (b) and (c) metal ions. A hard acid is a type of acid and a hard base is a ligand such as ammonia or the fluoride ion. Conversely, a soft acid is a type of base and a soft base is a ligand such as a phosphine or the chloride ion. A thorough discussion of the factors operating in hard and soft interactions can be found in the work of Pearson and his students. In addition to the hard and soft acids and bases, it is possible to classify any given acid or base as hard or soft by its apparent preference for hard or soft reactants. For example, a given acid can be classified as hard or soft by its apparent preference for hard or soft bases.

### Hard and Soft Acids and Bases

For some time coordination chemists were aware of certain trends in the stability of metal complexes. One of the earliest of these correlations was the Irving-Williams series of stability. For a given ligand, the stability of complexes with metal ions follows the order: $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Mn}^{2+} > \text{Fe}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$. This order arises in part from a decrease in size across the series and in part from ligand field effects (Chapter 11). A second observation is that certain ligands form their most stable complexes with metal ions such as $\text{Ag}^{+}$, $\text{Hg}^2+$, and $\text{Pt}^2+$, but other ligands seem to prefer ions such as $\text{Al}^{3+}$, $\text{Tl}^{3+}$, and $\text{Co}^{3+}$. Ligands and metal ions were classified as belonging to type (a) or (b) or (c) according to their apparent bonding. Class (a) metal ions include those of alkali metals, alkaline earth metals, and lighter transition metals in lower oxidation states such as $\text{Cu}^{+}$, $\text{Ag}^+$, $\text{Hg}^+$, $\text{Pt}^+$, and $\text{Pd}^2+$. Class (c) metal ions include those of the heavier transition metals and those in lower oxidation states such as $\text{Cu}^2+$, $\text{Ag}^+$, $\text{Hg}^2+$, $\text{Pt}^2+$, and $\text{Pd}^{2+}$. According to their preferences toward either class (a) or class (b) metal ions, ligands may be classified as type (a) or (b), respectively. Stability of these complexes may be summarized as follows:

<table>
<thead>
<tr>
<th>Tendency to complex with</th>
<th>Tendency to complex with</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class (a) metal ions</td>
<td>Class (b) metal ions</td>
</tr>
<tr>
<td>N $&gt;$ P $&gt;$ As $&gt;$ Sb</td>
<td>N $&lt;$ P $&gt;$ As $&gt;$ Sb</td>
</tr>
<tr>
<td>O $&gt;$ S $&gt;$ Se $&gt;$ Te</td>
<td>O $&lt;$ S $&lt;$ Se $&lt;$ Te</td>
</tr>
<tr>
<td>F $&gt;$ Cl $&gt;$ Br $&gt;$ I</td>
<td>F $&lt;$ Cl $&lt;$ Br $&lt;$ I</td>
</tr>
</tbody>
</table>

For example, phosphines ($\text{R}_3\text{P}$) and their orthoesters ($\text{R}_2\text{O}$) have a much greater tendency to coordinate with $\text{Hg}^{2+}$, $\text{Hg}^+$, and $\text{Pt}^2+$, but ammonia, amines ($\text{R}_2\text{N}$), water, and fluoride ions prefer $\text{Be}^{2+}$, $\text{Ti}^{4+}$, and $\text{Co}^{3+}$. Such a classification has proved very useful in accounting for and predicting the stability of coordination compounds.

Pearson suggested the terms "hard" and "soft" to describe the members of class (a) and (b). Thus a hard acid is a type (a) metal ion and a hard base is a ligand such as ammonia or the fluoride ion. Conversely, a soft acid is a type (b) metal ion and a soft base is a ligand such as a phosphine or the chloride ion. A thorough discussion of the factors operating in hard and soft interactions can be found in the work of Pearson and his students. In addition to the hard and soft acids and bases, it is possible to classify any given acid or base as hard or soft by its apparent preference for hard or soft reactants. For example, a given acid can be classified as hard or soft by its apparent preference for hard or soft bases.
A single example of the application of electrode potentials to chemistry in ammonia will suffice. The Latimer diagram for mercury in acidic solution is

\[
\begin{align*}
\text{Hg}^{2+} & \quad \text{Hg}^2+ \quad \text{Hg} \\
\end{align*}
\]

and for the insoluble mercury(I) iodide the diagram is

\[
\begin{align*}
\text{Hg}^2+ & \quad \text{HgI}^- \quad \text{HgI}_2 \\
\end{align*}
\]

It may readily be seen that the mercurous ion (whether free or in Hg-,I-) is thermodynamically unstable with respect to disproportionation in ammonia, in contrast to its stability in water.

Electrochemistry in nonaqueous solvents is not merely a laboratory curiosity. We have already seen batteries made with solid electrolytes (sodium beta alumina, see Chapter 7) that are certainly “nonaqueous.” In looking for high-efficiency cells one desires the cathode and anode to be highly reactive (large positive emf) and to have a low equivalent weight. In these terms, lithium appears to be highly desirable. Its very reactivity, however, precludes its use in aqueous systems or even liquid ammonia. One successful battery utilizing lithium has been developed using sulfur dioxide or thionyl chloride (OSCL) as solvent and oxidant. Others involve weight-efficient lithium metal with other oxidants and solvents.32 Highly efficient batteries of this sort are widely used in specialized applications where light weight and long life are important.

Hydrometallurgy

Traditionally the winning of metals from their ores has been achieved by pyrometallurgy: the reduction of relatively concentrated metallic ores at high temperatures. The reactions of the blast furnace form a typical example (see also page 377):

\[
\begin{align*}
\text{Fe}_2\text{O}_3 + 3\text{CO} & \rightarrow 2\text{Fe} + 3\text{CO}_2 \\
\text{CO}_2 + \text{C} & \rightarrow 2\text{CO} \\
\end{align*}
\]

Carbon monoxide for the reduction of the iron is formed not only from the recycling of carbon dioxide (Eq. 10.128) but also from the direct oxidation of the coke in the charge by hot air:

\[
\begin{align*}
2\text{C} + \text{O}_2 & \rightarrow 2\text{CO} \\
\end{align*}
\]

The energy released by the combustion is sufficient to raise the temperature well above the melting point of iron, 1535 °C. One of the incentives for development of alternative methods of producing metals is the hope of finding less energy-intensive processes.

Hydrometallurgy is not new; it has been used for almost a century in the separation of gold from low-grade ores. This process is typical of the methods used: Gold is normally a very unreactive metal:

\[
\begin{align*}
\text{Au} & \rightarrow \text{Au}^+ + e^- \quad E^\circ = -1.69 \text{ V} \\
\end{align*}
\]

With such a negative oxidation emf, it is too noble to react with either \( \text{O}_2 \) \((E^\circ = +1.185 \text{ V})\) or \( \text{Cl}_2 \) \((E^\circ = +1.36 \text{ V})\). By complexation of the \( \text{Au}(I) \) ion, however, the emf can be shifted until it is much more favorable:

\[
\begin{align*}
\text{Au} + 2\text{CN}^- & \rightarrow \text{Au(CN)}_2^- + e^- \\
\quad \quad E^\circ = +0.60 \text{ V} \\
\end{align*}
\]

Oxygen in the air is now a sufficiently strong (and cheap!) oxidizing agent to effect the solution of the gold. It may then be reduced and precipitated by an active metal such as zinc powder \((E^\circ = -0.763 \text{ V})\). Such hydrometallurgical processes offer definite advantages:

1. Low-grade ores may be leached, with complexing agents if necessary, and profitably exploited.
2. Complex ores may be successfully treated and multiple metals separated under more carefully controlled processes.
3. Since the reactions are carried out at room temperature, energy savings are possible.
4. Because no stack gases are involved, air pollution does not present the problem faced by pyrometallurgy.

These aspects do not form an unmixed blessing, however. If the metal must be reduced by electrolysis, the process may become energy intensive. Thus attractive solutions to this problem are reduction of more valuable gold by less expensive zinc and of more valuable copper by scrap iron. Finally, in view of the large amounts of waste water formed as by-product, one may be trading an air pollution problem for a water pollution problem. A comparison of the two types of processes is given in Table 10.6. Related hydrometallurgical methods may allow the use of bacteria to release copper from low-grade ores, or the use of algae to concentrate precious metals such as gold (see Chapter 19).33

Softness

If this equilibrium is studied in aqueous solution, as is usually the case, the acids will occur as CH₃HgBr⁺ and H₂SO₄ with additional waters of hydration. For data on equilibria of this type, see Schwarzenbach, G.; Schelterberg, M. Helv. Chim. Acta 1962, 45, 28.

32 If this equilibrium is studied in aqueous solution, as is usually the case, the acids will occur as CH₃HgBr⁺ and H₂SO₄ with additional waters of hydration. For data on equilibria of this type, see Schwarzenbach, G.; Schelterberg, M. Helv. Chim. Acta 1962, 45, 28.

33 An interesting historical sidelight on this type of soft-soft interaction is the origin of the name "mercaptan," a mercury capturer: Hg²⁺ + 2KRS → HgSR₂ + 2K⁺.
3. The Nernst equation applies to the potentials of both half-reactions and total redox reactions:

\[ E = E^0 \frac{RT}{nF} \ln Q \]  

where \( E^0 \) represents the overall potential with all species at unit activity and \( Q \) represents the reaction quotient.

4. Reactions resulting in a decrease in free energy (\( \Delta G < 0 \)) are spontaneous. This is a requirement of the second law of thermodynamics. Concomitantly, redox reactions in which \( \Delta G > 0 \) are therefore spontaneous.

5. In aqueous solutions two half-reactions are of special importance: (a) the reduction of hydrogen in water or hydronium ions:

1 M acid \( H_2O^+ + e^- \rightarrow H_2 + H^- \)  
Neutral solution \( H_2O + e^- \rightarrow OH^- + H_2 \)  
1 M base \( H_2O + e^- \rightarrow OH^- + H_2 \)  

and (b) the oxidation of oxygen in water or hydroxide ions:

1 M acid \( H_2O + I^- \rightarrow O_2^- + 2H^+ \)  
Neutral solution \( H_2O + I^- \rightarrow O_2^- + 2H^+ \)  
1 M base \( 2OH^- + I^- \rightarrow O_2^- + 2H_2O \)

These reactions limit the thermodynamic stability\(^{28}\) of species in aqueous solution.

6. In calculating the "skip-step emf" for a multivalent species it is necessary to take into account the total change in free energy. Suppose we know the emfs for the oxidation of Fe to Fe\(^{3+}\) and Fe\(^{2+}\) to Fe\(^{3+}\) and wish to calculate the skip-step emf for Fe to Fe\(^{3+}\):

\[ \begin{align*}
\text{Fe} & \rightarrow \text{Fe}^{2+} \quad E^0 = 0.44 \\
\text{Fe}^{2+} & \rightarrow \text{Fe}^{3+} \quad E^0 = -0.77 \\
\text{Fe} & \rightarrow \text{Fe}^{2+} \quad \Delta G^0 = -0.11 \ F
\end{align*} \]

\[ E^0 = -\frac{\Delta G^0}{nF} = 0.11/3 = 0.037 \ V \]  

Although the emfs are not additive, the free energies are, allowing simple calculation of the overall emf for the three-electron change.

7. Standard potential or "Latimer" diagrams are useful for summarizing a considerable amount of thermodynamic information about the oxidation states of an element in a convenient way. For example, the following half reactions may be taken from Table F.1, Appendix F:

\[ \begin{align*}
\text{Mn}^{2+} + 2e^- & \rightarrow \text{Mn} \quad E^0 = -1.18 \ V (10.118) \\
\text{Mn}^{3+} + e^- & \rightarrow \text{Mn}^{2+} \quad E^0 = +1.36 \ V (10.119) \\
\text{MnO}_2 + 4H^+ + e^- & \rightarrow \text{Mn}^{2+} + 2H_2O \quad E^0 = +0.90 \ V (10.120) \\
\text{HMnO}_4 + 3H^+ + 2e^- & \rightarrow \text{MnO}_2 + 2H_2O \quad E^0 = +0.29 \ V (10.121) \\
H^+ + \text{MnO}_4^- + e^- & \rightarrow \text{HMnO}_4^- \quad E^0 = +0.90 \ V (10.122) \\
\text{MnO}_2 + 4H^+ + 2e^- & \rightarrow \text{MnO}_2 + 2H_2O \quad E^0 = +1.23 \ V (10.123) \\
\text{MnO}_2 + 4H^+ + 2e^- & \rightarrow \text{MnO}_2 + 2H_2O \quad E^0 = +1.70 \ V (10.124) \\
\text{MnO}_2 + 8H^+ + 5e^- & \rightarrow \text{Mn}^{2+} + 4H_2O \quad E^0 = +1.51 \ V (10.125)
\end{align*} \]

By omitting species such as \( H_2O, H^+, \) and \( OH^- \), all of the above information can be summarized as:

\[ \begin{align*}
\text{Mn}^{2+} + 2e^- & \rightarrow \text{Mn} \quad E^0 = -0.18 \\
\text{Mn}^{3+} + e^- & \rightarrow \text{Mn}^{2+} \quad E^0 = +1.36 \\
\text{HMnO}_4^- + 3H^+ + 2e^- & \rightarrow \text{MnO}_2 + 2H_2O \quad E^0 = +0.29 \\
\text{HMnO}_4^- + 3H^+ + 2e^- & \rightarrow \text{MnO}_2 + 2H_2O \quad E^0 = +1.23 \\
\text{MnO}_2 + 4H^+ + 2e^- & \rightarrow \text{MnO}_2 + 2H_2O \quad E^0 = +1.70 \\
\text{MnO}_4^- + 8H^+ + 5e^- & \rightarrow \text{Mn}^{2+} + 4H_2O \quad E^0 = +1.51
\end{align*} \]

The highest oxidation state is listed on the left and the reduction emfs are listed between each species and the next reduced form, with the lowest oxidation state appearing on the right.\(^{29}\)

Although the entire discussion of electrochemistry thus far has been in terms of aqueous solutions, the same principles apply equally well to nonaqueous solvents. As a result of differences in solvation energies, electrode potentials may vary considerably from those found in aqueous solution. In addition the oxidation and reduction potentials characteristic of the solvent vary with the chemical behavior of the solvent. As a result of these two effects, it is often possible to carry out reactions in a nonaqueous solvent that would be impossible in water. For example, both sodium and beryllium are too reactive to be electroplated from aqueous solution, but beryllium can be electroplated from liquid ammonia and sodium from solutions in pyridine.\(^{30}\)

Unfortunately, the thermodynamic data necessary to construct complete tables of standard potential values are lacking for most solvents other than water. Jolly has compiled such a table for liquid ammonia. The hydrogen electrode is used as the reference point to establish the scale as in water:

\[ \text{NH}_3 + e^- \rightarrow \text{H}_2 + \text{NH}_2 \quad E^0 = 0.00 \ V (10.126) \]

\(^{28}\) As is always the case when dealing with thermodynamic stabilities, it must be borne in mind that a species may possibly be thermodynamically unstable yet kinetically inert. That is, no mechanism of low activation energy may exist for its decay.

\(^{29}\) This convention originated with Latimer and is widespread in the inorganic chemical literature. Unfortunately, Latimer used oxidation emfs, and so his diagram is a mirror image of the one drawn on the basis of reduction potentials. This has resulted in a wide variety of modified "Latimer diagrams," often with no indication of the convention employed concerning the spontaneity of the half-reaction. To avoid confusion, arrows (not present in the original Latimer diagram) are recommended. Further discussion of Latimer diagrams and related topics may be found in Chapter 14.


The Irving-Williams series of increasing stability from $\text{Ba}^{2+}$ to $\text{H}^+$ shows that the hydroxide ion is a strong base toward both acids, but in this case about a million times better toward the proton; hence it is hard. The aqueous fluoride ion, $\text{F}^-$, is not particularly good base toward either acid but slightly better toward the proton as expected from its hard character.

The importance of both inherent acidity and a hard-soft factor is well shown by the Irving-Williams series and some oxygen, nitrogen, and sulfur chelates (Fig. 9.5). The Irving-Williams series of increasing stability from $\text{Ba}^{2+}$ to $\text{Cu}^{2+}$ is a measure of increasing inherent acidity of the metal (largely due to decreasing size). Superimposed upon this is a hardness-softness factor in which the softer species coming later in the series (greater number of electrons, see page 350) favor ligands $\text{S} > \text{N} > \text{O}$. The harder alkaline earth and early transition metal ions (few or no soft electrons) favor ligands $\text{O} > \text{N} > \text{S}$. Bases such as the sulfide ion ($\text{S}^-$) and triethylphosphine ($\text{P}^-$) are good base toward either acid but slightly better toward the proton as expected from its soft character.

As noted above, the hardness or softness of an acidic or basic site is not an inherent property of the particular atom at that site, but can be influenced by the substituent atoms. The addition of soft, polarizable substituents can soften an otherwise hard center and the presence of electron-withdrawing substituents can reduce the softness of a site. The acidic boron atom is borderline between hard and soft. Addition of three soft, electronegative fluorine atoms hardens the boron and makes it a hard Lewis acid. Conversely, addition of three soft, electropositive hydrogens softens the boron and makes it a soft Lewis acid. Examples of the difference in hardness of these two boron acids are:

$$\text{R}_3\text{OBF}_3 + \text{R}_2\text{O} \rightarrow \text{R}_2\text{OBHF}_3 + \text{R}_3\text{S} \quad (9.76)$$
$$\text{R}_2\text{OBH}_3 + \text{R}_2\text{S} \rightarrow \text{R}_2\text{SBH}_3 + \text{R}_2\text{O} \quad (9.77)$$

In a similar manner, the hard $\text{BF}_3$ molecule will prefer to bond to another fluoride ion, but the soft $\text{BH}_3$ acid will prefer a softer hydride ion:$^{35}$

$$\text{BF}_3 + \text{F}^- \rightarrow \text{BF}_4^- \quad (9.78)$$
$$\text{B}_2\text{H}_6 + 2\text{H}^- \rightarrow 2\text{BH}_4^- \quad (9.79)$$

Therefore, the following competitive reaction will proceed to the right:

$$\text{BF}_3\text{H}^- + \text{BH}_3\text{F}^- \rightarrow \text{BF}_4^- + \text{BH}_4^+ \quad (9.80)$$

$^{34}$ In a manner analogous to the usual treatment of balancing redox equations, it is necessary here to do some careful "bookkeeping." Although this is strictly a formalism, it is necessary to make certain that the proper comparison is being made. In the present example, the formation of $\text{BF}_4^-$ is formally considered to be $\text{B}^{3+} + 3\text{F}^-$. The three $\text{F}^-$ ions harden the $\text{B}^{3+}$. The analogous comparison is $\text{B}^{3+} + \text{3H}^+ = \text{BH}_3$. In this case the soft hydride ions soften the $\text{B}^{3+}$. One must be careful to distinguish between the small, hard proton ($\text{H}^+$) and the large ($r_+ = 208 \text{ pm}$) soft hydride ion ($\text{H}^-$).

$^{35}$ The simple $\text{BH}_3$ molecule does not exist in appreciable quantities, but always dimerizes to $\text{B}_2\text{H}_6$. See Chapter 19.

Table 9.8 lists the strengths of various bases toward the proton ($\text{H}^+$) and the methylmercury cation ($\text{CH}_3\text{Hg}^+$). Bases such as the sulfide ion ($\text{S}^-$) and triethylphosphine ($\text{P}^-$) are very strong toward both the methylmercury ion and the proton, but about a million times better toward the former; hence they are considered soft. The hydroxide ion is a strong base toward both acids, but in this case about a million times better toward the proton; hence it is hard. The aqueous fluoride ion, $\text{F}^-$, is not particularly good base toward either acid but slightly better toward the proton as expected from its hard character.

Table 9.8 shows the relationship between the hardness-softness factor (greater number of soft electrons) and the basicity toward the proton ($\text{H}^+$) and the methylmercury cation ($\text{CH}_3\text{Hg}^+$). Bases such as the sulfide ion ($\text{S}^-$) and triethylphosphine ($\text{P}^-$) are very strong toward both the methylmercury ion and the proton, but about a million times better toward the former; hence they are considered soft. The hydroxide ion is a strong base toward both acids, but in this case about a million times better toward the proton; hence it is hard. The aqueous fluoride ion, $\text{F}^-$, is not particularly good base toward either acid but slightly better toward the proton as expected from its hard character.

Table 9.8

<table>
<thead>
<tr>
<th>Base</th>
<th>Linking atom</th>
<th>$pK_a$ ($\text{CH}_3\text{Hg}^+$)</th>
<th>$pK_a$ ($\text{H}^+$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{F}^-$</td>
<td>$\text{Cl}$</td>
<td>1.50</td>
<td>2.85</td>
</tr>
<tr>
<td>$\text{Br}^-$</td>
<td>$\text{Br}$</td>
<td>6.62</td>
<td>9.03</td>
</tr>
<tr>
<td>$\text{I}^-$</td>
<td>$\text{I}$</td>
<td>8.60</td>
<td>9.90</td>
</tr>
<tr>
<td>$\text{OH}^-$</td>
<td>$\text{O}$</td>
<td>9.37</td>
<td>15.7</td>
</tr>
<tr>
<td>$\text{HPO}_4^{2-}$</td>
<td>$\text{O}$</td>
<td>5.03</td>
<td>6.79</td>
</tr>
<tr>
<td>$\text{SO}_4^{2-}$</td>
<td>$\text{S}$</td>
<td>21.2</td>
<td>14.2</td>
</tr>
<tr>
<td>$\text{HOC}_2\text{H}_4\text{S}^-$</td>
<td>$\text{S}$</td>
<td>16.12</td>
<td>9.52</td>
</tr>
<tr>
<td>$\text{SCN}^-$</td>
<td>$\text{S}$</td>
<td>6.05</td>
<td>4.9</td>
</tr>
<tr>
<td>$\text{SO}_3^{2-}$</td>
<td>$\text{S}$</td>
<td>8.11</td>
<td>6.79</td>
</tr>
<tr>
<td>$\text{S}_2\text{O}_3^{2-}$</td>
<td>$\text{S}$</td>
<td>10.90</td>
<td>negative</td>
</tr>
<tr>
<td>$\text{NH}_3$</td>
<td>$\text{N}$</td>
<td>7.60</td>
<td>9.42</td>
</tr>
<tr>
<td>$\text{NH}_2\text{C}_2\text{H}_4\text{SO}_3^-$</td>
<td>$\text{N}$</td>
<td>2.60</td>
<td>3.06</td>
</tr>
<tr>
<td>$\text{PCl}_3\text{C}_2\text{H}_4\text{SO}_3^-$</td>
<td>$\text{P}$</td>
<td>9.15</td>
<td>0.0</td>
</tr>
<tr>
<td>$\text{Et}_3\text{P}$</td>
<td>$\text{P}$</td>
<td>14.6</td>
<td>8.1</td>
</tr>
<tr>
<td>$\text{CN}^-$</td>
<td>$\text{C}$</td>
<td>15.0</td>
<td>8.8</td>
</tr>
</tbody>
</table>

$^{34}$ In a manner analogous to the usual treatment of balancing redox equations, it is necessary here to do some careful "bookkeeping." Although this is strictly a formalism, it is necessary to make certain that the proper comparison is being made. In the present example, the formation of $\text{BF}_4^-$ is formally considered to be $\text{B}^{3+} + 3\text{F}^-$. The three $\text{F}^-$ ions harden the $\text{B}^{3+}$. The analogous comparison is $\text{B}^{3+} + \text{3H}^+ = \text{BH}_3$. In this case the soft hydride ions soften the $\text{B}^{3+}$. One must be careful to distinguish between the small, hard proton ($\text{H}^+$) and the large ($r_+ = 208 \text{ pm}$) soft hydride ion ($\text{H}^-$).

$^{35}$ The simple $\text{BH}_3$ molecule does not exist in appreciable quantities, but always dimerizes to $\text{B}_2\text{H}_6$. See Chapter 19.

Fig. 9.5 The Irving-Williams hard and soft acids bases series. The stability increases in the series $\text{Ba}^{2+}$ to $\text{Cu}^{2+}$ decreases with $\text{Zn}$ (From Sigel, H., McCormick, D. B. Acc. Chem. Res. 1970, 3, 201. Reproduced with permission.)
1. The standard hydrogen electrode (aH₂ = 1.00; fH₂ = 1.00) is arbitrarily assigned an electrode potential of 0.00 V.

2. If we construct a cell composed of a hydrogen electrode and a second electrode (M²⁺/M) of metal M immersed in a solution of M⁺⁺/M unit activity, we can measure the potential between the electrodes of the cell. Since the hydrogen electrode was assigned a potential of 0.00 V, the potential of the electrode, M⁺⁺/M, is by definition the same as the measured potential of the cell. If the metal electrode is positively charged with respect to the hydrogen electrode (e.g., Cu²⁺/Cu), the electrode potential of the metal is assigned a negative sign (E(M⁺⁺/M) = -0.337 V). If the metal tends to lose electrons more readily than hydrogen and thus becomes negatively charged (e.g., Zn²⁺/Zn), the electrode is assigned a positive sign (E(Zn²⁺/Zn) = 0.763 V). This convention is convenient in that it results in a single, invariant quantity for the electrode potential for each electrode (the zinc electrode is always electrostatically negative whether the reaction under consideration occurs in a galvanic cell or an electrolytic cell). Most physical and inorganic chemists are more interested in the thermodynamics of half-reactions rather than the electrostatic potential that obtains in conjunction with the standard hydrogen electrode. The convention related to thermodynamics may be termed the thermodynamic convention. This convention assigns to the electromotive force (E) a sign such that

\[ \Delta G = -nFE \]

where \( \Delta G \) is the change in Gibbs free energy, \( n \) is the number of equivalents reacting, and \( F \) is Faraday’s constant, 96,485 coulombs equivalent⁻¹. It is necessary to specify the direction in which a reaction is proceeding. Thus, if we consider the reaction

\[ \text{Zn} + 2\text{H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2 \]

and find that for the reaction, as written, \( \Delta G < 0 \), then (since \( H^+/H_2 \) is defined as 0.00 V)

\[ \text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \quad E > 0 \]

For the spontaneous reaction:

\[ H_2 + 2\text{Zn}^{2+} \rightarrow \text{Zn} + 2\text{H}^+ \]

\[ \Delta G > 0 \] and so for

\[ \text{Zn}^{2+} + 2e^- \rightarrow \text{Zn} \quad E < 0 \]

Accordingly, the sign of the emf of either a half-reaction (“electrode”) or the overall redox reaction depends upon the direction in which the equation for the reaction is written (as is true for any thermodynamic quantity such as enthalpy, entropy, or free energy). The sign of the reduction electrode is always algebraic the same as that of the electrostatic potential.\(^{27}\)

---

27 In the past the electrostatic convention has often been called the “European convention” and the thermodynamic convention popularized by Latimer (The Oxidation Potentials of the Elements and Their Valences in Aqueous Solution; Prentice-Hall: Englewood Cliffs, NJ, 1952) the “American convention.” In an effort to reduce confusion, the IUPAC adopted the “Stockholm convention” in which electrode potentials refer to the electrostatic potential and emf refers to the thermodynamic quantity. Furthermore, the recommendation is that standard reduction potentials be listed as “electrode potentials” to avoid the possibility of confusion over signs.
The ioelectronic fluorinated methanes behave in a similar manner.\textsuperscript{56}

\[
\text{CF}_3\text{H} + \text{CH}_3\text{F} \rightarrow \text{CF}_4 + \text{CH}_4
\]

(9.81)

Jorgensen\textsuperscript{55} has referred to this tendency of fluoride ions to favor further coordination by a fourth fluoride (the same is true for hydrides) as "syntasis." Although other factors can work to oppose the syntactic tendency, it has widespread effect in inorganic chemistry and helps to explain the tendency for compounds to be symmetrically substituted rather than to have mixed substituents. We have seen (Chapter 5) that the electronstatic stabilization of $C=\text{F}$ bonds (ionic resonance energy) energy will be maximized in $\text{CF}_4$, and similar arguments can be made for maximizing hard-hard or soft-soft interactions.

Although the hard-soft rule is basically a pragmatic one allowing the prediction of chemical properties, it is of interest to investigate the theoretical basis of the effect. In this regard there is no complete unanimity among chemists concerning the relative importance of the various possible factors that might affect the strength of hard-hard and soft-soft interactions. Indeed, it is probable that the various factors may have differing importance depending upon the particular situation.

A simple explanation for hard-hard interactions would be to consider them to be primarily electrostatic or ionic interactions. Most of the typical hard acids and bases are those that we might suppose to form ionic bonds such as $\text{Li}^+$, $\text{Na}^+$, $\text{K}^+$, $\text{F}^-$, and $\text{OH}^-$. Because the electrostatic or Madelung energy of an ion pair is inversely proportional to the interatomic distance, the smaller the ions involved, the greater is the attraction between the hard acid and base. Since an electrostatic explanation cannot account for the apparent stability of soft-soft interactions (the Madelung energy of a pair of large ions should be relatively small), it has been suggested that the predominant factor here is a covalent one. This would correlate well for transition metals, $\text{Ag}$, $\text{Hg}$, etc., since it is usually assumed that bonds such as $\text{Ag}-\text{Cl}$ are considerably more covalent than the corresponding ones of the alkali metals. In this regard the polarizing power and the polarizability of electrons becomes important. It has been pointed out that all really soft acids are transition metals with six or more $d$-electrons becomes important. It is natural, since a typical hard-hard interaction is $\text{Li}^+\text{F}^-$. But the $\text{Li}^+$ ion has a relatively high electronegativity resulting from the extremely high second ionization potential. In contrast, transition metals in low oxidation states (Cu, Ag, etc.) have relatively low ionization energies and low electronegativities. The same may be said of hard and soft bases. This relation between hardness and softness helps explain the fact that the trifluoromethyl group is considerably harder than the methyl group and that the trifluoroacetic acid is harder than formic acid.

Recall that the Mulliken-Jaffe definition of electronegativity involves two parameters, $\alpha$, the first derivative of the ionization energy-electron affinity curve, and $\beta$, the second derivative (see page 186). The $\alpha$ term is identical with the original Mulliken electronegativity, and the $\beta$ term is the inverse of the charge capacity of an atom or group. It appears that the association between electronegativity and hardness actually refers to the $\beta$ parameter, but the values of $\alpha$ and $\beta$ for elements tend to parallel each other, hence the similarity. It was early suggested that since the $\beta$ parameter is the inverse of the charge capacity, hard atoms will have high values of $\beta$, and soft atoms will have smaller values.$\textsuperscript{53}$ Thus, although not only forms a hard ion (note the very high value of $\beta$ in Table 5.6) but is likewise harder the trifluoromethyl group by contributing to a higher $\beta$ value for it than for methyl.

Recently Parr and Pearson$\textsuperscript{38}$ have used the $\beta$ parameter to investigate the hard and soft properties of metal ions and ligands. They have termed this the absolute hardness in comparison to the Mulliken-Jaffe parameter which they call absolute electronegativity. They provide strong arguments for the use of the absolute hardness parameter in treating hard soft acid-base (HSAB) interactions.

Almost from the beginning of HSAB theory, attention has been directed to frontier orbitals.$\textsuperscript{60}$ These are the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). According to Koopmans' theorem, the energy of the HOMO should represent the ionization energy and the LUMO the electron affinity for a closed-shell species. These orbitals are thus involved in the electronegativity and HSAB relationships discussed. Hard species have a large HOMO-LUMO gap whereas soft species have a small gap. The presence of low-lying unoccupied MOs capable of mixing with the ground state accounts for the polarizability of soft atoms and, indeed, Politzer has shown a close correlation between atomic polarizabilities and the $\beta$ parameter.$\textsuperscript{59}$ Such mutual polarizability allows distortion of electron clouds to reduce repulsion. In addition, for polarizable species synergistically coupled donor and backbone bonding will be enhanced.$\textsuperscript{59}$

The idea of equaling hard-hard interactions with electrostatics has probably been overemphasized. It is natural, since a typical hard-hard interaction is $\text{Li}^+\text{F}^-\text{Li}^+\text{F}^-$. But the isoelectronic series $\text{Li}^-\text{F}$, $\text{Be}^-\text{O}$, $\text{B}^-\text{N}$, $\text{C}^-\text{C}$ all form strong bonds. The $\text{Li}^-\text{F}$ bond is the strongest since it is its resonance hybrid of $\text{Li}^-\text{F}^-\text{Li}^-\text{F}^-$. Some calculations based on electronegativity theory and a simple bonding model suggested that in LiF about one-fourth of the bond energy comes from covalent bonding, one-half from ionic bonding, and one-fourth from the transfer of electron density from the less electronegative lithium atom to the more electronegative fluorine atom.$\textsuperscript{59}$ The latter corresponds roughly to Pauling's iononic resonance energy.\textsuperscript{59}

\begin{itemize}
  \item Equation 9.81 is not meant to imply that a mixture of trifluoromethane and fluoromethane would react to form transfluoromethane and methane, although the reaction would be synthetically if it occurred. In this case, as in many others in chemistry, kinetic considerations (such as a steric effect) favor a suitable mechanism over a favorable thermodynamics.
  \item Equations 10.5 and 10.6 have been given by Jorgensen$\textsuperscript{55}$ for transfluoromethane and methane, although the reaction would be synthetically if it occurred. In this case, as in many others in chemistry, kinetic considerations (such as a steric effect) favor a suitable mechanism over a favorable thermodynamics.
  \item Backbonding in metal complexes is discussed in Chapter 11. For a clear discussion of HOMOs, LUMOs, and HSAB, see Pearson, R. G. J. Am. Chem. Soc. 1962, 107, 6081-6086; 1966, 88, 6109-6114; and Footnote 50.
  \item See Footnote 38 and the associated discussion of strong covalent bonding by fluoride (fluorine).
\end{itemize}
of magnesium and aluminum and the removal of silica impurities (in a blast furnace, for example) by a high-temperature solid-base reaction:

\[
\text{SiO}_2 + \text{CaO} \rightarrow \text{CaSiO}_3
\]  

(10.94)

One of the most interesting aspects of molten salt chemistry is the readiness with which metals dissolve. For example, the alkali halides dissolve large amounts of the corresponding alkali metal, and some systems (e.g., cesium in cesium halides) are completely miscible at all temperatures above the melting point. On the other hand, the halides of zinc, lead, and tin dissolve such small amounts of the corresponding free metal that special analytical techniques must be devised in order to estimate the concentration accurately.

At one time solutions of metals in their molten salts were thought to be colloidal in nature, but this has been shown not to be true. However, no completely satisfactory theory has been advanced to account for all the properties of these solutions. One hypothesis involves reduction of the cation of the molten salt to a lower oxidation state. For example, the solution of mercury in mercuric chloride undoubtedly involves reduction:

\[
\text{Hg} + \text{HgCl}_2 \rightarrow \text{Hg}_2\text{Cl}_2
\]  

(10.95)

and mercury(II) chloride remains when the melt is allowed to solidify. For most transition and posttransition metals the evidence for the formation of "subhalides" is considerably weaker. The \(\text{CuCl}_2^+\) ion is believed to exist in solutions of cadmium chloride but can be isolated only through the addition of aluminum chloride:

\[
\text{Cd} + \text{CdCl}_2 \rightarrow [\text{Cd}_2\text{Cl}_4]^- + \text{AlCl}_3
\]  

(10.96)

In many cases, although the presence of reduced species is suspected, it is impossible to isolate them. On solidification the melts disproportionate to solid metal and solid cadmium(II) salt.

In solutions of alkali metals in alkali halides, reduction of the cation, at least in the sense of forming discrete species such as \(\text{M}^+\), is untenable. It is probable that in these salts ionization takes place upon solution:

\[
\text{M} \rightarrow \text{M}^+ + e^-
\]  

(10.97)

The presence of free electrons thus bears a certain similarity to solutions of these same metals in liquid ammonia. If the electrons are thought to be trapped in anion vacancies in the melt, an analogy to F-centers (see Chapter 7) may be made. Undoubtedly the situation is considerably more complex with the possibility of the electron being delocalized in energy levels or bands characteristic of several atoms, but a thorough discussion of this problem is beyond the scope of this book.25

Molten salts provide a medium in which the concentration of anionic ligands can be much higher than is possible in aqueous solutions. The concentration of the chloride ion in concentrated aqueous hydrochloric acid is about 12 M, for example. In contrast,

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The HSAB rule works and the reaction is exothermic as written. If we look at the individual heats of atomization of the species (from bond energies, Appendix E) we find BrF\(_2\) \(\Delta H_\text{f} = +1264\); HgF\(_2\) \(\Delta H_\text{f} = +536\); Be\(_2\) \(\Delta H_\text{f} = +578\); Hg\(_2\) \(\Delta H_\text{f} = +391\) kJ mol\(^{-1}\). The driving force in Eq. 9.82 is almost entirely the strong bonding in the hard-hard interaction.

One advantage that softer acids and bases generally do have is the ability to form \(\pi\)-bonds. This is made possible by large numbers of electrons in \(\pi\) orbitals on the metals and empty, low-lying acceptor orbitals on the ligands. Once again, "bigger" is not necessarily "better": Once an atom is large enough, that is, has \(n > 3\), it will have available \(d\) orbitals. Sulfur and phosphorus are exemplars of soft-atom behavior. They are much better at binding soft metals than are their larger congeners such as selenium, arsenic, tellurium, and antimony. This is for the same reason we have seen before: Long \(\pi\) bonds are not very strong just as long \(\sigma\) bonds are not very strong, but the effect is even more pronounced because of the sideways overlap to form \(\pi\) bonds. The premier soft ligand and \(\pi\) bonder is carbon monoxide which has low-lying \(\pi\) acceptor orbitals and which has the advantage of small size to obtain good overlap. 

The HSAB rule works in the gas phase, by far its greatest usefulness lies in the interpretation of only two species at a time; to the extent that the nonpolar solvents used in these studies minimize solvation effects, the results are comparable to gas-phase proton affinities. The early 1970s showed repeated attempts to correlate the two ideas, prove one superior to the other, or to improve their theoretical basis. For example, both Drago and Pearson have discussed the possibility of quantifying the HSAB principle along the lines of the \(E\)-\(C\) system were proposed and developed in the 1960s. Insofar as the HSAB principle employs ideas of electrostatic and covalent bonding to account for hardness and softness, it was natural to attempt a correlation with the \(E\) and \(C\) parameters. The early 1970s showed repeated attempts to correlate the two ideas, prove one superior to the other, or to improve their theoretical basis. For example, both Drago and Pearson have discussed the possibility of quantifying the HSAB principle along the lines of the \(E\)-\(C\) system, but have come to diametrically opposed conclusions. Drago and coworkers have even suggested that the HSAB model is no longer tenable.

Some typical anionic bases are plotted with their proton affinities for the reaction of hard and soft acids and bases. 

\[
\begin{align*}
\text{Hard-soft} & \quad \text{Hard-hard} & \quad \text{Soft-soft} \\
\text{Soft-hard} & \quad \text{Hard-soft} & \quad \text{Hard-hard} \\
\text{Soft-hard} & \quad \text{Soft-soft} & \quad \text{Hard-hard} \\
\text{Soft-soft} & \quad \text{Hard-soft} & \quad \text{Hard-hard}
\end{align*}
\]

We have already seen that in the gas phase the stability of all metal halides follows the order \(F^->Cl^->Br^->I^->\), contrary to the simplest possible interpretation of the HSAB rule. Perhaps the rule should be restated as follows: Soft acids prefer to bond to soft bases when hard acids are preferentially bonding to hard bases. Although the HSAB rule works in the gas phase, by far its greatest usefulness lies in the interpretation of complexes in aqueous solution. These ions will always be hydrated though this may not be explicitly stated. Under these circumstances, it is somewhat surprising that the HSAB rule works as well as it does.

McDaniel and coworkers\(^{66}\) have provided a graphical means of portraying some of the ideas discussed in this chapter. For the reaction of hard and soft acids and bases:

\[
A_1B_1 + A_2B_2 \rightarrow A_1B_2 + A_2B_1
\]

it can be shown that the enthalpy change for this reaction, \(\Delta H\), can be related to the affinities of the bases for the two acids as shown in Fig. 9.6. If the affinities for a hard acid (e.g., \(H^+\)) and a softer acid (e.g., \(CH_3^+\)) are plotted and lines of unit slope are drawn through them, \(\Delta H\), for the reaction can be measured by the distance between the lines in either the \(x\) or \(y\) direction. Furthermore, if two bases were to fall on the same line in Fig. 9.6, they would be equally soft. If the line for a given base lies above and to the left of that for another, the first base is softer and the second is harder. Finally, since strength is related to the magnitude of acid-base interactions, the further a given base lies from the origin, the stronger it is. 

Some typical anionic bases are plotted with their proton affinities and their methyl cation affinities in Fig. 9.7. The solid line was drawn by the original investigators as a least squares fit of all of their data. The dashed line was added for this discussion, and it is arbitrarily drawn through \(F^->\) and \(OH^-\) (the archetypical hardest bases) with unit slope. Hard bases lie close to the dashed line, soft bases lie further away from it. The reader is urged to find analogous pairs, such as \(CN^-\) and \(OH^-\), \(CN^-\) and \(NH_3^+\), and interpret their positions on this graph in terms of inherent strength, hardness, and softness.

Staley and coworkers\(^{67}\) have provided direct measurement of HSAB effects in gas-phase dissociation energies between transition metals (where the principle has

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Solvent Properties

The chemistry of molten salts as nonaqueous solvent systems is one that has developed extensively from the 1960s to the present, and only a brief survey can be given. The most obvious difference when compared with the chemistry of aqueous solutions is the strongly bonded and stable nature of the solvent, a concomitant resistance to destruction of the solvent by vigorous reactions, and higher concentrations of various species, particularly coordinating anions, than can be obtained in saturated solvents in water.

Solvent Types

On the basis of the structure of the liquid, molten salts can be conveniently classified into two groups although there is no distinct boundary between the two. The first consists of compounds such as the alkali halides that are bonded chiefly by ionic forces. On melting, very little change takes place in these materials. The coordination of the ions tends to drop from six in the crystal to about four in the melt and the long-range order found in the crystal is destroyed; but a local order, each cation surrounded by anions, etc., is still present. These fused salts are all very good electrolytes because of the presence of large numbers of ions. They behave normally with respect to cryoscopy and this is a useful means of study. The number of ions, n, may be determined in these systems just as in the sulfuric acid system (page 305). For example, if sodium chloride is the solvent, \( n_{Na^+} = 2 \), \( n_{Cl^-} = 3 \), etc. One interesting point is that a salt with a common ion behaves somewhat anomalously in that the common ion does not behave as a "foreign particle" and \( n \) is correspondingly lower. In sodium chloride solutions, \( n_{Na^+} = 2 \).

The second group consists of compounds in which covalent bonding is important. These compounds tend to melt with the formation of discrete molecules although autoionization may occur. For example, the mercury(II) halides ionize as follows:

\[
2HgX_2 \rightarrow HgX^+ + HgX^2^- \quad (10.73)
\]

This is analogous to the aprotic halide solvents discussed in the previous section. Acidic solutions may be prepared by increasing the concentration of \( HgX^+ \) and basic solutions by increasing the concentration of \( HgX^2^- \).

\[
Hg(ClO_3)_2 + HgX_2 \rightarrow 2HgX^+ + 2ClO_4^- \quad (10.74)
\]

and neutralization reactions occur on mixing the two:

\[
HgX^+ + ClO_4^- + K^+ + HgX_2 \rightarrow 2HgX_2 + K^+ + ClO_4^- \quad (10.75)
\]

If aluminum chloride is added to an alkali metal chloride melt, an alkali metal tetrachloroaluminate forms:

\[
2M^+Cl^- + AlCl_3 \rightarrow 2M^+ + 2AlCl_4^- \quad (10.77)
\]

The tetrachloroaluminate ion undergoes autoionization

\[
2AlCl_4^- \rightarrow Al_2Cl_7^2- + Cl^- \quad K_{eq} = 1.06 \times 10^{-7} \quad (10.78)
\]

and one can clearly relate similarity to the concentration of the chloride ion. At 175 °C the neutral melt has \( [AlCl_3^-] = [Cl^-] = 3.26 \times 10^{-4} \) and a pCl scale can be set up with a neutral point of 3.5. Basic solutions have lower values of pCl (a saturated solution of NaCl has pCl = 1.1) and acidic solutions (made by adding excess AlCl_3) have higher values. The pCl can be monitored electrochemically with an aluminum electrode.22

Although the term "molten salts" conjures up images of very high-temperature fused systems, some salts are liquid at or near room temperature. For example, if alkylpyridinium chlorides are added to aluminum chloride, the resultant compounds are very similar to the alkali metal tetrachloroaluminates, but they are often liquids.22

\[
2[R(NMe_2)KHgCl] + AlCl_3 \rightarrow 2[R(NMe_2)KHgCl]_2 + [AlCl_4^-] \quad (10.79)
\]

The chemistry in these melts is very similar to that in MgCl_2 except that it can be carried on at about 25 °C instead of 175 °C.

One problem with chloroaluminate melts is that aluminum chloride and most transition metal chlorides (cf., Eqs. 10.99 to 10.101) are hygroscopic, and even if very carefully handled will hydrolyze from any moisture in the atmosphere:

\[
[AlCl_4^-] + H_2O \rightarrow [Al(OH)_2Cl_2] + 2HCl \quad (10.80)
\]

\[
[Cl_2AlOCl]_2^2- + [TiCl_4]_2^- \rightarrow [TiCl_4]_2^2- + [AlCl_4^-] \quad (10.81)
\]

Such impurities are, of course, a problem whenever careful measurements are attempted. It has been found23 that phosgene quantitatively removes the oxide impurities

\[
[TiCl_4]_2^2- + OCCl_2 \rightarrow [TiCl_4]_2^3- + CO_2 \quad (10.82)
\]

\[
[NbOCl_4]_2^2- + OCCl_2 \rightarrow [NbOCl_5]_2^3- + CO_2 \quad (10.83)
\]

and this has proved a useful way to keep the systems anhydrous.

Although the chloroaluminates are the best known room-temperature molten salts, there are several other interesting systems. For example, if one mixes the crystalline solids triethylammonium chloride and copper(I) chloride, an endothermic reaction takes place to form a light green oil. The most reasonable reaction is the coordination of a second chloride ion to the copper(I) ion

\[
[Et_3NH]Cl + CuCl \rightarrow [Et_3NH][CuCl_2] \quad (10.84)
\]

to form the dichlorocuprate(I) ion. The source of the low melting point seems to be the following equilibria:

\[
\begin{align*}
\text{CuCl}_2 & \rightarrow \text{Cu}^{2+} + \text{Cl}^- \\
\text{Cu}^{2+} + \text{Cl}^- & \rightarrow \text{CuCl}_2
\end{align*}
\]

Fig. 9.7 Methyl cation affinity vs. proton affinity of a series of anionic bases of varying hardness. The solid line is a least-squares fit of the data drawn by the original investigators. The dashed line has been arbitrarily drawn through F\textsuperscript{-} and OH\textsuperscript{-} with unit slope (see Fig. 9.6). Hard bases lie close to the dashed line, soft bases lie further away from it. [From Brauman, J. I.; Han, C.-C. J. Am. Chem. Soc. 1988, 110, 5612. Reproduced with permission.]

Fig. 9.8 Comparison of relative ligand dissociation energies for Mn\textsuperscript{3+} and Co\textsuperscript{2+}. Zero points for the scales have been arbitrarily chosen. Note that for the soft ligands, MeS\textsubscript{2}, HCN, and Me\textsubscript{2}S, the data points lie above and to the left of those for the oxygen bases. This indicates relatively stronger hard-hard bonding (O—Mn\textsuperscript{3+}) or soft-soft bonding (S—Co\textsuperscript{2+}), or both. [Modified from Jones, R. W.; Staley, R. H. J. Phys. Chem. 1982, 86, 1387. Reproduced with permission.]

Problems

9.1 Use the Lewis definition of acids and bases to explain the examples given for the Brønsted-Lowry, Lux-Flood, and solvent system definitions (Eqs. 9.1-9.4, 9.5-9.8, 9.9-9.36).

9.2 Use the generalized definition of acids and bases to explain the examples given for the Brønsted-Lowry, Lux-Flood, solvent system, and Lewis definitions (Eqs. 9.1-9.4, 9.5-9.8, 9.9-9.36, 9.37-9.40).

9.3 Which would you expect to be a better Lewis acid, BC\textsubscript{3} or B(CH\textsubscript{3})\textsubscript{3}? Explain.

9.4 The order of acidity of boron halides is BF\textsubscript{3} < BG\textsubscript{3} < BBr\textsubscript{3}. Is there anything unexpected in this order? Suggest possible explanations.

9.5 Plot the acidity parameters, a, from Table 9.1 vs. the pA\textsubscript{H} values in Table 9.3 for those metals that occur in both tables. Interpret your plot.

9.6 B-stress can occur in amines to lower their basicity. Will B-stress inhibit or enhance the acidic behavior of boranes?

9.7 Predict which way the following reactions will go (left or right) in the gas phase:

\[
\begin{align*}
\text{HI} + \text{NaF} & = \text{HF} + \text{NaI} \\
\text{AlF}_3 + 3\text{NaF} & = \text{AlF}_4 + 3\text{NaI} \\
\text{Cu}_2 & = 2\text{CuF} = \text{CuF}_2 + 2\text{Cu} \\
\text{TiF}_4 + 2\text{Ti}_4 & = \text{Ti}_4 + 2\text{TiF}_3 \\
\text{CoF}_2 & + \text{HgBr}_2 = \text{CoBr}_2 + \text{HgF}_2 \\
\end{align*}
\]

9.8 Calculate the values for the proton affinities of the halide anions shown in Table 9.5 from a Born-Haber thermochémical cycle and values for ionization energies, electron affinities, and bond energies.

9.9 a. Using Eq. 9.61, calculate the proton affinities of the following bases: NH\textsubscript{3}, CH\textsubscript{3}NH\textsubscript{2}, (CH\textsubscript{2})\textsubscript{2}NH, (CH\textsubscript{2})\textsubscript{3}N, py, H\textsubscript{2}O, (CH\textsubscript{2})\textsubscript{4}O, H\textsubscript{2}S, (CH\textsubscript{2})\textsubscript{4}SH, and (CH\textsubscript{2})\textsubscript{6}SO.

b. Compare your answers with experimental values as given in Table 9.5. Which compounds show the greatest differences between \(\Delta P_{A,H}\) and \(\Delta E_{PA}\)? Discuss possible reasons for the differences.
Most molecular chlorides behave as acids:

\[
\begin{align*}
\text{FeCl}_3 & \overset{\text{oxo}}{\longrightarrow} \text{OPCl}_3 + \text{FeCl}_4^- \\
\text{SCl}_3 & \overset{\text{oxo}}{\longrightarrow} \text{OPCl}_3 + \text{SCl}_4^-
\end{align*}
\]  
(10.66, 10.67)

As might be expected, basic solutions may be titrated with acidic solutions and the neutralization followed by conductometric, potentiometric, photometric, and similar methods. Some metal and nonmetal chlorides are amphoteric in phosphorus oxychloride:

\[
\begin{align*}
\text{K}^+ + \text{Cl}^- + \text{AlCl}_3 & \overset{\text{oxo}}{\longrightarrow} \text{K}^+ + \text{AlCl}_4^- \\
\text{SCl}_3 + \text{AlCl}_3 & \overset{\text{oxo}}{\longrightarrow} \text{SCl}_4^-
\end{align*}
\]  
(10.68, 10.69)

A table of relative chloride ion donor and acceptor abilities can be established from equilibrium and displacement reactions (Table 10.5). As expected, good donors are generally poor acceptors and vice versa with but few exceptions (e.g., HgCl₂).

There has been some controversy in the literature over the proper interpretation of reactions in solvents such as phosphorus oxychloride. Dragó and coworkers have suggested the "coordination model" as an alternative to the solvent system approach. They have stressed the errors incurred when the solvent system concept has been generally poor acceptors and vice versa with but few exceptions (e.g., HgCl₂).

They have pointed out that iron(III) chloride dissolves in triethyl phosphate with the formation of tetrachloro-

\[
\text{FeCl}_3 + \text{OPCl}_3 \rightarrow \text{FeCl}_4^-(\text{solvent})
\]

This equilibrium will lie to the right if the dichlorophosphoryl ion and to the left if the acid strengths are reversed. The important point is that neither the solvent system approach nor the coordination model can, a priori, predict the nature of the equilibrium in Eq. 10.72. To make this prediction, one must turn to the generalized acid-base definition given above together with some knowledge of the relative electron densities on the central atoms in FeCl₃.

Dragó and coworkers argue that in view of the similarity in physical and chemical properties between phosphorus oxychloride, OP(OEt)₃, and triethyl phosphate, OP(OEt)₃, it is probable that the formation of FeCl₄⁻ in phosphorus oxychloride proceeds by a reaction similar to Eq. 10.70.

\[
\begin{align*}
2\text{FeCl}_3 & \overset{\text{oxo}}{\longrightarrow} \left[\text{FeCl}_3(\text{OP(OEt)})_3\right]^{3+} + \text{FeCl}_4^-(10.70)
\end{align*}
\]

They argue that the similar coordinating ability of these phosphorus (—P=O) solvents (and to a lesser extent their dielectric constants) is more important than their chemical differences (supposed autoionization and chloride ion transfer in phosphorus oxychloride).

Gutmann has rejoined that the dichloroiron(III) ion, [FeCl₂(solv.)]⁺, is not found in dilute solutions in phosphorus oxychloride but only in concentrated solutions or those to which a strong acid such as SbCl₅ has been added. In such cases the chloride donor ability of the solvent has been exceeded and chloride ions are abstracted from the iron(III) chloride. This point was made earlier by the observation that the controversy is at least partly a semantic one. The only "characteristic property" of the solvo-cations and solvo-anions in the solvent system autoionization is that they are the stronger acids and bases that can exist in that particular solvent without being leveled.

In triethyl phosphate (a nonleveling solvent) the dichloroiron(III) ion is perfectly stable. In phosphorus oxychloride a mechanism for leveling exists, namely:

\[
\text{FeCl}_3 + \text{OPCl}_3 \rightarrow \text{OPCl}_3^- + \text{FeCl}_4^-(10.73)
\]

This equilibrium will lie to the right if the dichloroiron(III) ion is a stronger acid than the dichlorophosphoryl ion and to the left if the acid strengths are reversed. The important point is that neither the solvent system approach nor the coordination model can, a priori, predict the nature of the equilibrium in Eq. 10.72. To make this prediction, one must turn to the generalized acid-base definition given above together with some knowledge of the relative electron densities on the central atoms in FeCl₃ and OP(OEt). The essence of the acidity of iron(III) chloride lies in its tripositive ion of rather small radius and high charge, which is compensated only in part by three coordinated chloride ions and which seeks electrons for electron density to reduce its positive character. It is thus an acid irrespective of the solvent chosen and will accept the strongest base available to it. If the basicity of the phosphoryl group is sufficient (as it must of necessity be in triethyl phosphate or in phosphorus oxychloride if the chloride ion concentration is too low), then the iron(III) chloride is less acidic than if it can abstract a chloride ion (possible only in phosphorus oxychloride).
9.10 a. Do you expect dimethylsulfide, (CH₃SO₂, to bind to H⁺ through the sulfur or the oxygen atom? Support your prediction with numbers.

b. Calculate the affinities of the following bases for trimethylsilylammoniog: (CH₃)₃N⁺.

9.11 In general, the best data for correlating acid-base phenomena are obtained in gas-phase experiments rather than in solution. Discuss factors present in solution, especially in polar solvents, that make solution data suspect.

9.12 In contrast to the generalization made in Problem 9.11 there is reason to believe the gas-phase work. Can you suggest a reason? (Hint: Consider the possibilities for hydrogen bonding.)


9.14 Complete and balance the following equations, identifying the acids and the bases.

9.15 When you read Chapter 5, do so now.

9.16 The discussions of basicity of amides on pages 334 and 342 are based upon the carbonyl bonding.)

9.17 a. 9.18 b. Calculate the affinities of the following bases for trimethylstannyl cation. (CH₃)₃Sn⁺:

9.19 i. K. Will this material act as an acidic or basic catalyst?

9.20 a. b. (Hint: Remember that the current chapter deals with Lewis acid–base interactions.)

9.21 Predict the order of proton affinities for the following bases: NR₂, S⁻², N⁺F-, O⁻², NH₃, OH⁻, NC.O, N⁺². Pick any pair of bases from this series and explain why you decided that one was stronger than the other.

9.22 There is a strong chemical bond between the coordinated nitrogen and the iron.

9.23 a. b. c. d. e. f. Calculate the enthalpies for all of the possible 1:1 reactions between the acids H⁺, CH₃CO₂H, FF, CF₃CH₂OH, and the bases OH⁻, NH₃, (CH₃)₃N, and C²⁺. You may check some of your answers against Table 9.5. How accurate are your calculations?

9.24 Examine Fig. 9.2 and provide a rationale for the relationship therein.

9.25 a. We learn in organic chemistry that C₆H₅N⁺ and C₆H₅O⁻ are weaker bases than NH₃, and Table 9.5 indicates similarly. Discuss, including the important molecular attributes of each molecule. (Hint: See RO₂⁻, page 344.)

b. Water is a weak acid, but most hydrocarbons are usually considered to have virtually no acidity whatsoever. However, in the gas phase C₂H₅OH is 10⁻¹¹ stronger as an acid than H₂O. Discuss the particular molecular properties that cause the gas-phase values to be different from solution data and to differ so much between these two species.

9.26 a. The change in frequency of the carbonyl group upon coordination to a Lewis acid is stated in terms of bond order. Develop such an argument.

b. The proton affinities of pyridine (953 kJ mol⁻¹) and ammonia (872 kJ mol⁻¹) with the argument on page 343 concerning the relationship between pKₐ and electronegativity. The latter argument seems to go with the "conventional wisdom" rather than the discussion in this chapter. Continue.

9.27 Reconcile the values of the proton affinities of pyridine (953 kJ mol⁻¹) and ammonia (872 kJ mol⁻¹) with the argument on page 343 concerning the relationship between pKₐ and electronegativity.

9.28 Examine Fig. 9.2 and provide a rationale for the relationship therein.

9.29 a. a. Dioxygen, O₂, is not a very good ligand, but it is fairly soft. Hemoglobin contains Fe⁺⁺, which is only of borderline softness.

b. a. Look at the structure of the hemoglobin and suggest how the iron in hemoglobin is softened.

c. a. Carbon monoxide is poisonous because it bonds more tightly to the hemoglobin in red blood cells than does dioxygen. Why does carbon monoxide out-compete dioxygen as a ligand?

9.30 How is it possible for the noble gases to have exothermic proton affinities, indicating the formation of X⁻+H⁺ chemical bonds?

9.31 a. Presumably, in the gas phase IF₃O₂⁻ has the same structure as CF₃O₂⁻, but the structure of the solid is not a bit of a surprise. Suggest possibilities. (Hint: Remember that the current chapter deals with Lewis acid–base interactions.)

9.32 b. Some ill effects of acid rain come not from the low pH, per se, but from the toxicity of metals ions. Explain.
selected solvents
relative permittivity
(\varepsilon/\varepsilon_0)
of acceptor number (AN), and Donor number (DN),


Molecular Interactions', Chimia, 1977, I; The Donor-Acceptor Approach to


371

Table 10.4

<table>
<thead>
<tr>
<th>Solvent</th>
<th>DN</th>
<th>AN</th>
<th>(\varepsilon/\varepsilon_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>52.9</td>
<td>6.2</td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>12.5</td>
<td>20.7</td>
<td></td>
</tr>
<tr>
<td>Acetonic acid</td>
<td>19.3</td>
<td>56</td>
<td></td>
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<tr>
<td>Antimony pentachloride</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
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<td>2.3</td>
<td></td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
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<td>2.2</td>
<td></td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>23.1</td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>20.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diethyl ether</td>
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<td>4.3</td>
<td></td>
</tr>
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<td></td>
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</tr>
<tr>
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<td></td>
</tr>
<tr>
<td>Dioxane</td>
<td>18.0</td>
<td>3.3</td>
<td></td>
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<tr>
<td>Nitromethane</td>
<td>2.7</td>
<td>38.6</td>
<td></td>
</tr>
<tr>
<td>Phosphorus oxychloride</td>
<td>11.7</td>
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</tr>
<tr>
<td>Propylene carbonate</td>
<td>15.1</td>
<td></td>
<td></td>
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<tr>
<td>Pyridine (py)</td>
<td>14.2</td>
<td>12.3</td>
<td></td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>20.0</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>Trichloroacetic acid</td>
<td>105.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trichloroacetic acid</td>
<td>129.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>15</td>
<td>54.8</td>
<td>81.7</td>
</tr>
</tbody>
</table>

* The ratio \(\varepsilon/\varepsilon_0\) is more convenient to use than the value of the permittivity in absolute units.


370 10. Chemistry in Aqueous and Nonaqueous Solvents

Fluoride salts dissolve unchanged except for fluoride ion transfer to form conducting solutions:

- KF + BrF_4^- = K^+ + BrF_4^- (10.54)
- AgF + BrF_4^- = Ag^+ + BrF_4^- (10.55)
- SnF_4 + BrF_4^- = 2BrF_4^- + SnF_4^- (10.56)
- SnF_4 + BrF_4^- = 2BrF_4^- + SnF_4^- (10.57)

These solutions can be considered acids or bases by analogy to the presumed autoionization of BrF_4^-:

- 2BrF_4^- = BrF_4^- + BrF_4^- (10.58)

Reactions 10.50 to 10.52, 10.56, and 10.57 above may be considered to form acid solutions (BrF_4^- ions formed) and reactions 10.53 to 10.55 may be considered to form basic solutions (BrF_4^- ions formed). Acid solutions may be readily titrated by bases:

- (BrF_3)SnF_4 + AgBrF_4 = AgSnF_4 + 2BrF_3 (10.59)

Such reactions may be followed conveniently by measuring the conductivity of the solution: A minimum occurs at the 1:1 endpoint. Solutions of SnF_4 behave as dibasic acids:

- (BrF_3)SnF_4 + 2KBrF_4 = K_2SnF_4 + 4BrF_3 (10.60)

with minimum conductivities corresponding to 1:2 mole ratios.

A similar, although less reactive, aprotic solvent is phosphorus oxychloride (phosphoryl chloride). A tremendous amount of work on the properties of this solvent has been done by Gutmann and coworkers. They have interpreted their results in solvent system terms based on the supposed autoionization:

- OPCl_3 = OPCl_3^- + Cl^- (10.61)

or the more general solvated forms:

- \((m + n)OPCl_3 = \{OPCl_3[OPCl_3]\}^\cdot + \{Cl[OPCl_3]\}^- (10.62)\)

It is extremely difficult to measure this autoionization because contamination with traces of water yields conducting solutions which may be described approximately as:

- \(3H_2O + OPCl_3 = 2H_2OCl + Cl^- + (OPCl_3)\) (10.63)

If autoionization does occur, the ion product, \([OPCl_3[Cl^-])\), is equal to or less than \(5 \times 10^{-14}\).

Salts which dissolve in phosphoryl chloride to yield solutions with high chloride ion concentrations are considered bases:

- KCl = K^+ + Cl^- (10.64)
- Et_3N = [Et_3N][Cl^-]^- (10.65)

13 This expression for the autoionization of BrF_3 is based on the conductivity of pure BrF_3 and the characterization of the BrF_4^- salts such as KBrF_4. The evidence for BrF_4^- is weaker. Further support for this formulation is obtained from the ICl_3 system where X-ray evidence for ICl_3^- has been obtained.

9.34 Explain what effect acid rain would have on the condition of each of the following and why:

a. The Taj Mahal, at Agra, India
b. A limestone barn near Antietam Battlefield, Maryland, dating from the Civil War
c. The Parthenon, Athens, Greece
d. The ability of an aquatic snail to form its shell in a lake in the Adirondack Mountains
e. The asbestos-shingled roof on the house of one of the authors in College Park, Maryland
f. The integrity of the copper eaves-troughs and downspout on that house
g. The integrity of the brick siding of that house
h. The growth of the azaleas planted along the foundation of that house
i. The integrity of the aluminum siding on a neighbor’s house
j. The slate roof on another neighbor’s house
k. The longevity of galvanized steel fencing in the neighborhood

9.35 Throughout this chapter, the fluoride ion is referred to as a strong base, yet good, illustrative examples are seemingly not common. Suggest a few such examples. Why are there not more simple examples of $F^-$ acting as a strong base or nucleophile? Suggest ways of making strong $F^-$ bases.

---

Fig. 10.1 Relative acidity and basicity of solvents. Solvents and solutes are listed from top to bottom in order of decreasing basicity and increasing acidity. Solutes are listed in order of decreasing $pK_u$ as determined in water. Some values of $pK_u$ are estimated. In ideal aqueous solutions, equimolar mixtures of an acid and its conjugate base will have a pH equal to the $pK_a$.

The range of acidity and basicity over which a particular solvent is differentiating is shown at the right. All acids lying below and all bases lying above the enclosed box will be leveled to the characteristic cation and anion of the solvent. The arrows involving CH$_3$COOH and NH$_3$ illustrate the fact that an acid will readily donate a proton to a base above it and to the right.

Aprotic Solvents

Thus far, the solvents discussed have had one feature in common with water, namely, the presence of a transferable hydrogen and the formation of ionic ions. In this section we shall look briefly at solvents which do not ionize in this way. These may be conveniently classified into three groups. The first group consists of solvents such as carbon tetrachloride and cyclohexane which are nonpolar, essentially nonsolvating, and do not undergo autoionization. These are useful when it is desired that the solvent play a minimal role in the chemistry being studied, for example, in the determination of $E$ and $C$ parameters discussed in the previous chapter.

The second group consists of those solvents that are polar, yet do not ionize.

Some examples of solvents of this type are acetone, CH$_3$COCH$_3$; dimethylformamide, (CH$_3$)$_2$CONH$_2$; dimethyl sulfoxide (DMSO), (CH$_3$)$_2$SO; and sulfur dioxide, SO$_2$. Although these solvents do not ionize to a significant extent, they are highly coordinating solvents because of their polarity. The polarity ranges from low (SO$_2$) to extremely high (DMSO). Most are basic solvents tending to coordinate strongly with cations and other acidic centers:

\[
\text{CoBr}_2 + 6\text{DMSO} \rightarrow \text{Co(DMSO)}_6^{2+} + 2\text{Br} \tag{10.46}
\]

\[
\text{SbCl}_5 + \text{CH}_3\text{C}=\text{N} \rightarrow \text{SbCl}_5\text{CH}_3\text{C}=\text{N} \tag{10.47}
\]

A few, the nonmetal oxides and halides, can behave as acceptor solvents, reacting with anions and other basic centers:

\[
\text{Ph}_2\text{CCI} + \text{SO}_2 \rightarrow \text{Ph}_2\text{CCl}^+ + \text{SO}_2\text{Cl}^- \tag{10.48}
\]

This group of solvents ranges from the limiting case of a nonpolar solvent (Group I) to an autoionizing solvent (Group III, see below). Within this range a wide variety of reactivity is obtained. Gutmann\(^1\) has defined the donor number (DN) as a measure of the basicity or donor ability of a solvent. It is defined as the negative enthalpy of reaction of a base with the Lewis acid antimony pentachloride, SbCl$_5$:

\[
E + \text{SbCl}_5 \rightarrow E\text{SbCl}_5^+ \rightarrow \Delta H \tag{10.49}
\]

These donor numbers provide an interesting comparison of the relative donor abilities of the various solvents (Table 10.4), ranging from the practically nonpolar 1,2-dichloroethane to the highly polar hexamethylphosphoramide, (CH$_3$)$_6$P=O. Note, however, that there is no exact correlation between donor number and permittivity.

Some solvents with relatively high permittivities such as nitromethane and propylene carbonate ($\varepsilon/\varepsilon_0 = 36.8$ and 65.1) may be very poor donors (DN = 2.7 and 13.1). Conversely, the best donors do not always have high permittivities: pyridine (DN = 33.1, $\varepsilon/\varepsilon_0 = 12.5$) and diethyl ether (DN = 19.2, $\varepsilon/\varepsilon_0 = 4.1$). This should serve to remind us that solubility is not merely an electrostatic interaction but that solvation also involves the ability to form covalent donor bonds. Note that pyridine may be considered to be a relatively soft base (Chapter 9). Gutmann has extended the concept

Water will be discussed only briefly here, but a summary of its physical properties is given in Table 10.1 for comparison with the nonaqueous solvents to follow. One notable property is the very high permittivity which makes it a good solvent for ionic and polar compounds. The solvating properties of water and some of the related effects have been discussed in Chapter 8. Electrochemical reactions in water are leveled (to form ammonium ions):

\[ \text{HCIO}_4 + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{ClO}_4^- \]  
\[ \text{HNO}_3 + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{NO}_3^- \]

All acids that behave as strong acids in water react completely with ammonia (are leveled) to form ammonium ions:

\[ \text{HClO}_4 + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{ClO}_4^- \]  
\[ \text{HNO}_3 + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{NO}_3^- \]

In addition, some acids which behave as weak acids in water (with \( pK_a > 12 \)) react completely with ammonia and hence are strong acids in this solvent:

\[ \text{H}_3\text{CNO}_2 + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{C}_2\text{H}_5\text{O}_2^- \]  
\[ \text{HNO}_2 + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{NO}_2^- \]

Neutralization reactions can be run that parallel those in water:

\[ \text{KNO}_2 + \text{NH}_4\text{Cl} \rightarrow \text{KCl} + \text{NH}_4\text{NO}_2 \]  
\[ \text{KNO}_2 + \text{NH}_4\text{NO}_3 \rightarrow \text{KNO}_3 + \text{NH}_4\text{Cl} \]

Furthermore, amphoteric behavior resulting from complex formation with excess amide also parallels that in water:

\[ \text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn} \left( \text{OH} \right)_2 \downarrow \]  
\[ \text{Zn}^{2+} + 2\text{NH}_3 \rightarrow \text{Zn} \left( \text{NH}_2 \right)_2 \downarrow \]

Precipitation reactions take place in ammonia just as they do in water. Because of the differences in solubility between the two solvents, the results may be considerably different. As an example, consider the precipitation of silver chloride in aqueous solution:

\[ \text{KCl} + \text{AgNO}_3 \rightarrow \text{AgCl} + \text{KNO}_3 \]  
\[ \text{KCl} + \text{AgNO}_3 \rightarrow \text{AgCl} + \text{KNO}_3 \]

In ammonia solution, the direction of the reaction is reversed so that:

\[ \text{AgCl} + \text{KNO}_3 \rightarrow \text{AgNO}_3 + \text{KCl} \]  
\[ \text{AgCl} + \text{KNO}_3 \rightarrow \text{AgNO}_3 + \text{KCl} \]

Ammonia undergoes autolysis with the formation of ammonium and amide ions:

\[ 2\text{NH}_3 \rightarrow \text{NH}_4^+ + \text{NH}_2^- \]  
\[ 2\text{NH}_3 \rightarrow \text{NH}_4^+ + \text{NH}_2^- \]

Ammonia has probably been studied more extensively than any other nonaqueous solvent. Its physical properties resemble those of water except that the permittivity is considerably smaller (Table 10.2). The lower dielectric constant results in a generally decreased ability to dissolve ionic compounds, especially those containing highly charged ions (e.g., carbonates, sulfates, and phosphates are practically insoluble). In some cases the solubility is higher than might be expected on the basis of the permittivity alone. In these cases there is a stabilizing interaction between the solute and the ammonia. One type of interaction is between certain metal ions such as \( \text{Ni}^{2+} \), \( \text{Cu}^{2+} \), and \( \text{Zn}^{2+} \) and the ammonia molecule, which acts as a ligand to form stable ammine complexes. A second type is between the polarizing and polarizable ammonia molecule and polarizable solute molecules or ions. Ammonia may thus be a better solvent than water toward nonpolar molecules. Ionic compounds containing large, polarizable ions such as iodide and thiocyanate also are quite soluble.

Table 10.1

<table>
<thead>
<tr>
<th>Physical properties of water</th>
<th>100 °C</th>
<th>0 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling point</td>
<td>100 °C</td>
<td>0 °C</td>
</tr>
<tr>
<td>Freezing point</td>
<td>1.00 g cm(^{-3}) (4 °C)</td>
<td>81.7 °C (18 °C)</td>
</tr>
<tr>
<td>Density</td>
<td>4.10 \times 10^{-8} \text{ g cm}^{-1} (18 °C)</td>
<td>1.01 \mu \text{ cm}^{-1} \text{ s}^{-1} (78 °C)</td>
</tr>
<tr>
<td>Viscosity</td>
<td>1.008 \times 10^{-3} \text{ mol L}^{-1} (25 °C)</td>
<td>1.008 \times 10^{-3} \text{ mol L}^{-1} (25 °C)</td>
</tr>
<tr>
<td>Ion product constant</td>
<td>1.008 \times 10^{-3} \text{ mol L}^{-1} (25 °C)</td>
<td>1.008 \times 10^{-3} \text{ mol L}^{-1} (25 °C)</td>
</tr>
</tbody>
</table>

Table 10.2

<table>
<thead>
<tr>
<th>Physical properties of ammonia</th>
<th>-33.38 °C</th>
<th>-77.7 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling point</td>
<td>-33.38 °C</td>
<td>-77.7 °C</td>
</tr>
<tr>
<td>Freezing point</td>
<td>0.725 g cm(^{-3}) (-70 °C)</td>
<td>26.74 g cm(^{-3}) (-60 °C)</td>
</tr>
<tr>
<td>Density</td>
<td>1.90 \times 10^{-11} \text{ g cm}^{-1}</td>
<td>0.2546 \mu \text{ cm}^{-1} (-31 °C)</td>
</tr>
<tr>
<td>Viscosity</td>
<td>5.1 \times 10^{-7} \text{ mol L}^{-1}</td>
<td>5.1 \times 10^{-7} \text{ mol L}^{-1}</td>
</tr>
<tr>
<td>Ion product constant</td>
<td>5.1 \times 10^{-7} \text{ mol L}^{-1}</td>
<td>5.1 \times 10^{-7} \text{ mol L}^{-1}</td>
</tr>
</tbody>
</table>
Perchloric acid is one of the strongest acids known, but in sulfuric acid it is practically a nonelectrolyte, behaving as a very weak acid:

\[
\text{HClO}_4 + \text{H}_2\text{SO}_4 \rightleftharpoons \text{H}_3\text{SO}_4^+ + \text{ClO}_4^- \quad (10.38)
\]

One of the few substances found to behave as an acid in sulfuric acid is disulfuric (pyrosulfuric) acid. It is formed from sulfur trioxide and sulfuric acid:

\[
\text{SO}_3 + \text{H}_2\text{SO}_4 \rightleftharpoons \text{H}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} \quad (10.39)
\]

\[
\text{H}_2\text{S}_2\text{O}_3 + \text{H}_2\text{SO}_4 \rightleftharpoons \text{H}_3\text{S}_2\text{O}_4^- + \text{H}_2\text{O} \quad (10.40)
\]

An exceptionally strong acid in sulfuric acid is hydrogen tetraakis(hydrogensulfato)borate, \(\text{H}_4\text{B(SO}_4\text{)}_4\). The compound has not been prepared and isolated in pure form, but solutions of it may be prepared in sulfuric acid:

\[
\text{H}_2\text{B(SO}_4\text{)}_4 + \text{H}_2\text{SO}_4 \rightleftharpoons \text{H}_2\text{B(SO}_4\text{)}_4^+ + 3\text{HSO}_4^- \quad (10.41)
\]

\[
\text{H}_2\text{B(SO}_4\text{)}_4^+ + 3\text{HSO}_4^- \rightleftharpoons \text{H}_2\text{B(SO}_4\text{)}_4 + 5\text{H}_2\text{O} \quad (10.42)
\]

Even such unlikely bases as \(\text{Xe, H}_2\text{, Cl}_2\text{, Br}_2\text{, and CO}_2\) have been shown to accept \(\text{H}^+\) ions from superacidity, though perhaps only to a small extent. There is no evidence that \(\text{Ar, O}_2\), or \(\text{N}_2\) become protonated.

Summary of Protonic Solvents

Despite certain differences, the three protonic solvents discussed above (water, ammonia, and sulfuric acid) share a similarity in their acid-base behavior. All are autoionizing, with the ionization taking place through the transfer of a proton from one molecule of solvent to another with the formation of a solvated proton (Bronsted acid, solvent system acid) and a deprotonated anion (Bronsted and Lewis base, solvent system base). The inherent acidities and basicities of these three solvents differ, however, and so their tendencies to protonize or deprotonate solutes differ. It is possible to list solvents in order of their inherent acidity or basicity. Water is obviously less acidic than sulfuric acid but more so than ammonia. Glacial acetic acid lies between water and sulfuric acid in acidity. Figure 10.1 graphically illustrates the relative acidities and basicities of four solvents, together with various acid-base conjugate pairs. They are listed in order of the \(pK_a\) in water. In an ideal aqueous solution the pH of an equimolar mixture of conjugates is given by the \(pK_a\) and similar acidity scales may be used in other solvents. The \(pK_a\) is thus a rough estimate of acidity in solvents other than water. Any given acid is stronger than the acids listed above it and, conversely, any base is stronger than the bases below it. All species that lie within the extremes of a particular solvent behave as weak electrolytes in that solvent and form weakly acidic or weakly basic solutions. All species that lie beyond the enclosed range are leveled by the solvent.

An example may serve to illustrate the information that may be obtained from Fig. 10.1. Consider acetic acid. In water, acetic acid behaves as an acid, or, to be more precise, an equimolar mixture of acetic acid and an acetic anion will have a pH of 4.74. If acetic acid is added to sulfuric acid, it will behave as a base and be leveled to \(\text{CH}_3\text{COO}^-\), the acetic acid ion, and \(\text{HSO}_4^-\) (cf. Eq. 10.36; note the equilibrium lying at about \(-9\) on the scale in Fig. 10.1).

If dissolved in ammonia, acetic acid will behave as a strong acid and be leveled to \(\text{NH}_3^-\) and \(\text{CH}_3\text{COO}^-\) (cf. Eq. 10.11; note equilibrium lying at about 4.7 on the scale in Fig. 10.1). The different behavior of acetic acid as a base (sulfuric acid), a strong acid (ammonia), or a weak acid (water) depends upon the acidity or basicity of the solvent.

The "equilibrium boxes" for the solvents (Fig. 10.1) indicate the range over which differentiation occurs: outside the range of a particular solvent, all species are leveled. For example, water can differentiate species (i.e., they are weak acids and bases) with \(pK_a\)'s from about 0 to 14 (such as acetic acid). Ammonia, on the other hand, behaves the same toward acetic acid and sulfuric acid because both lie below the differentiating limit of \(-12\). The extent of these ranges is determined by the autoionization constant of the solvent (e.g., \(-14\) units for water). The acid-base behavior of several species discussed previously may be seen to correlate with Fig. 10.1.

A complete discussion of relative acidities and basicities would be too extensive to be covered here. Nevertheless it is possible to summarize the behavior of acids and bases as involving (1) the inherent acidity--basicity of the solvent, (2) the inherent acidity--basicity of the solute, and (3) the interaction of solute and solvent to form an...
**Solutions of Metals in Ammonia**


2. Certain elements do not form this type of solution. Although the solution changes from blue to bronze with increasing concentration, a two-phase system is always obtained.

3. One must be very careful to exclude water and other materials which might react with the alkali metal and thus prevent the reversibility of the solution.

Cl₂ + 2NH₃ → HClO + H₂O⁺ + Cl⁻  \(\text{(10.15)}\)

Cl₂ + 2NH₃ → NH₃Cl + NH₄⁺ + Cl⁻  \(\text{(10.16)}\)

Since it is more basic than water, ammonia can cause the disproportionation of sulfur:

S₈ + 16NH₃ → 4S₂N⁺ + 4S²⁻ + 12NH₂⁺  \(\text{(10.17)}\)

The hexafulvene ion is in dissociative equilibrium:

\[S_2^{1-} \rightleftharpoons 2S\]  \(\text{(10.18)}\)

The \(S_2\) ion is responsible for the deep blue color of these solutions \((\lambda_{max} = 610 \text{ nm})\). This ion is also responsible for the color of sulfur dissolved in chlorinated solvents (see below) and in the aluminosilicate known as aluminomica (see Chapter 10). Many nonmetal halides behave as acid halides in solvolysis reactions:

\[\text{OPC}_2 + 6\text{H}_2\text{O} \rightarrow \text{OP(OH)}_2 + 3\text{H}_2\text{O}^+ + 3\text{Cl}^-\]  \(\text{(10.19)}\)

\[\text{OPC}_2 + 5\text{NH}_3 \rightarrow \text{OP(NH)}_3 + 2\text{NH}_2^+ + 3\text{Cl}^-\]  \(\text{(10.20)}\)

The resemblance of these reactions and the structural resemblance between phosphoric acid \((\text{OP(OH)}_2)\) and phosphonamide \((\text{OP(NH)}_3)\) has led some people to use the term "ammonio acid" to describe the latter.

In a manner analogous to that used for water, a \(p_H\) scale can be set up for ammonia: \(p_H = 0 (1 \text{ M NH}_3); \quad p_H = 13 (\text{[NH}_2] = [\text{NH}_3]), \quad \text{neutrality}; \quad p_H = 26 (1 \text{ M NH}_3)\). Likewise oxidation-reduction potentials may be obtained, based on the hydroxide electrode (see page 379):

\[\text{NH}_4^+ + e^- = \text{NH}_3 + \text{H}_2 \quad \epsilon^0 = 0\]  \(\text{(10.21)}\)

In summary, the chemistry of ammonia solutions is remarkably parallel to that of aqueous solutions. The principal differences are in the increased basicity of ammonia and its reduced dielectric constant. The latter not only reduces the solubility of ionic materials, but also promotes the formation of ion pairs and ion clusters. Hence even strong acids, bases, and salts are highly associated.

If a small piece of an alkali metal is dropped into a Dewar flask containing liquefied ammonia, the solution immediately assumes an intense deep blue color. If more alkali metal is dissolved in the ammonia, eventually a point is reached where a bronze-colored phase separates and floats on the blue solution. Further addition of alkali metal results in the gradual conversion of blue solution to bronze solution until the former disappears. Evaporation of the ammonia from the bronze solution allows one to recover the alkali metal unchanged. This unusual behavior has fascinated chemists since its discovery in 1864. Complete agreement on the theoretical interpretation of experimental observations made on these solutions has not been achieved.

The blue solution is characterized by (1) its color, which is independent of the metal involved; (2) its density, which is very similar to that of pure ammonia; (3) its conductivity, which is in the range of electrolytes dissolved in ammonia; and (4) its paramagnetism, indicating unpaired electrons, and its electron paramagnetic resonance \(g\)-factor, which is very close to that of the free electron. This has been interpreted as indicating that in dilute solution, alkali metals dissociate to form alkali metal cations and solvated electrons:

\[\text{M}^{3+} (\text{ammonia}) \quad \text{M}^+ [\text{e(NH}_3)_2]^-\]  \(\text{(10.22)}\)

The dissociation into cation and anion accounts for the electrolytic conductivity. The solution contains a very large number of unpaired electrons, hence the paramagnetism, and the \(g\)-value indicates that the interaction between solvent and electrons is rather weak. It is common to talk of the electron existing in a cavity in the ammonia, loosely solvated by the surrounding molecules. The blue color is a result of a broad absorption peak that has a maximum at about 1500 nm. This peak results from an absorption of photons by the electron as it is excited to a higher energy level, but not all absorptions are in agreement as to the nature of the excited state.

The very dilute solutions of alkali metals in ammonia thus come close to presenting the chemist with the hypothetical "ultimate" base, the free electron (Chapter 9). As might be expected, such solutions are metastable, and when catalyzed, the electrons are "leveled" to the amide ion:

\[\text{[e(NH}_3)_2]^- \rightarrow 2\text{H}^+ + 2\text{NH}_2^+ + (x - 1)\text{NH}_3\]  \(\text{(10.23)}\)

The bronze solutions have the following characteristics: (1) a bronze color with a definite metallic luster; (2) very low densities; (3) conductivities in the range of metals; and (4) magnetic susceptibilities similar to those of pure metals. All of these properties are consistent with a model describing the solution as a "dilute metal" or an "alloy" in which the electrons behave essentially as in a metal, but the metal atoms have been moved apart (compared with the pure metal) by interspersed molecules of ammonia.

The nature of these two phases helps to throw light on the metal-nonmetal transition. For example there has been much speculation that hydrogen molecules at high pressure, such as those occurring on the planet Jupiter, might undergo a transition to an "alkali metal." The fundamental transition is one of a dramatic change in the van der Waals interactions of \(H_2\) molecules into metallic cohesion.

Solutions of alkali metals in ammonia have been the best studied, but other metals and other solvents give similar results. The alkaline earth metals except beryllium form similar solutions readily, but upon evaporation a solid "ammonia." \(\text{M(NH}_3)_2\) is formed. Lanthanide elements with stable +2 oxidation states (europium, ytterbium) also form solutions. Cathodic reduction of solutions of aluminum iodide, beryllium chloride, and tetraethylammonium halides yields blue solutions, presumably containing \(\text{Al}^{3+}, \text{Be}^{2+}, \text{Mg}^{2+}\), and \(\text{R}_2\text{N}^+, \text{c}\) respectively. Other solvents such as aromatics, ethers, and hexamethyldisiloxane have been investigated and show some propensity to form this type of solution. Although none does so as readily as ammonia, stabilization of the color by complexation results in typical blue solutions.

---


The chemistry of metal electrides has been extensively studied and although the formulation \( \text{M}^{+}e^{-} \) is undoubtedly the best, most chemists have the all-too-human emotion of feeling more secure in their science if they have something more tangible than solutions and equations on paper. Therefore the isolation and structural characterization of cesium electride, \( \text{Cs}^{+}e^{-} \), is single crystals was welcome, indeed.\(^7\) The crystals are dark blue with a single absorption maximum at 1500 nm, have no likely anions present (the empirical formula is \( 1:1, \text{Cs}:\text{ligand} \)), with a trace of lithium (based on X-ray diffraction data), and are most readily formulated as a complex of cesium electride.

The crystals are dark blue with a single absorption maximum at 1500 nm, have no likely anions present (the empirical formula is \( 1:1, \text{Cs}:\text{ligand} \)), with a trace of lithium (based on X-ray diffraction data), and are most readily formulated as a complex of cesium electride.

The physical properties of sulfuric acid are listed in Table 10.3. The dielectric constant is even higher than that of water, making it a good solvent for ionic substances and leading to extensive autoionization. The high viscosity, some 25 times that of water, introduces experimental difficulties: Solutes are slow to dissolve and slow to crystallize. It is also difficult to remove adhering solvent from crystallized materials. Furthermore, solvent that has not drained from prepared crystals is not readily removed by evaporation because of the very low vapor pressure of sulfuric acid.

### Table 10.3

<table>
<thead>
<tr>
<th>Physical properties of sulfuric acid</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling point</td>
<td>300 °C (with decomposition)</td>
</tr>
<tr>
<td>Freezing point</td>
<td>10.71 °C</td>
</tr>
<tr>
<td>Density</td>
<td>1.83 g cm(^{-3}) (25 °C)</td>
</tr>
<tr>
<td>Permittivity (dielectric constant)</td>
<td>110 (20 °C)</td>
</tr>
<tr>
<td>Specific conductance</td>
<td>1.04 ( \times 10^{-3} ) ( \Omega^{-1} ) cm(^{-1}) (25 °C)</td>
</tr>
<tr>
<td>Viscosity</td>
<td>24.54 ( \times 10^{-3} ) cm(^{2}) s(^{-1}) (20 °C)</td>
</tr>
<tr>
<td>Ion product constant</td>
<td>2.7 ( \times 10^{-4} ) mol L(^{-1}) (25 °C)</td>
</tr>
</tbody>
</table>

---


\(^7\) Issa, D.; Dye, J. L. J. Am. Chem. Soc. 1982, 104, 3781. For the crystal structure of this compound, see Chapter 12, Fig. 12.30b.

---

**Autoionization of sulfuric acid results in the formation of the hydrogen sulfate (bisulfate) ion and a solvated proton:**

\[
\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}_2\text{SO}_4^+ + \text{HSO}_4^- \quad (10.29)
\]

As expected, a solution of potassium hydrogen sulfate is a strong base and may be treated with a solution containing \( \text{H}_3\text{PO}_4 \) ions. Such a titration may readily be followed conductometrically with a minimum in conductivity at the neutralization point.\(^8\)

Another method that has proved extremely useful in obtaining information about the nature of solutions in sulfuric acid solution is the measurement of freezing point depressions. The freezing point constant (4) for sulfuric acid is 6.13 °C mol\(^{-1}\) dm\(^3\) kg\(^{-1}\). For ideal solutions, the depression of the freezing point is given by

\[
\Delta T = \frac{nM}{m \kappa} 
\]

where \( n \) is the stoichiometric molarity and \( \kappa \) is the number of particles formed when one mole of solute dissolves in sulfuric acid. For example, ethanol reacts with sulfuric acid as follows:

\[
\text{C}_2\text{H}_5\text{OH} + 2\text{H}_2\text{SO}_4 \rightleftharpoons \text{C}_2\text{H}_5\text{HSO}_4 + \text{HSO}_4^- \quad \nu = 3 \quad (10.31)
\]

It is found that all species that are basic in water are also basic in sulfuric acid:

\[
\text{OH}^- + 2\text{H}_2\text{SO}_4 \rightleftharpoons \text{HSO}_4^- + \text{H}_3\text{O}^+ \quad \nu = 3 \quad (10.32)
\]

\[
\text{NH}_3 + \text{H}_2\text{SO}_4 \rightleftharpoons \text{HSO}_4^- + \text{NH}_4^+ \quad \nu = 2 \quad (10.33)
\]

Likewise, water behaves as a base in sulfuric acid:

\[
\text{H}_2\text{O} + \text{H}_2\text{SO}_4 \rightleftharpoons \text{H}_3\text{O}^+ + \text{HSO}_4^- \quad \nu = 2 \quad (10.34)
\]

Amides, such as urea, which are nonelectrolytes in water and acids in ammonia accept protons from sulfuric acid:

\[
\text{NH}_2\text{C}(\text{NH}) \text{NH}_2 + \text{H}_2\text{SO}_4 \rightleftharpoons \text{HSO}_4^- + \text{NH}_2\text{C}(\text{NH}) \text{NH}_3^+ \quad \nu = 2 \quad (10.35)
\]

Acetic acid is a weak acid in aqueous solution and nitric acid is a strong acid, but both behave as bases in sulfuric acid:

\[
\text{CH}_3\text{COO}^- + \text{H}_2\text{SO}_4 \rightleftharpoons \text{CH}_3\text{COOH}^- + \text{HSO}_4^- \quad \nu = 2 \quad (10.26)
\]

\[
\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightleftharpoons 2\text{HSO}_4^- + \text{NO}_3^- + \text{H}_3\text{O}^+ \quad \nu = 4 \quad (10.37)
\]

Sulfuric acid is a very acidic medium, and so almost all chemical species which react upon solution do so with the formation of hydrogen sulfate ions and are bases.

Because of the extreme tendency of the \( \text{H}_2\text{SO}_4 \) molecule to donate protons, molecules exhibiting basic tendencies will be leveled to \( \text{H}_2\text{SO}_4^- \).
452 11 • Coordination Chemistry: Bonding, Spectra, and Magnetism

As we have seen (Table 11.21), all of the $MI_2$ complexes that are susceptible to Jahn-Teller distortion have octahedral configurations that involve asymmetric electron occupation of either the $e^1$ or $e^2$ orbitals. Generally speaking, the former leads to considerably more pronounced distortions than does the latter. This occurs because the $e^1$ level is much more involved in the bonding than is the $e^2$. Hence complexes with $e^1$ or $e^2$ configurations (from high spin $d^4$ and $d^5$, low spin $d^4$, or $d^5$) often exhibit substantial distortions. It is not uncommon for these complexes to have bond length differences (two longer and four shorter or vice versa) that can be detected crystallographically at room temperature. In fact, some of the strongest evidence for Jahn-Teller effects in transition metal compounds comes from structural studies of solids containing the $d^4$ Co$^{2+}$ ion. Distortion by either elongation or compression will lead to stabilization of a copper(II) complex. However, experimental measurements show that the distortion is generally elongation along the $z$ axis (Fig. 11.49). Table 11.22 lists some bond distances found in crystals containing hexacoordinate Cu(II) ions. Each compound has both shorter and longer bonds. It is of interest that the "short" bonds represent a lower limit or starting point from which various degrees of distortion in the form of bond lengthening can occur.

We have fewer data to support Jahn-Teller distortion in high spin $d^4$ or low spin $d^6$ complexes. Chromium(II) and manganese(III) are $d^4$ ions, and both have been found to be distorted in some compounds (see Table 11.22). Furthermore, extensive studies of six-coordinate manganese(III) compounds have shown that their spectra can be readily interpreted in terms of elongation along the $z$ axis. The $d^6$ configuration of low spin Co$^{2+}$ is less straightforward. With ligands that are sufficiently strong field, the ion tends to form five- or four- rather than six-coordinate complexes. For example, the expected hexacyano complex, [Co(CN)$_6$]$^{3-}$, is not found, but instead the principal species in solution has five cyano groups per cobalt and is probably [Co(CN)$_5$]ClO$_4$$_2$. This might be viewed as an extreme form of Jahn-Teller distortion, namely complete dissociation of one cyanide from the hypothetical [Co(CN)$_6$]$^{3-}$ ion. Six-coordinate Co$^{2+}$ complexes are observed for the ligands bis(salicylidene)ethylamine (H$_2$salen) and nitrite. The spectra for these species are quite complicated, but they are consistent with axially elongated structures.

Table 11.22

<table>
<thead>
<tr>
<th>Compound</th>
<th>Short distances</th>
<th>$\alpha^\circ$</th>
<th>Long distances</th>
<th>$\alpha^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuF$_3$</td>
<td>4F at 153</td>
<td>122</td>
<td>2F at 227</td>
<td>156</td>
</tr>
<tr>
<td>CuF$_2$H$_2$O</td>
<td>2F at 150</td>
<td>119</td>
<td>2F at 247</td>
<td>176</td>
</tr>
<tr>
<td>Na$_2$CuF$_4$</td>
<td>4F at 151</td>
<td>120</td>
<td>2F at 237</td>
<td>166</td>
</tr>
<tr>
<td>K$_2$CuF$_4$</td>
<td>4F at 152</td>
<td>121</td>
<td>2F at 222</td>
<td>151</td>
</tr>
<tr>
<td>Na$_2$CuF$_3$</td>
<td>2F at 158</td>
<td>117</td>
<td>2F at 226</td>
<td>152</td>
</tr>
<tr>
<td>KCuF$_3$</td>
<td>2F at 159</td>
<td>118</td>
<td>2F at 225</td>
<td>154</td>
</tr>
<tr>
<td>CuCl$_2$</td>
<td>4Cl at 230</td>
<td>122</td>
<td>2Cl at 235</td>
<td>156</td>
</tr>
<tr>
<td>CuCl$_2$-2H$_2$O</td>
<td>2Cl at 229</td>
<td>120</td>
<td>2Cl at 234</td>
<td>193</td>
</tr>
<tr>
<td>CuCl$_2$-2Cu$_2$H$_2$N</td>
<td>2Cl at 230</td>
<td>123</td>
<td>2Cl at 305</td>
<td>206</td>
</tr>
<tr>
<td>Cu(NH$_3$)$_2$Cl$_3$</td>
<td>4N at 207</td>
<td>123</td>
<td>2N at 262</td>
<td>187</td>
</tr>
<tr>
<td>CrF$_3$</td>
<td>4F at 200</td>
<td>119</td>
<td>2F at 243</td>
<td>172</td>
</tr>
<tr>
<td>KCrF$_3$</td>
<td>2F at 200</td>
<td>119</td>
<td>2F at 244</td>
<td>143</td>
</tr>
<tr>
<td>NaXuF$_4$</td>
<td>4F at 217</td>
<td>108</td>
<td>2F at 229</td>
<td>138</td>
</tr>
<tr>
<td>NaCuF$_3$</td>
<td>2F at 191</td>
<td>120</td>
<td>2F at 209</td>
<td>138</td>
</tr>
<tr>
<td>K$_2$MnF$_4$H$_2$O</td>
<td>4F at 183</td>
<td>112</td>
<td>2F at 207</td>
<td>130</td>
</tr>
</tbody>
</table>

+ All distances are in picometers. The radius of the metal was obtained by subtracting the covalent radius of the ligating atom (Table 8.1) from the M-X distance.

Complexes having measurable bond-length differences, such as those reported in Table 11.22, are examples of static Jahn-Teller behavior. In some other complexes, no distortion can be detected in the room temperature crystal structure, but additional evidence shows that the Jahn-Teller effect is nonetheless operative. The supplementary evidence may consist of a low-temperature crystal structure showing distortion or spectroscopic data consistent with tetragonal geometry. These complexes are displaying dynamic Jahn-Teller behavior. In its simplest form, this can be thought of as a process in which a complex oscillates among three equivalent tetragonal structures. At any instant, the complex is distorted, but if the oscillation between forms is rapid enough, the structure observed by a particular physical method may be time-averaged and therefore appear undistorted. Sometimes cooling a sample will slow the oscillations enough that a single distorted structure is "frozen out." In some instances, however, a distorted structure produced upon cooling does not represent a true static condition but rather a different form of dynamic behavior.

There is an interesting series of compounds, all of them containing the hexa-nitroacetate(II) ion (IO$_6$). Some exhibit the full range of static and dynamic Jahn-Teller effects described above. In some members of the series, such as...

substitution of Cr$^{3+}$ for Al$^{3+}$. In this case the two cations have the same charge and similar radii (r$_{Cr}^{3+} = 69.3$ pm; r$_{Al}^{3+} = 75.5$ pm). There are also examples of resemblance between Mg$^{2+}$ (r = 71 pm), Mn$^{2+}$ (r = 80 pm), and Zn$^{2+}$ (r = 74 pm). Despite the fact that one has a noble gas configuration (Zn$^{2+}$) and the others do not (Cr$^{3+}$ and Al$^{3+}$), the resemblance among the lanthanides bears witness to the overwhelming influence of electronic charge and similar size in these species. Like-nesses that depend more on charge than on electron configuration might be termed physical. They relate to crystal structure and hence to solubilities and tendencies to precipitate. Coprecipitation is often more closely related to oxidation state than to family relationships. Thus carriers for radioactive tracers need not be of the same chemical family as the radioisotope. Technetium(VII) may be carried not only by perchlorate but also by peroxide, periodate, and tetafluoroborate. Lead(II) has the same solubility characteristics as the heavier alkaline earth metals. Thallium(I) (r = 104 pm) often resembles potassium ions (r = 151 pm), especially in association with oxygen and other highly electronegative elements. Thus, like K$^+$, Tl$^+$ forms a soluble nitrate, carbonate, phosphate, sulfate, and fluoride. Thallium(I) can also be incorporated into many potassium enzymes and is exceedingly poisonous. Of course, some properties of cations (especially polarization of anions) are affected by electronic structure (see Chapter 4). Thus we should not be surprised that with respect to the heavier homologues, Ti$^+$ resembles Ag$^+$ more closely than it does K$^+$.

Finally, another chemical property that depends on the cationic charge is the coordination number. Although it is generally influenced by size (Chapter 4), there is a tendency for cations with larger charges to have larger coordination numbers, e.g., Cu$^{2+}$ (C.N. = 4 and 6) versus Cu$^{+}$ (C.N. = 6), Mn$^{3+}$ (C.N. = 4 in [MnCl$_2$]) versus Mn$^{2+}$ (C.N. = 6 in [MnF$_2$]). This is a consequence of the electronegativity principle (see Chapter 11). On the other hand, metals in extremely high oxidation states [Cr(VI), Mn(VII), Os(VIII)] have a tendency to form metal-oxygen double bonds (considerable π bonding from the oxygen to the metal), and four-coordinate tetrahedral species ([COO]$_4^{3-}$, [MnO$_4$]$_2^{3-}$, [OsO$_4$]$_2^{3-}$) result.

Although there are resemblances that depend only on the charge or oxidation state, transition metal chemistry is more often governed by the electron configurations of the metal ions. Thus, despite a natural tendency for lower oxidation states to be reducing in character and higher ones to be oxidizing, the electron configuration may well make the divalent, tetravalent, or even higher oxidation states the most stable for a particular metal. In this section the properties of the metals of the first transition series are briefly examined in terms of electron configuration.

The $d^3$ Configuration

This configuration occurs for simple ions such as K$^+$, Cu$^{2+}$, and Zn$^{2+}$ and for the formal oxidation states equal to the group numbers for many of the transition metals. This holds true as far as Mn(VII) (Fe(VII) is unknown). All metal ions with $d^3$ configurations are hard acids and prefer to interact with hard bases such as oxide, hydroxide, or fluoride. Complexation chemistry is less extensive than for other configurations, but work in this area continues to expand. There is no tendency for metals with this configuration to behave as reducing agents (there are no electrons to lose) and little tendency for them to behave as oxidizing agents unless species such as [CrO$_4$]$_3^{3-}$, [CrO$_4$]$^{3-}$, [MnO$_4$]$_2^{3-}$, and [MnO$_4$]$^{3-}$ are reached. In general, therefore, their aqueous chemistry may be described simply: the lower charged species (K$^+$, Cu$^{2+}$, Zn$^{2+}$) behave as simple, uncomplexed (other than by water) free ions in aqueous solution. Complex ions of scandium, such as [ScF$_4$]$^{3-}$ and [Sc(OH)$_4$]$^{3-}$, are known and result when excess F$^-$ or OH$^-$ is added to insoluble ScF$_3$ or Sc(OH)$_3$. The "crown" complexes of the alkali metals have been discussed previously (Chapter 12), and Cu$^{2+}$ may be complexed by polydentate ligands such as edta.

The higher oxidation states [Cr(VI), Mn(VII)] tend to form oxoanions, which are good oxidizing agents, especially in acidic solution. the oxides of the intermediate species are insoluble (TiO$_2$) or amphoteric (V$_2$O$_5$).

A quick survey of the metals with the $d^3$ configuration yields the following descriptive information. For potassium, calcium, and scandium it is the only stable electron configuration. It is by far the most stable for titanium (e.g., TiO$_2$, TiH$_2$F$_2$). Vanadium(V) occurs in the vanadyl ion, [VO]$_3^{2-}$, and a variety of poly vanadates. It is a mild oxidizing agent giving way to vanadium(VI) as the most stable oxidation state. The strongly oxidizing species [CrO$_4$]$_3^{3-}$ (to Cr$^{6+}$) is I.37 V and [MnO$_4$]$_2^{3-}$ (to Mn$^{7+}$) is 1.51 V are unstable relative to lower oxidation states.

This does not tend to be a stable configuration. It is completely unknown for scandium and strongly reducing in Ti(III). The later members of the series tend to disproportionate or to more stable configurations:

$$3[CrO_4]^{2-} + 10H^+ \rightarrow 2[CrO_2]^{2-} + Cr^{3+} + 4H_2O \quad (14.5)$$

$$3[MnO_4]^{2-} + 4H^+ \rightarrow 2[MnO_2]^{2-} + Mn^{3+} + 2H_2O \quad (14.6)$$

The only $d^3$ species of importance is the vanadyl ion, VO$_2^{++}$, which is the most stable form of vanadium in aqueous solution.

This configuration ranges from Ti(III), very strongly reducing, to Fe(III), very strongly oxidizing. It is not a particularly stable configuration. Both Ti(III) and V(III) are reducing agents and Cr(IV) and Mn(IV) are relatively unimportant. The ferric(VI) ion,
K,[Sb(Cu(NO₃)₄)], K,[Cu(Cu(NO₃)₄)], and K,[Sr(Cu(NO₃)₄)]—the Cu(II) anions are elongated at room temperature (398 K), while in others, such as K,[Pb(Cu(NO₃)₄)], they are undistorted. In yet a third category are Cu₂[Ca(Cu(NO₃)₄)] and Rb₂Ba[Ca(Cu(NO₃)₄)₂], for which the room temperature structures appear to be usually compressed octahedra but actually are the dynamic averages of two tetragonally elongated structures. Upon being cooled to 276 K, K,[Pb(Cu(NO₃)₄)] also assumes this “pseudo compressed” geometry. The subtle structural variations in these and other complexes exhibiting similar behavior have been elucidated with a combination of physical methods, most often crystallography in conjunction with EPR and electronic spectroscopies.

No discussion of the Jahn-Teller effect in coordination compounds would be complete without including the spectral features of chelated compounds (see Chapter 12 for a more thorough discussion of chelated complexes). The very nature of the chelated ring tends to restrict the distortion of a complex from a perfect octahedron because the ligand will have a preferred “bite” or distance between the coordinating atoms:

```
CH₂ — CH₂ — NH₂
```

An example of the conflict between stabilization from the Jahn-Teller effect and chelate geometrical requirements is found in the ethylenediamine complexes of Cu(II). Most divalent transition metal ions form complexes with ethylenediamine (en) by stepwise replacement of water:

```
[M(H₂O)₆]²⁺ + en → [M(en)]⁺ + 2H₂O
```

Each step has associated with it an equilibrium or stability constant, K₁, K₂, or K₃, which measures the tendency for formation of a mono-, bis-, or tris(ethylenediamine) complex, respectively. The values of these constants for ions Mn²⁺ to Zn²⁺, which measures the tendency for formation of a mono-, bis-, or tris(ethylenediamine) complex, are shown in Table 11.22. The Cu(II) ion has a fairly uniform trend of gradually increasing stability from left to right across the series (the Irving-Williams order) (Fig. 11.50). The Cu²⁺ ion provides a striking example, as shown in Table 11.22. One oxygen atom from each hexafluoroacetylacetonate ligand binds to the copper at a distance of 206 pm, consistent with the short bonds from other nitrogen ligands to copper(II). The two nitrogen atoms of bipyridine bind to the copper at a distance of 200 pm, consistent with short Cu-N bond. The two remaining oxygen atoms form Cu-O bonds which are some 33 pm longer, indicating severe Jahn-Teller distortion. Despite the restraining influence of a bidentate ligand, a number of distorted chelated structures are known. For example, [Cu(bpy)(hfa)] is known to be tetragonally distorted. Both bipyridine and hexafluoroacetylacetonate are chelating ligands that form bonds through nitrogen and oxygen atoms, respectively. The structure of this molecule is shown in Fig. 11.51. The two nitrogen atoms of bipyridine bind to the copper at a distance of 200 pm, consistent with the short bonds from other nitrogen ligands to copper(II). The two remaining oxygen atoms form Cu-O bonds which are some 33 pm longer, indicating severe Jahn-Teller distortion.

Although most of the visible spectra studied by inorganic chemists in evaluating coordination compounds have been of the d-d (or ligand field) type, perhaps more...
transitional Metals

Oxidation States

Some oxidation states of the metals of the first transition series

<table>
<thead>
<tr>
<th>Oxidation state</th>
<th>III</th>
<th>IVB</th>
<th>VB</th>
<th>VIIB</th>
<th>VIIIB</th>
</tr>
</thead>
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<tr>
<td>+7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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<td></td>
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<tr>
<td>+5</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>+4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>+3</td>
<td>TiCl₄⁺⁺⁺⁺</td>
<td>VO₂⁺⁺⁺⁺</td>
<td>CrCl₃⁺⁺⁺⁺</td>
<td>MnCl₂⁺⁺⁺⁺</td>
<td>NiCl₂⁺⁺⁺⁺</td>
</tr>
<tr>
<td>+2</td>
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<td>VO₂⁺⁺⁺⁺</td>
<td>CrCl₂⁺⁺⁺⁺</td>
<td>MnCl₂⁺⁺⁺⁺</td>
<td>NiCl₂⁺⁺⁺⁺</td>
</tr>
<tr>
<td>+1</td>
<td>Ti(bpy)₃⁺⁺⁺⁺</td>
<td>V(bpy)₃⁺⁺⁺⁺</td>
<td>Cr(bpy)₃⁺⁺⁺⁺</td>
<td>Mn(bpy)₃⁺⁺⁺⁺</td>
<td>Ni(bpy)₃⁺⁺⁺⁺</td>
</tr>
<tr>
<td>0</td>
<td>Ti(bpy)₃⁺⁺⁺⁺</td>
<td>V(bpy)₃⁺⁺⁺⁺</td>
<td>Cr(bpy)₃⁺⁺⁺⁺</td>
<td>Mn(bpy)₃⁺⁺⁺⁺</td>
<td>Ni(bpy)₃⁺⁺⁺⁺</td>
</tr>
<tr>
<td>-1</td>
<td>Ti(bpy)₃⁻⁻⁻⁻</td>
<td>V(bpy)₃⁻⁻⁻⁻</td>
<td>Cr(bpy)₃⁻⁻⁻⁻</td>
<td>Mn(bpy)₃⁻⁻⁻⁻</td>
<td>Ni(bpy)₃⁻⁻⁻⁻</td>
</tr>
<tr>
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<td>V(bpy)₃⁻⁻⁻⁻</td>
<td>Cr(bpy)₃⁻⁻⁻⁻</td>
<td>Mn(bpy)₃⁻⁻⁻⁻</td>
<td>Ni(bpy)₃⁻⁻⁻⁻</td>
</tr>
<tr>
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<td>Ti(bpy)₃⁻⁻⁻⁻</td>
<td>V(bpy)₃⁻⁻⁻⁻</td>
<td>Cr(bpy)₃⁻⁻⁻⁻</td>
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<td>Ni(bpy)₃⁻⁻⁻⁻</td>
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<td>V(bpy)₃⁻⁻⁻⁻</td>
<td>Cr(bpy)₃⁻⁻⁻⁻</td>
<td>Mn(bpy)₃⁻⁻⁻⁻</td>
<td>Ni(bpy)₃⁻⁻⁻⁻</td>
</tr>
</tbody>
</table>

* The +8 oxidation state is found in ReO₄ and OsO₄ and the +7 oxidation state is found in their anions, [ReO₄]⁻ and [OsO₄]⁻.

Chemistry of the Various Oxidation States of Transition Metals

Low and Negative Oxidation States

The entire question of oxidation state is arbitrary and one and the assignment of appropriate oxidation states is often merely a matter of convenience (or inconveniency). The concept of oxidation state is best defined in compounds between elements of considerably different electronegativity in which the resulting molecular orbitals are clearly more closely related to the atomic orbitals of one atom than another. In those cases in which the differences in electronegativity are small and especially those in which there are extensive delocalized molecular orbitals that are nonbonding, weakly bonding, or antibonding, the situation becomes difficult. The former situation is found with complexes containing halogen, oxygen, or nitrogen σ-bonding ligands. The latter condition is common among organometallic complexes for which no attempt is made to assign oxidation states. Ligands stabilizing low (if imprecise) oxidation states are cyanide and phosphorus trifluoride, both excellent σ-bonding ligands. Hence, it is possible to prepare zero-valent nickel complexes with these ligands:

\[
\text{Ni(CO)}_4 + 4\text{PF}_3 \rightarrow \text{Ni}([\text{PF}_3])_4 + 4\text{CO} \quad \text{(14.3)}
\]

\[
\text{Ni}^{2+} + 5\text{KCN} \rightarrow \text{K}_5[\text{Ni(CN)}_5]^{-5} + \text{K}_2[\text{Ni(CN)}_4] \quad \text{(14.4)}
\]

Ligands with extensively delocalized molecular orbitals that are essentially nonbonding can make the assignment of precise oxidation states difficult or impossible. For example, we have already seen this in the thiolene-thiolate ligands (see Chapter 12). A similar ligand is bipyridine, which forms complexes that may formally be classified as containing +1,0, or even -1 oxidation states for the metal. A substantial portion of the electron density on the metal in these low oxidation states is delocalized over the ligand π-system. Other instances of extensive delocalization stabilizing metals in low oxidation states are often encountered in biological systems (see Chapter 19).

Although the definition of low oxidation states is somewhat subjective, it is possible to discuss the range of oxidation states exhibited by various metals. When the metals of the first transition series are examined, the results shown in Table 14.2 are found. There is a general trend between a minimum number of oxidation states (one or two) at each end of the series (Sc²⁺ and Zn²⁺) to a maximum number in the middle (manganese, -3 to +7). The paucity of oxidation states at the extremes stems from either too few electrons to lose or share (Sc, Ti) or too many d electrons (and hence fewer open orbitals through which to share electrons with ligands) for high valency (Cu, Zn). A second factor tending to reduce the stability of high oxidation states toward the end of the transition series is the steeper increase in effective atomic number. This aids to decrease the energies of the d orbitals and draw them into the core of electrons not readily available for bonding. Thus, early in the series it is difficult to form species that do not utilize the d electrons. Scandium(II) is virtually unknown and Ti(IV) is more stable than Ti(III), which is much more stable than Ti(I). At the other extreme, the only oxidation state for zinc is +2 (no d electrons are involved) and for nickel, Ni(II) is much more stable than Ni(III). As a result, maximum oxidation states of reasonable stability occur equal in value to the sum of the s and d electrons through manganese (Ga²⁺, Fe³⁺, Cr³⁺, Mn²⁺), followed by a rather abrupt decrease in stability for higher oxidation states, so that the typical species available are Fe(II, III), Co(II, III), Ni(II), Cu(II, I), ZnII.

There are certain resemblances among metal ions that can be discussed in terms of oxidation state but which are relatively independent of electron configuration. They relate principally to size and charge phenomena. For example, the ordinary alums, KA₄SO₄·12H₂O, are isomorphous with the chrome alums, KCr₂(SO₄)₃·12H₂O, and mixed crystals of any composition between the two extremes may be prepared by...
imported from an applied standpoint have been those involving charge transfer transitions. As the term implies, these transitions involve electron transfer from one part of a complex to another. More specifically, an electron moves from an orbital that is mainly ligand in character to one that is mainly metal in character (ligand-to-metal charge transfer, LMCT) or vice versa (metal-to-ligand charge transfer, MLCT). Unlike \( d \)-d transitions, those involving charge transfer are fully allowed and hence give rise to much more intense absorptions (see Table 11.16). When these absorptions fall within the visible region, they often produce rich colors and therein lies the source of practical interest in these types of transitions.\(^{55}\)

In a primitive sense, a charge transfer transition may be regarded as an internal redox process. This makes it possible to use familiar ideas, such as ionization energies and electron affinities, to predict the conditions that will favor such a transition. Consider a crystal of sodium chloride. Imagine ionizing an electron from a chloride ion (\( A_H \) = electron affinity) and transferring it to the sodium ion (\( A_H \) = negative of ionization energy). It could be imagined that the overall energy (including \( U^0 \)) required to effect this process might be supplied by a photon. Indeed such photons exist, but their energy is so high that they belong to the ultraviolet portion of the spectrum. Hence, sodium chloride does not absorb visible light: It is colorless.

Now consider how we might modify the metal-ligand combination to make the electron transfer from ligand to metal more favorable. We would want a metal with a relatively high ionization energy so that it would have empty orbitals at fairly low energies. Good candidates would be transition or posttransition metals, especially in higher oxidation states. An ideal ligand would be a nonmetal with a relatively low electron affinity, which would mean that it would have filled orbitals of fairly high energy and would be readily oxidizable. Chalcogenides or heavier halides would be examples of good choices. The net result of such a metal-ligand combination would be that the orbitals involved in a LMCT process would be close enough in energy that the transition could be induced by a photon in the visible or near-ultraviolet region.\(^{56}\)

The permanganate ion, \( \text{MnO}_4^- \), meets the criteria set forth in the preceding paragraph: Manganese is in a formal oxidation state of +7 and combined with four oxide ions. The molecular orbital diagram for tetrahedral complexes in Fig. 11.52 allows us to identify possible LMCT transitions. In any tetrahedral complex, the four lowest energy \( \sigma \)-bonding orbitals will be filled and will be primarily ligand in character. Next there are two sets of \( \pi \)-nonbonding MO's, one ligand-centered and one metal-centered. In permanganate, these orbitals would correspond to filled oxygen \( n_p \) orbitals and empty manganese \( 3d \) orbitals, respectively. All of the higher energy antibonding molecular orbitals would be unoccupied for a manganese(VII) complex. Hence there are four possible ligand-to-metal transitions:

\[
\begin{align*}
L(\pi) &\rightarrow M(e) \\
L(\pi^*) &\rightarrow M(e) \\
L(\sigma) &\rightarrow M(e) \\
L(\sigma^*) &\rightarrow M(e)
\end{align*}
\]

For \( \text{MnO}_4^- \) all four of these transitions have been observed: 17,700 cm\(^{-1} \) (\( \pi \rightarrow e \)); 29,500 cm\(^{-1} \) (\( \pi \rightarrow \pi^* \)); 30,300 cm\(^{-1} \) (\( \sigma \rightarrow e \)); and 44,400 cm\(^{-1} \) (\( \sigma \rightarrow \pi^* \)).\(^{56}\) Only the absorption at 17,700 cm\(^{-1} \) falls within the visible range (14,000–28,000 cm\(^{-1} \)), and it is responsible for the familiar deep purple color of \( \text{MnO}_4^- \).


Even so, it sometimes seems as though no facts are retained. Each of us has a "silver chloride is a pale green gas" story. Our local one concerns the organic chemistry graduate student who reported that he couldn't get bromine to dissolve in carbon tetrachloride (1). He even tried "grinding" with a mortar and pestle (!!). When his professor investigated, it turned out that the bromine was still in an unopened container in the bottom of the packing case, and the material in question, being subjected to grinding and solubilization tests, was the vermiculite packing material (!!). Truly, A little learning is a dangerous thing; Drink deep, or taste not the Pierian spring.2

In this chapter the theories developed previously will be used to help correlate the important facts of the chemistry of groups I-12. Much of the chemistry of these elements, in particular the transition metals, has already been included in the chapters on coordination chemistry (Chapters 11, 12, and 13). More will be discussed in the chapters on organometallic chemistry (Chapter 15), clusters (Chapter 16), and the descriptive biological chemistry of the transition metals (Chapter 19). The present chapter will concentrate on the trends within the series (Sc to Zn, Y to Cd, Lu to Hg, Ag — Au), the differences between groups (Ti — Zr — Hf, Cu — Ag — Au), and the stable oxidation states of the various metals.

General Periodic Trends

As the effective atomic number increases across a series of transition metals, the size decreases from near shielding by the d electrons. For transition metal ions the results of ligand field effects override a smooth decrease and so minimum in the ionic radii curves are found for d0 low spin ions, etc. (Fig. 11.15). The decrease in ionic radii favors the formation of stable complexes, and this, together with ligand field stabilization energies (LFSEs) arising from incompletely filled d orbitals, is responsible for the general order of stability of complexes. The increasing availability of d electrons for back bonding via σ orbitals (especially in low oxidation states) increases the softness of the metal ions in going from left to right in a series. However, the d orbitals in ions such as Cu2+ and Zn2+ have become so stabilized that σ bonding for them becomes relatively unimportant.

The differences between one series and another are discussed later in this chapter, but we may note some seeming paradoxes: The heavier metals tend to be somewhat less reactive as elements, and yet they are more easily oxidized to higher oxidation states; the first and second series appear to be more closely related to each other than to the third on the basis of ionization energies, and yet it is common to group the second and third series together on the basis of chemical properties and to differentiate them from the first series.

The first ionization energies of the main group and transition metals are listed in Table 14.1. The first two series do not differ significantly from each other — sometimes an element of one series is higher, sometimes the other. Beginning with cesium the period increases from left to right in a series. However, the orbitals in ions such as Cu2+ and Zn2+ have become so stabilized that σ bonding for them becomes relatively unimportant.

Comparisons of gold and silver further illustrate the point. The Au—H bond is much stronger than the Ag—H bond and AuCl5 is much more stable than AgCl5. The relatively high effective nuclear charge leads to relativistic stabilization (contraction) of 6s orbitals and destabilization (expansion) of 5d orbitals. The net result is greater participation in M—L bonding by the 5d orbitals and thus stronger bonds.4


In a similar way, the charge transfer spectrum of orange CrO$_4^{2-}$ ion can be analyzed, the LMCT process being facilitated by the high oxidation state of chromium(VI). Many iodide salts are also colored because of charge transfer transitions of this type. Examples are Hgl$_2$ (red), Bi$_3$ (orange-red), and PbI$_2$ (yellow). The metal ions in these substances certainly are not outstanding oxidizing agents, but the transitions occur because the iodide ion is easily oxidized.

If the energy difference between the lowest unoccupied molecular orbital (LUMO) centered on the metal ion and the highest occupied molecular orbital (HOMO) centered on the ligand is very small (less than 10,000 cm$^{-1}$), total electron transfer between the two may occur. This will be the case if the metal ion is a sufficiently good oxidizing agent and the ligand a good enough reducing agent to cause a spontaneous redox process. The result is breakdown of the complex. Examples of complexes in which this occurs are [Co(H$_2$O)$_6$]$_2^+$ and Fe$_3$$^+$ Water is oxidized by Co$_{3+}$ and the iodide ion is oxidized by Fe$^{2+}$. Despite the thermodynamic instability of these complexes, however, it has been possible to isolate both of them by procedures that take advantage of their kinetic inertness.\(^{57}\)

Some examples of pigments that owe the nature and intensity of their colors to ligand-to-metal charge transfer transitions are listed in Table 11.23. Some of these have been long known and used by people in their efforts to beautify their immediate environments. The use of ochres as pigments, dating from prehistoric times, followed from their natural abundance [the reds and yellows of the deserts and some other soils are caused by iron(III) oxide]. Pigments used in antiquity included orpiment found in Tutankhamun’s tomb near Thebes and lead antimonate (later dubbed "Naples yellow").\(^{58}\)"}

---

### Table 11.23

<table>
<thead>
<tr>
<th>Pigment</th>
<th>Primary orbitals involved*</th>
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</thead>
<tbody>
<tr>
<td>Cadmium yellow (CJS)</td>
<td>Ligand $\sigma_\pi$ → metal 5s</td>
</tr>
<tr>
<td>Vermilion (HgS)</td>
<td>Ligand $\sigma_\pi$ → metal 6s</td>
</tr>
<tr>
<td>Naples yellow (Pb$_2$Sb$_2$O$_7$)</td>
<td>Ligand $\sigma_\pi$ → metal 5s or 5p</td>
</tr>
<tr>
<td>Manganous (PbCO$_3$)</td>
<td>Ligand $\sigma_\pi$ → metal 6s</td>
</tr>
<tr>
<td>Chrome yellow (PbCrO$_4$)</td>
<td>Ligand $\sigma_\pi$ → metal 3d</td>
</tr>
<tr>
<td>Red and yellow ochres (iron oxides)</td>
<td>Ligand $\sigma_\pi$ → metal 3d</td>
</tr>
</tbody>
</table>

* Simplified notation. See text and Fig. 11.52.

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\(^{57}\)"The synthesis of Co(CrH$_2$O)$_6$NO$_2$-H$_2$O is repeated in Johnson, D. A.; Sharpe, A. G. J. Chem. Soc. (A), 1964, 798-801. The preparation of FeI$_2$ is described in Yoan, K. B.; Kochi, J. K. Inorg. Chem. 1966, 5, 869-874. This report dispelled a long-held assumption that the compound could not exist.


\(^{59}\)"For an interesting discussion of inorganic pigments and their relation to art, see Brill, T. B. *Light, Its Interaction with Art and Antiquities.* Plenum: New York, 1980."
13.31 If reaction 13.76 proceeds by an inner sphere mechanism with the formation of \((\text{NC})_5\text{Fe—CN—Co(CN)}_3\) as an intermediate, what can you say about the rate of Fe—C bond breaking relative to the rate of Co—N bond breaking?

13.32 The reaction of \(\text{Cr}^{2+}\) with

\[
[\text{RN}]\text{Cr}^2+ \rightarrow \text{C} = \text{O} \rightarrow [\text{Cr(OH)}_3]^{3+}
\]

Can we conclude that this reaction proceeds by remote attack?*

13.33 Define the following terms: fluorescence, phosphorescence, luminescence, photoluminescence, and chemiluminescence.

13.34 If 1 mol of 452-nm photons are absorbed by \([\text{Ru(bpy)}_3]^{2+}\), how many kJ are absorbed? How many eV does this correspond to? If \([\text{Ru(bpy)}_3]^{2+}\) lies 2.1 eV higher in energy than \([\text{Ru(bpy)}_3]^{3+}\), what wavelength of light will be emitted when the excited state relaxes to the ground state?

13.35 What wavelength of light would be needed to provide the minimum energy for the reaction

\[
\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g) + \text{O}_2(g)
\]

for which \(\Delta G^0 = 678\) kJ mol\(^{-1}\)?

13.36 The intervalence spectrum of \([\text{Ru(NH}_3_3])_2(N_1)\] consists of an absorption at 1050 nm. In what part of the electromagnetic spectrum is it found? Explain how this absorption arises.

13.37 A cyclic voltammogram of \([\text{Ru(bpy)}_3]^{2+}\) in acetonitrile is shown below.†

![Cyclic voltammogram](image)

How do you account for the observation of three reduction potentials?

13.38 If the potentials for Eqs. 13.62 and 13.63 had not been given, could you have calculated them (Chapter 10)?

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**Some Descriptive Chemistry of the Metals**

In the preceding chapters principles guiding the structure and reactions of transition metal complexes have been considered. The present chapter will concentrate on the properties of individual metals in various oxidation states. The stabilities of these oxidation states will be examined and the similarities and differences compared. The material in this chapter and much of the next may be characterized as the "descriptive chemistry" of the alkali, alkaline earth, transition, lanthanide, and actinide metals. Unfortunately, descriptive chemistry has not always been especially popular with students and teachers. Admittedly, complete mastery of all the properties and all the reactions of the compounds of one element would be an impossible task, to say nothing of attempting it with 109. Furthermore, new reactions and properties are constantly being discovered that require the continual revision of one's knowledge. Nevertheless, it is impossible to ignore descriptive chemistry and try only for mastery of the theoretical side of chemistry. Theory can only be built upon and checked against facts. Actually, in reading this book you will encounter a vast body of descriptive chemistry, perhaps without consciously being aware of it. As each theory or model has been presented, an appeal has been made to the real world to support or modify that concept. Much of this descriptive chemistry may go unnoticed, but consider that almost all metal carbonyls are diamagnetic (Chapter 15), that magnetite has an inverse spinel structure (Chapter 11), and that potassium permanganate is purple (Chapter 11) or that it is a strong oxidizing agent (Chapter 10). Furthermore (Chapter 13),

\[
[\text{PtCl}_4]^{2-} + 2\text{NH}_3 \rightarrow \text{cis-} \text{PtCl}_4(\text{NH}_3)_2 + 2\text{Cl}^-
\]

When it comes to what is "important" descriptive chemistry, chacun a son goû,!

---

Substances were first classified as diamagnetic or paramagnetic by Michael Faraday in 1845, but it was not until many years later that these phenomena came to be understood in terms of electronic structure. When any substance is placed in an external magnetic field, there is an induced circulation of electrons producing a net magnetic moment aligned in opposition to the applied field. This is the diamagnetic effect and it arises from paired electrons within a sample. Since all compounds contain some paired electrons, diamagnetism is a universal property of matter. If a substance has only paired electrons, this effect will dominate, the material will be classified as diamagnetic, and it will be slightly repelled by a magnetic field.

Paramagnetism is produced by unpaired electrons in a sample. The spins and orbital motions of these electrons give rise to permanent molecular magnetic moments that tend to align themselves with an applied field. Because it is much larger than the diamagnetic effect, the paramagnetic effect overshadows any repulsions between an applied field and paired electrons in a sample. Thus even substances having only one unpaired electron per molecule will show a net attraction into a magnetic field. The paramagnetic effect is observed only in the presence of an external field: When the field is removed, individual molecular moments are randomized by thermal motion and the bulk sample has no overall moment. When a field is present, there is competition between the thermal tendency toward randomness and the field's capacity to force alignment. Consequently, paramagnetic effects decrease in magnitude as the temperature is increased.

When any substance is placed in a magnetic field, the field produced within the sample will either be greater than or less than the applied field, depending on whether the material is paramagnetic or diamagnetic. The difference between the two \( \Delta H \) can be expressed as

\[
\Delta H = B - H_0
\]

where \( B \) is the induced field inside the sample and \( H_0 \) is the free-field value, \( \Delta H \) will be negative \( (B < H_0) \) for a diamagnetic substance and positive \( (B > H_0) \) for one that is paramagnetic. More commonly the difference between the applied field and that induced in the sample is expressed in terms of \( f \), the intensity of magnetization, which is the magnetic moment per unit volume:

\[
4\pi \sigma = B - H_0
\]

Because both \( B \) and \( f \) will tend to be proportional to an external field, dividing Eq. 11.32 by \( H_0 \) yields ratios \( \frac{B}{H_0} \) and \( \frac{B}{H_0} \) that will be essentially constant for a given substance. The term \( B/H_0 \), called the magnetic permeability, is a ratio of the density of the magnetic force lines in the presence of the sample to the same density with no sample; for a vacuum this ratio will be equal to 1. The term \( B/H_0 \) is the magnetic susceptibility per unit volume \( (\chi) \), which expresses the degree to which a material is subject to magnetization:

\[
4\pi \sigma = \frac{B}{H_0} - 1
\]

The value of \( \chi \) will be negative for a diamagnetic substance and positive for one that is paramagnetic.

The quantity that is most frequently obtained from experimental measurements of magnetism is the specific (or mass) susceptibility, \( \chi \). It is related to the volume susceptibility through the density, \( d \):\n
\[
\chi = \frac{\chi}{d}
\]

By multiplying the specific susceptibility of a compound by its molecular weight, we can obtain the molar susceptibility, \( \chi_m \):

\[
\chi_m = \chi \cdot MW
\]

A number of methods exist for laboratory measurement of magnetic susceptibilities. Two that are very common and quite similar to each other are the Gouy and Faraday methods. Both techniques are based on the determination of the force exerted on a sample by an inhomogeneous magnetic field and both of them involve measuring the weight of a substance in the presence and absence of the field. The Faraday method has two distinct advantages over the Gouy method. The first pertains to sample size: The Faraday method requires several milligrams of material whereas the Gouy technique requires approximately 1 gram. A second advantage of the Faraday method is that it gives specific susceptibility directly. The Gouy experiment yields volume susceptibility, which must in turn be converted to specific susceptibility. This conversion can be problematic because it requires an accurate value for density, which can be difficult to obtain for solids because the value varies according to how the material is packed.

The setup for a Faraday experiment is represented schematically in Fig. 11.54. If a sample of mass \( m \) and specific susceptibility \( \chi \) is placed in a nonuniform field \( H \) that has a gradient in the \( x \) direction \( (\frac{dH}{dx}) \) the sample will experience a force \( f \) along \( x \) due to the gradient:

\[
f = \frac{(m\chi H_0)(dH)}{dx}
\]

This force can be measured by weighing the sample both in the field and out of the field, the difference between the two weights being equal to \( f \). Commonly the experiment is simplified by determining the force exerted on a standard of known suscept-
In the synthesis of cis-[PtMe2(S2N2)]+, from cis-[PtNH2(S2N2)2], the reaction is first treated with AgClO4 and then with Me2S. What role does silver perchlorate play in this reaction?

The rate constant for the formation of IMolH2OMNCS at 298 K is 0.317 M⁻¹s⁻¹, and the volume of activation for the NCS⁻ reaction is -11.4 cm³/mol. Explain how each of these facts contribute to the energies of activation.

Account for the following: (a) Differences in A and A for the exchange reaction proceeds It) times faster than predicted by the Marcus equation. What does this suggest about the mechanism of electron transfer?

Self-exchange rates for the oxidant and reductant are 4.2 M⁻¹s⁻¹ and 4.0 x 10⁻3 M⁻¹s⁻¹, respectively. The equilibrium constant for the reaction is 2.1 x 10⁻².

The [Co(H₂O)₆]⁺⁺⁺ electron exchange reaction proceeds 10³ times faster than predicted by the Marcus constant. What does this suggest about the mechanism of electron transfer?

The rate constant for the formation of [M(H₂O)₆(NCS)]₂⁻ at 298 K is 0.317 M⁻¹s⁻¹, and for [M(H₂O)₆(NCS)]⁺⁺⁺ is 4.6 x 10⁻³ M⁻¹s⁻¹. Seven-coordinate molybdenum(III) complexes are known. The volume of activation for the NC⁻ reaction is -11.4 cm³/mol. Explain how each of these factors contribute to the energies of activation.

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The [Co(H₂O)₆]⁺⁺⁺ electron exchange reaction proceeds 10³ times faster than predicted by the Marcus constant. What does this suggest about the mechanism of electron transfer?
Coordination Chemistry: Bonding, Spectra, and Magnetism

The theoretical paramagnetic moment for such a complex is given by

$$\mu = \frac{J}{m_s}$$

(Solving this equation for the susceptibility of the unknowns gives)

$$\chi_a = \frac{N \mu^2}{3kT}$$

The molar susceptibility of the sample, \(\chi_m\), can be obtained from \(\chi_a\) by applying Eq. 11.35.

Once an experimental value of \(\chi_m\) has been obtained for a paramagnetic substance, it can be used to determine how many unpaired electrons there are per molecule or ion. In order to translate the experimental result into the number of unpaired spins, it must first be recognized that a measured susceptibility will include contributions from both paramagnetism and diamagnetism in the sample. Even though the latter will be small, it is not always valid to consider it negligible. The most common procedure is to correct a measured susceptibility for the diamagnetic contribution. Compilations of data from susceptibility measurements on a number of diamagnetic materials make it possible to estimate the appropriate correction factors. The diamagnetic susceptibility for a particular substance can be obtained as a sum of contributions from its constituent units: atoms, ions, bonds, etc. (Table 11.24). The basic assumption underlying such a procedure, namely, that the diamagnetism associated with an individual atom or other unit is independent of environment, has been shown to be valid.

The next step is to connect the macroscopic susceptibility to individual molecular moments and finally to the number of unpaired electrons. From classical theory, the corrected or paramagnetic molar susceptibility is related to the permanent paramagnetic moment of a molecule, \(\mu\), by:

$$\chi_m = \frac{3N\mu^2}{RT}$$

As we know, this paramagnetic moment originates in the spins and orbital motions of the unpaired electrons in the substance. There are three possible modes of coupling between these components: spin-spin, orbital-orbital, and spin-orbital. For some complexes, particularly those of the lanthanides, we must consider all three types of coupling. The theoretical paramagnetic moment for such a complex is given by

$$\mu = g[J(J+1)]^{1/2}$$

where \(J\) is the total angular momentum quantum number and \(g\) is the Landé splitting factor for the electron, defined as

$$g = 1 + \frac{3J(J+1) - LL + 1}{2J(J+1)}$$

The value of \(J\) depends on the total orbital angular momentum quantum number, \(L\), and the total spin angular momentum quantum number, \(S\) (Appendix C). Some calculated and experimental magnetic moments for lanthanide complexes are shown in Table 11.25.

For complexes in which spin-orbit coupling is nonexistent or negligible but spin and orbital contributions are both significant, the predicted expression for \(\mu\) is

$$\mu = 4g[S(S+1) + LL + 1]$$

Equation 11.43 describes a condition that is never fully realized in complexes because the actual orbital contribution is always somewhat less than the ideal value. This
13.1 Metal-halogen bonds are more labile than metal-nitrogen bonds. Use this information and the trans effect to devise syntheses for the following geometric isomers from \([\text{PtCl}_4]^-\).

a. Cl Br

b. Cl Br


13.2 Predict the geometries of the complexes which result from the following reactions:

a. \([\text{Pt(NO)}_3\text{Cl}_3]^- + \text{NH}_3 \rightarrow [\text{Pt(NO)}_3(\text{NH}_3)\text{Cl}_2]^+ + \text{Cl}^-\)

b. cis-\([\text{Pt(RNH}_2)_2\text{Cl}_2](\text{NH}_3)(\text{NO})_2\)]^+ + \text{Cl}^- \rightarrow Pt(\text{RNH}_2)(\text{NH}_3)(\text{NO})_2\text{Cl} + \text{RNH}_2

13.3 Predict the products of the following reactions (1 mol of each reactant):

a. \([\text{Pt(CO)}\text{Cl}_3]^- + \text{NH}_3 \rightarrow [\text{Pt(CO)}\text{Cl}_3(\text{NH}_3)]^+\)

b. \([\text{Pt(NH}_3]\text{Br}_3]^- + \text{NH}_3 \rightarrow [\text{Pt(NH}_3]\text{Br}_3(\text{NH}_3)]^+\)

13.4 Trialkyl phosphines are rather good trans directors and, as expected, the reaction of \(\text{Bu}_3\text{P}\) with \([\text{PtCl}_4]^-\) gives the trans isomer as a major product. However, when one uses Ph\(_3\)P in this reaction, only the soluble cis product is obtained. Offer an explanation for this apparent violation of the trans-effect prediction. (Problem 13.5 may be helpful.)

13.5 When pure Ph\(_3\)P-\(\text{PtCl}_4\)(\text{Bu}_3\text{P}) is placed in solution with a trace of \(\text{Bu}_3\text{P}\), isomerization occurs to give a mixture of cis and trans isomers. Provide a plausible mechanism.

13.6 Nickel complexes are observed to undergo substitution much faster than platinum complexes. Offer an explanation.

13.7 The following data were observed for the reaction (dien = diethylenetriamine, HNN(CH\(_2\)CH\(_2\)NH\(_2\)):\n
\([\text{Pt(dien)}\text{SCN}]^+ + \text{py} \rightarrow [\text{Pt(dien)}\text{py}]^+ + \text{SCN}^-\)

\(k_{\text{obs}} \quad [\text{py}]\)

<table>
<thead>
<tr>
<th></th>
<th>6.6 (\times) (10^{-3})</th>
<th>1.24 (\times) (10^{-3})</th>
<th>2.48 (\times) (10^{-3})</th>
<th>2.5 (\times) (10^{-2})</th>
<th>1.24 (\times) (10^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O</td>
<td>1900</td>
<td>10</td>
<td>0.05</td>
<td>0.017</td>
<td></td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>35</td>
<td>23</td>
<td>10</td>
<td>0.000001</td>
<td></td>
</tr>
<tr>
<td>Br(^-)</td>
<td>23</td>
<td>10</td>
<td>0.05</td>
<td>0.000001</td>
<td></td>
</tr>
<tr>
<td>I(^-)</td>
<td>10</td>
<td>10</td>
<td>0.05</td>
<td>0.000001</td>
<td></td>
</tr>
<tr>
<td>NO(_3)(^-)</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.000001</td>
<td></td>
</tr>
<tr>
<td>CN(^-)</td>
<td>0.017</td>
<td>0.017</td>
<td>0.017</td>
<td>0.000001</td>
<td></td>
</tr>
</tbody>
</table>

Use the data to calculate \(k_1\) and \(k_2\) for substitution in this square planar complex.

13.8 Sketch plots of \(k_{\text{obs}}\) versus [\(Y\)] for two cases of substitution of a square planar complex: (a) one in which the solvent pathway is insignificant and (b) one in which the solvent pathway is exclusive.

13.9 The rate of substitution in a square planar complex often depends on the identity of the leaving group, \(X\). For the reaction:

\([\text{Pt(dien)}X]^+ + \text{py} \rightarrow [\text{Pt(dien)}\text{py}]^+ + X^-\)

the following data were collected:

Of these ligands, CN\(^-\) has the least effect and H\(_2\)O has the greatest effect on the rate of the reaction. Yet as trans directors, just the opposite order is observed for these two ligands. Explain.

13.10 The hydroxide ion is a stronger base than ammonia, and yet it reacts more slowly than ammonia with a square planar complex. Explain.

13.11 Rationalize the order of the following values for the reaction of cis-\(\text{Pt(PF}_3\text{C}_6\text{H}_5\text{Cl})\) with \(\text{py}\):

\(L \quad k_{\text{obs}} \quad [\text{py}]\)

<table>
<thead>
<tr>
<th></th>
<th>phenyl</th>
<th>0.08</th>
<th>0.0002</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-tolyl</td>
<td>0.0002</td>
<td></td>
<td></td>
</tr>
<tr>
<td>mesityl</td>
<td>0.000001</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

13.12 Sketch a reaction profile for substitution in a square planar complex in which (a) a five-coordinate intermediate exists, but bond breaking is more important than bond making; (b) a five-coordinate intermediate exists, but bond making is more important than bond breaking.

13.13 Substitution reactions of dinuclear platinum(I) complexes have been investigated.\(^{11}\) The rate constant for the reaction below is \(93 \pm 10 \text{ M}^{-1} \text{s}^{-1}\) at \(10 \text{°C}\) in dichloromethane. Rate constants for halide substitution in trans-\(\text{Pt}3\text{P}2\text{X}_2\) complexes are typically \(10^{-4} \text{ M}^{-1} \text{s}^{-1}\).

Magnetic properties

<table>
<thead>
<tr>
<th>Central metal</th>
<th>No. of d electrons</th>
<th>Ground state</th>
<th>Compound</th>
<th>(\mu) (exp)</th>
<th>BM</th>
<th>(\mu) (calc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(II)</td>
<td>1</td>
<td>(3d^6)</td>
<td>FeCl(_3)</td>
<td>1.73</td>
<td>1.73</td>
<td></td>
</tr>
<tr>
<td>Cr(III)</td>
<td>2</td>
<td>(3d^{4})</td>
<td>CrCl(_3)</td>
<td>2.75</td>
<td>2.23</td>
<td></td>
</tr>
<tr>
<td>Mn(II)</td>
<td>3</td>
<td>(3d^{5})</td>
<td>MnCl(_3)</td>
<td>3.70</td>
<td>3.88</td>
<td></td>
</tr>
<tr>
<td>Co(II)</td>
<td>4</td>
<td>(3d^{6})</td>
<td>CoCl(_3)</td>
<td>4.75</td>
<td>4.90</td>
<td></td>
</tr>
<tr>
<td>Ni(II)</td>
<td>5</td>
<td>(3d^{7})</td>
<td>NiCl(_3)</td>
<td>5.65</td>
<td>5.92</td>
<td></td>
</tr>
<tr>
<td>Zn(II)</td>
<td>6</td>
<td>(3d^{10})</td>
<td>ZnCl(_2)</td>
<td>5.70</td>
<td>5.92</td>
<td></td>
</tr>
<tr>
<td>Cu(II)</td>
<td>7</td>
<td>(3d^{9})</td>
<td>CuCl(_2)</td>
<td>5.10</td>
<td>4.90</td>
<td></td>
</tr>
<tr>
<td>Hg(II)</td>
<td>8</td>
<td>(3d^{10})</td>
<td>HgCl(_2)</td>
<td>4.30</td>
<td>3.88</td>
<td></td>
</tr>
<tr>
<td>Ag(II)</td>
<td>9</td>
<td>(3d^{10})</td>
<td>AgCl(_2)</td>
<td>3.86</td>
<td>3.88</td>
<td></td>
</tr>
</tbody>
</table>

*Table 11.25: Magnetic properties of some complexes of the first-row transition metals.*

**Magnetic Properties of Complexes**

<table>
<thead>
<tr>
<th>High spin complexes</th>
<th>Low spin complexes</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\mu) (exp)</td>
<td>BM</td>
</tr>
<tr>
<td>T(_2^+)</td>
<td>1</td>
</tr>
<tr>
<td>V(_2^+)</td>
<td>2</td>
</tr>
<tr>
<td>V(_3^+)</td>
<td>3</td>
</tr>
<tr>
<td>Cr(_3^+)</td>
<td>3</td>
</tr>
<tr>
<td>Mn(_3^+)</td>
<td>4</td>
</tr>
<tr>
<td>Fe(_4^+)</td>
<td>5</td>
</tr>
<tr>
<td>Co(_5^+)</td>
<td>6</td>
</tr>
<tr>
<td>Ni(_6^+)</td>
<td>7</td>
</tr>
<tr>
<td>Zn(_7^+)</td>
<td>8</td>
</tr>
<tr>
<td>Cu(_8^+)</td>
<td>9</td>
</tr>
</tbody>
</table>

*Table 11.26: Magnetic properties of some complexes of the lanthanide metals.*

\(\mu\) is effectively a free metal ion by the presence of ligands. In the extreme case, where \(L\) is effectively zero, the orbital contribution to the magnetic moment is said to be quenched. This is the general situation in complexes having \(A\) or \(E\) ground states, which would include octahedral \(d^1\), \(d^4\) (high spin), \(d^6\) (low spin), \(d^7\) (low spin), and \(d^8\) cases. Furthermore, when a complex involves a first-row transition element, even if the ground state is \(T\), the orbital contribution generally may be ignored. For the \(L = 0\) condition, Eq. 11.43 reduces to

\[
\mu = |S(S+1)|^{1/2} = [(S(S+1)+1)^{1/2}] \quad (11.44)
\]

which is known as the spin-only formula for magnetic moment. By recognizing that \(S\) will be related to the number of unpaired electrons \((n)\) by \(S = n/2\), the expression may be further simplified to

\[
\mu = |n(n+2)|^{1/2} \quad (11.45)
\]

A number of calculated and experimental magnetic moments for first-row transition metal complexes are given in Table 11.26, showing that the spin-only formula gives results that are in reasonably good agreement.

As we know, a number of transition metal ions form both high and low spin complexes, and we have now seen that magnetic susceptibility measurements allow us to experimentally distinguish one from the other. Within ligand field theory, these two spin configurations in octahedral complexes are explained in terms of relative magnitudes of \(A_o\) and pairing energy \((P)\). We associate high spin complexes with the condition \(A_o < P\) and low spin complexes with \(A_o > P\). For complexes in which the energy difference between \(A_o\) and \(P\) is relatively small, an intermediate field situation, it is possible for the two spin states to coexist in equilibrium with each other. Consider the Fe\(^{3+}\) ion. At the two extremes, it forms high spin paramagnetic \([Fe(H_2O)_6]^{3+}\) \((S = 2)\) and low spin diamagnetic \([Fe(CN)_6]^{3+}\) \((S = 0)\). The Tanabe-Sugano diagram pertaining to these \(d^6\) complexes (Appendix G) shows that near the crossover point between weak and strong fields the difference in energy between the spin-free \((T_{2g})\) and spin-paired \((A_{2u})\) ground states becomes very small (Fig. 11.55). Within this region, it is reasonable to expect that both spin states may be present simultaneously and that the degree to which each is represented will depend on the temperature \((A_o - P = kT)\). A complex illustrating these effects is \([Fe_{(phen)(NCS)}_2]_2\). A plot of its magnetic moment against temperature appears in Fig. 11.56. At high temperatures a moment consistent with four unpaired electrons is observed, but as the temperature is...
branched). It is an electron carrier for oxidative phosphorylation, transferring electrons to O₂. The energy released in this process is used to synthesize ATP. The heme group of cytochrome c lies near the surface of the protein. The iron atom is six-coordinate, with bonds to five nitrogen atoms (four from the porphyrin, one from a histidine nitrogen) and one sulfur atom from a cysteine. Since all six iron coordination sites are occupied, direct electron transfer to iron is not possible, and the electron must pass through the surrounding protein bridgework (see Fig. 13.15). Electron transfer rates between horse heart cytochrome c (very stable and commercially available) and many transition metal complexes have been studied. For example, the observed rate constant for reduction by [Ru(NH₃)₅Cl]²⁺ (Eₜ = 0.8 V) is 3.8 x 10⁷ s⁻¹, which compares well with the value of 7.8 x 10⁶ M⁻¹ s⁻¹ calculated from the Marcus cross-reaction equation.

Calculating rate constants for electron transfers between two metalloproteins is a much more complicated affair. Distances between metal sites of two such proteins are often large and uncertain. A clever approach to gaining information about the distance dependence of electron transfer in these systems is to bind a second metal center to the surface of a single metalloprotein. A number of different electron transfer proteins (including horse heart cytochrome c, cytochrome Cyt b₅, azurin, plastocyanin, and an iron-sulfur protein) as well as sperm whale myoglobin have been modified by attaching [Ru(NH₃)₅Cl]²⁺ to a surface histidine nitrogen atom. The distance between metal centers is thereby fixed and can be determined. In cytochrome c, for example, both the Ru of the surface [Ru(NH₃)₅Cl]²⁺ and the heme Fe begin in the +3 oxidation state. The ruthenium moiety is reduced to [Ru(NH₃)₅Cl]⁺ by ruthenium-modified myoglobin with another metal system gives one a generated view of the heme group and four ruthenium surface histidines in sperm whale myoglobin. Closest heme-α-Ru(His) edge-to-edge distances are 14.6 (His40), 19.1 (His31), 20.1 (His146), and 22.1 Å (His127). (From Mayo, S. L.; Elms, W. R., Jr.; Crutchley, R. J.; Gray, H. B. Science 1986, 233, 948-952. Used with permission.)


---

**Table 13.10**

<table>
<thead>
<tr>
<th>L⁻¹</th>
<th>r, Å</th>
<th>k₀ s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>6.8</td>
<td>3 x 10⁸</td>
</tr>
<tr>
<td>Pb</td>
<td>7.1</td>
<td>1 x 10⁸</td>
</tr>
<tr>
<td>N</td>
<td>6.0</td>
<td>6 x 10⁸</td>
</tr>
<tr>
<td>N</td>
<td>11.3</td>
<td>1 x 10⁸</td>
</tr>
<tr>
<td>N</td>
<td>13.8</td>
<td>2 x 10⁷</td>
</tr>
</tbody>
</table>

---

**Fig. 13.15** Computer-generated view of the heme group and four ruthenium surface histidines in sperm whale myoglobin. Closest heme-α-Ru(His) edge-to-edge distances are 14.6 (His40), 19.1 (His31), 20.1 (His146), and 22.1 Å (His127). (From Mayo, S. L.; Elms, W. R., Jr.; Crutchley, R. J.; Gray, H. B. Science 1986, 233, 948-952. Used with permission.)

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**Mechanisms of Redox Reactions**

Transfer rates depend upon distance in these sorts of systems. However, not all pathways are identical so it is possible for a particular situation to be an exception to this rule. A theory has been developed that suggests that electron transfer in proteins is regulated by pathways that are optimal combinations of through-bond, hydrogen bond, and through-space links. According to this model, the electron transfer will follow the best overall linkage. Hydrogen bond bridges will be less efficient than through-bond linkages, but much better than through-space electron transport. Thus the optimum pathway will be the one with the best compromise of minimizing distance (covalent link) and avoiding, if possible, hydrogen bond linkages and, especially, through-space gaps. These optimum pathways can be computed making use of assumptions about the relative effectiveness of through-bond, hydrogen bond, and through-space links. Figure 13.16 illustrates such a pathway.

The driving force of a reaction, as noted earlier and as predicted by Marcus theory, also affects the rate of electron transfer in and between proteins. Replacing the heme in a ruthenium-modified myoglobin with another metal system gives one a chance to evaluate these effects. When the heme is replaced with a photoactive palladium porphyrin, which is a good example of an electronic excited state, the electron transfer driving force increases. Studies such as these allow reorganization energies, which strongly influence reaction rates, to be evaluated.

---

64 In many ways, the electronic coupling pathway is analogous to various electric circuits with different resistors. The longer the "circuit" in these systems, the greater the resistance. Hydrogen bonds tend to increase resistance and open space has the greatest of all.
11.9 Why is a solution of copper(II) sulfate blue?

11.10 If one CuCl₂ solution is blue and another is green, which would be expected to have the higher value of \( \Delta_\alpha \)?

11.11 Consider the following electronic transition frequencies (in cm⁻¹) for a series of nickel(II) complexes (ada = diethylnicotinate):

<table>
<thead>
<tr>
<th>Complex</th>
<th>( \delta_1 )</th>
<th>( \delta_2 )</th>
<th>( \delta_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni(ada)₂Cl]²⁺</td>
<td>8500</td>
<td>15,400</td>
<td>76,000</td>
</tr>
<tr>
<td>[Ni(ada)Cl₂]⁴⁻</td>
<td>10,750</td>
<td>17,000</td>
<td>28,200</td>
</tr>
<tr>
<td>[NiOSMes₂Cl]²⁺</td>
<td>7720</td>
<td>12,970</td>
<td>24,038</td>
</tr>
<tr>
<td>[NiOSMes₂Br]²⁻</td>
<td>7576</td>
<td>12,738</td>
<td>23,369</td>
</tr>
</tbody>
</table>

Determine appropriate values of \( \Delta_\alpha \) and \( \beta \) for these complexes.

11.12 The following absorption bands are found in the spectrum of [Cr(CN)₆]³⁻: 2691, 1970, 23.809, 26.000, 8500, 12,970, 17.500, 15.400, 15.150 cm⁻¹. For which complex is \( \delta \) largest? Why? How can you account for the presence of two bands in each spectrum?

11.13 When visible light passes through a solution of nickel(II) sulfate, a green solution results. When visible light passes through a solution of nickel(II) chloride, a red solution results. Explain why different colors are observed.

11.14 Explain the following experimental results. When cobalt(II) is heated in a vacuum, a 0.192-g sample of CoH₂BrCl₂ is obtained. The sample shows that it contains 15.16% Ni, 12.13% C, 5.09% H, and 53.70% Cl. The effective magnetic moment measured is 4.6 BM. The blue complex dissolves in water to give a pink solution, the conductivity of which is 382 ohm⁻¹ cm⁻¹. The solution is purple in color. The volume spectrum of the blue solution of the complex has bands centered at 3217, 5601, and 15.150 cm⁻¹ (molar absorptivity = 5080 mol⁻¹ cm⁻¹), but for a water solution, the absorptions occur at 9900, 19,000, and 19,400 cm⁻¹ (molar absorptivity = 3 mol⁻¹ cm⁻¹). In a titration with sodium hydroxide, each mole of the complex neutralizes four moles of hydroxide. Determine the formula and structure of the complex. Account for all reactions and observations.

11.15 Show that the ground state term of Er⁺⁺⁺ is \( ^{2}I_{15/2} \). What magnetic moment would you expect for Er₂SO₄·3H₂O?

11.16 The complexes [MnH₂O₄]²⁺, [FeH₂O₄]²⁺, [CoH₂O₄]²⁺, and [FeH₂O₄]²⁻ all have magnetic moments of nearly 3.92 BM. What does this tell you about the geometric and electronic structures of these complexes? Why is the spin-only formula so precise in these cases?

11.17 One way of determining the magnetic susceptibility of a transition metal complex, the Evans method, utilizes NMR. As an illustration of the procedure, consider the following experiment utilizing a 60-MHz spectrometer. A capillary tube is filled with a solution containing 6.0 mg/mL of \( \text{Co}^{2+} \) in 2% ethanol solution with no \( \text{Fe}^{3+} \). The volume susceptibility of the two solutions differs and as a result the ethyl alcohol group shows a different proton chemical shift in each. For this particular experiment, the chemical shift of the ethyl alcohol group in the copper solution is 5.6 Hz upfield from this in the noncomplex solution at 310 K. Use these data and help from Lojel, J.; Scheffold, R. J. Chem. Educ. 1972, 49, 646-647, to determine the magnetic moment of \( \text{Co}^{2+} \). How does the value you obtain compare to that expected from the spin-only formula?

11.18 Explain the following experimental results. At ambient temperature a 0.192-g sample of Fe(III)Br₃·pyrazolylBr₂ is obtained. The sample shows that it contains 15.16% Ni, 12.13% C, 5.09% H, and 53.70% Cl. The effective magnetic moment measured is 4.6 BM. The blue complex dissolves in water to give a pink solution, the conductivity of which is 382 ohm⁻¹ cm⁻¹. The solution is purple in color. The volume spectrum of the blue solution of the complex has bands centered at 3217, 5601, and 15.150 cm⁻¹ (molar absorptivity = 5080 mol⁻¹ cm⁻¹), but for a water solution, the absorptions occur at 9900, 19,000, and 19,400 cm⁻¹ (molar absorptivity = 3 mol⁻¹ cm⁻¹). In a titration with sodium hydroxide, each mole of the complex neutralizes four moles of hydroxide. Determine the formula and structure of the complex. Account for all reactions and observations.

11.19 Addition of TCI to an aqueous solution of acetone followed by addition of KI gave deep blue crystals of a complex containing titanium, water, and iodine. The visible spectrum of the material showed one absorption at 19,000 cm⁻¹ and its magnetic moment was determined to be 1.76 BM. When 1.00 g of the compound was decomposed at high temperatures in an oxygen atmosphere, all ligands volatilized and 0.101 g of TiO₂ (molar absorptivity = 15,150 cm⁻¹) was formed. Determine the formula and structure of the complex. What magnetic moment would you expect for this complex? How does the value you obtain compare to that expected from the spin-only formula?

11.20 Show that the ground state term of Er⁺⁺⁺ is \( ^{2}I_{15/2} \). What magnetic moment would you expect for Er₂SO₄·3H₂O?

11.21 Explain the following experimental results. When cobalt(II) is heated in a vacuum, a 0.192-g sample of CoH₂BrCl₂ is obtained. The sample shows that it contains 15.16% Ni, 12.13% C, 5.09% H, and 53.70% Cl. The effective magnetic moment measured is 4.6 BM. The blue complex dissolves in water to give a pink solution, the conductivity of which is 382 ohm⁻¹ cm⁻¹. The solution is purple in color. The volume spectrum of the blue solution of the complex has bands centered at 3217, 5601, and 15.150 cm⁻¹ (molar absorptivity = 5080 mol⁻¹ cm⁻¹), but for a water solution, the absorptions occur at 9900, 19,000, and 19,400 cm⁻¹ (molar absorptivity = 3 mol⁻¹ cm⁻¹). In a titration with sodium hydroxide, each mole of the complex neutralizes four moles of hydroxide. Determine the formula and structure of the complex. Account for all reactions and observations.
Mixed Valence Complexes

Theoretical treatments of electron transfer between two transition metal ions in solution are complicated by contributions arising from solvent reorganization and by transfer pathway uncertainties. If, however, the reducing and oxidizing agents are separated by a bridge within a single bimetallic complex, there will be no solvent molecules between the metal ions and the pathway will be defined. Furthermore, electron transfer over various distances can be studied by varying the length of the bridge, and this can provide some insight into important biological processes. Complexes that contain a metal atom in more than one oxidation state are referred to as mixed valence complexes. One could envision some systems in which the two metal ions are so far removed from one another that electron transfer does not take place nor can it be induced:

\[
\text{M}^{2+} - \text{M}^{3+}
\]

In other systems the two metal ions may be so strongly coupled that properties of the separate +2 and +3 ions are lost and the entire unit is best represented as two +2 ions:

\[
\text{M}^{2+2} - \text{M}^{2+3}
\]

Of greater interest are systems in which modest coupling exists between metal centers, for in these it is possible to photolytically induce electron transfer. The potential energy diagram in Fig. 13.13 shows by means of a vertical arrow the photochemical energy necessary for an electron to pass from the potential energy surface of \( \text{M}^{2+2} - \text{M}^{2+3} \) to the potential energy surface for \( \text{M}^{2+} - \text{M}^{3+} \). This means that intervalence transitions are observed in the electronic spectra (often in the near-infrared region) of these complexes but are not found in the spectra for monometallic complexes of either \( \text{M}^{2+} \) or \( \text{M}^{3+} \). Of course the electron could also pass thermally from one surface to the other, as for outer sphere electron transfer, through equalization of orbital energies by vibrational elongation and contraction of metal-ligand bonds. A comparison of optical and thermal electron transfer is shown in Fig. 13.14. In the optical process depicted in the top part of the figure, we see that transfer occurs prior to bond length adjustment, but in the thermal process (bottom of diagram), bond length changes take place (as required by the Franck-Condon principle) prior to electron transfer.

Fig. 13.14 A comparison of photochemical and thermal electron-transfer processes in mixed valence systems. The photochemical pathway (top) allows electron transfer prior to bond-length adjustment, while the thermal route (bottom) requires adjustment prior to electron transfer. [Creutz, C. Proc. Inorg. Chem., 1983, 30, 1-73. Used with permission.]

One photoactive system which has been extensively studied is a binuclear complex of \( \text{Ru}^{2+}/\text{Ru}^{3+} \) in which 4,4'-bipyridine functions as the bridge.

\[
\begin{align*}
\text{[Ru(NH}_3)_2\text{Ru}^{2+} \text{N}^\text{3+} \text{Ru(NH}_3)_2\text{]} & - \rightarrow \\
\text{[Ru(NH}_3)_2\text{Ru}^{2+} \text{N}^\text{3+} \text{Ru(NH}_3)_2\text{]} & - \rightarrow
\end{align*}
\]

An absorption (1050 nm) found in the near-infrared spectrum of this complex arises from a mixed valence transition. Light-induced metal-to-metal charge transfer was predicted by Hush for systems of this type before it was observed experimentally. Further, his theory relates the energy of absorption to that required for thermal electron transfer \((h\nu = 4 \times E_0)\) and from this it is possible to calculate the thermal electron transfer rate constant \( (5 \times 10^{-10} \text{s}^-) \).7

The expectation that the rate of electron transfer will slow with increasing distance between the two ions is realized, as shown for \( \text{Ru(bpy)}_2\text{Cl}_2 \text{Li}^+ \) complexes in Table 13.10. Distance alone, of course, does not determine how quickly an electron can pass through a bridge. The nature of the bridge itself is important with some bridges being more resistant to electron transport than others. A comparison of the diphosphine and pyrazine bridges, which are nearly the same length, shows the rate constant of the latter to be 30 times that of the former.38

Cytochrome \( c \), discussed more extensively in Chapter 19, is an important biological intermediate in electron transfer.39 This metalloprotein, found in all cells, has a molecular weight of approximately 12,800 and contains 104 amino acids in verte-

---

Chapter 12

Coordination Chemistry:
Structure

The previous chapter described the bonding principles responsible for the energetics and structure of coordination compounds. In this chapter the resulting structures will be examined in more detail with particular regard to the existence of various coordination numbers and molecular structures, and the effect of these structures on their chemical and physical properties.

The coordination numbers of metal ions range from 1, as in ion pairs such as Na"Cl in the vapor phase, to 12 in some mixed metal oxides. The lower limit, 1, is barely within the realm of coordination chemistry, since the Na"Cl ion pair would not normally be considered a coordination compound, and there are few other examples. Likewise, the upper limit of 12 is not particularly important since it is rarely achieved in discrete molecules, and the treatment of solid crystal lattices such as hexagonal BaTiO3 and perovskite as coordination compounds is not done frequently. The lowest and highest coordination numbers found in "typical" coordination compounds are 2 and 9 with the intermediate number 6 being the most important.

We have seen in Chapter 4 that the coordination number of ions in lattices is related to the ratio of the ionic radii. The same general principles apply to coordination compounds, especially when a single coordination number, such as 4, has two common geometries—tetrahedral and square planar. An extended list of coordination numbers and molecular structures, and the effect of these structures on their chemical and physical properties, can be found in the margin.

Typical examples include the cyano complexes, although silver(I) and gold(I) form discrete bis(cyanide) complexes, solid KCu(CN)2 possesses a chain structure in which the coordination number of the copper(I) is 3.

If the ligand is sterically hindered sufficiently, such as [N(SiMePh)3]+, [N(SiMePh2)2]+, [NPhMes]+, and [NPhBXY]+, two-coordinate complexes may also be formed by ions such as Me2+, Fe3+, Cu2+, and Ag+." The last two ligands have the advantage that the boryl group draws off one of the lone pairs on the nitrogen through N→B dative bonding and reduces the tendency of the nitrogen to bridge through N→M dative bonding. The geometry of coordination number 2 would be expected to be linear, either from the point of view of simple electrostatics or from the use of sp hybrid by the metal (but there are exceptions; see Chapter 5). If the (n-1) orbitals of the metal are sufficiently close in energy to the ns and np orbitals, the d1 orbital can enter into this hybridization to remove electron density from the region of the ligands. The tendency for this to occur will be in the order Hg = Au > Ag > Cu because of relativistic effects (see Chapter 18). This, in turn, may be partially responsible for the increased softness of Au(I) and Hg(II) (see Chapter 9).

As mentioned above, ion pairs in the gas phase may be considered as examples of coordination number 1. There are a few other examples known. For instance, the aryliodonium radical derived from the highly sterically hindered 1,1,3,5-triphenylbenzene. forms one-to-one organometallic compounds of the type CuC5H5(C5H5)2 and AgC5H5(C5H5)2, as shown in the margin.

Note, however, that some of the properties of metal ions in these systems can be described in terms of coordination chemistry. See Chapter 7.

<table>
<thead>
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<th>Coordination Number 1</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Structure" /></td>
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</tbody>
</table>

1. Note, however, that some of the properties of metal ions in these systems can be described in terms of coordination chemistry. See Chapter 7.

2. Lingens, R.; Strable, J. Angew. Chem. Int. Ed. Engl. 1984, 23, 436. Note that what we often naively write as "[LiCH3]" and "[LiC2H5]" and "KCH3" and "CuCl2" are often more complex. LiCH3 is a dimeric molecule in hydrocarbon solvents, isomerizes in THF and the solid, K CH3 is a cationic solid, and CuCl2 is a bridging polymeric solid. See Ettchenspacher, C.; Salzer, A. Organometallics, 2nd ed., VCH Weisbaden, Germany, 1992; pp 26-21.

Table 12.1

<table>
<thead>
<tr>
<th>Coordination Number 2</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Table" /></td>
</tr>
</tbody>
</table>


two metals is intimately involved in the electron transfer. The classic example of this type of mechanism was provided by Taube and coworkers. Their system involved the reduction of cobalt(III) (in \([\text{Co(NH}_3)_6\text{Cl}_3]^{2+}\)) by chromium(III) (in \([\text{Cr(OH)}_2\text{Cl}]^{3+}\)) and was specifically chosen because (1) both Co(III) and Cr(III) form inert complexes and (2) the complexes of Co(II) and Cr(II) are stable (see page 549). Under these circumstances the chlorine atom, while remaining firmly attached to the inert Co(II) ion, can displace a water molecule from the labile Cr(III) complex to form a bridged intermediate:

\[
[\text{Co(NH}_3)_6\text{Cl}_3]^{2+} + [\text{Cr(OH)}_2\text{Cl}]^{3+} \rightarrow [\text{H}_2\text{N}_2\text{Co-Cl-Cr(OH)}_2\text{Cl}]^{4+} + \text{H}_2\text{O}
\] (13.73)

The redox reaction now takes place within this dinuclear complex with formation of reduced Co(II) and oxidized Cr(III). The latter species forms an inert chloroaqua complex, but the cobalt(II) is labile, so the intermediate dissociates with the chlorine atom remaining with the chromium:

\[
[\text{H}_2\text{N}_2\text{Co-Cl-Cr(OH)}_2\text{Cl}]^{4+} \rightarrow [\text{H}_2\text{N}_2\text{CoCl}^{2+}] + [\text{CrCl(OH)}_2\text{Cl}]^{3+}
\] (13.74)

The five-coordinate cobalt(II) species presumably immediately picks up a water molecule to fill its sixth coordination position and then hydrolyzes rapidly to \([\text{CoCl(OH)}_2\text{Cl}]^{3+}\). Formally, such an inner sphere reaction consists of the transfer of a chlorine atom from cobalt to chromium, decreasing the oxidation state of the former but increasing that of the latter. In addition to the self-consistency of the above model (inert and labile species) and the observed formation of a chloroaqua complex, further evidence for this mechanism has been obtained by monitoring the reaction in the presence of free radiosotopes of chloride ion in the solution. Very little of this labeled chloride is ever found in the product, indicating that the chloride transfer has indeed been through the bridge rather than indirectly through free chloride.

![Fig. 13.12](image_url)

Fig. 13.12 A system for the photochemical conversion of \(\text{N}_2\) to \(\text{NH}_3\). Electrons (\(e^-\)) are promoted to the conduction band (CB) leaving holes (\(h^+\)) in the valence band (VB). (Modified from Khan, M. M. T.; Bhardwaj, R. C.; Bhardwaj, C. Angew. Chem., Int. Ed. Engl. 1998, 27, 923-925. Reproduced with permission.)

### Table 13.9

<table>
<thead>
<tr>
<th>X</th>
<th>(k, \text{M}^{-1} \cdot \text{s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{NH}_3)</td>
<td>(8.9 \times 10^{-3})</td>
</tr>
<tr>
<td>(\text{H}_2\text{O})</td>
<td>(0.5)</td>
</tr>
<tr>
<td>(\text{OH}^-)</td>
<td>(1.5 \times 10^4)</td>
</tr>
<tr>
<td>(\text{F}^-)</td>
<td>(2.5 \times 10^5)</td>
</tr>
<tr>
<td>(\text{Cl}^-)</td>
<td>(6 \times 10^6)</td>
</tr>
<tr>
<td>(\text{Br}^-)</td>
<td>(1.4 \times 10^7)</td>
</tr>
<tr>
<td>(\text{I}^-)</td>
<td>(3 \times 10^7)</td>
</tr>
<tr>
<td>(\text{N}_2)</td>
<td>(3 \times 10^7)</td>
</tr>
</tbody>
</table>


The importance of the nature of the bridging ligand in an inner sphere reaction is shown in Table 13.9. The reduction of \([\text{Co(NH}_3)_6\text{Cl}_3]^{2+}\) is about \(10^6\) faster than the reduction of \([\text{Co(NH}_3)_6\text{Cl}_3]^{3+}\). The bound ammonia ligand has no nonbonding pairs of electrons to donate to a second metal. Thus the reduction of the hexaammine complex cannot proceed by an inner sphere mechanism. If ligands are not available which can bridge two metals, an inner sphere mechanism can always be ruled out. A second important feature of an inner sphere reaction is that its rate can be no faster than the rate of exchange of the ligand in the absence of a redox reaction, since exchange of the ligand is an intimate part of the process. As was noted earlier, electron transfer reactions must be outer sphere if they proceed faster than ligand exchange.

It is often difficult to distinguish between outer and inner sphere mechanisms. The rate law is of little help since both kinds of electron transfer reactions usually are second order (first order with respect to each reactant):

\[
\text{rate} = k(\text{oxidant}) (\text{reductant})
\] (13.75)

Furthermore, although the chloro ligand in Eqs. 13.73 and 13.74 is transferred from oxidant to reductant, it is not always the case that the bridging ligand is transferred in an inner sphere reaction. After electron transfer takes place in the dinuclear complex, the subsequent dissociation may leave the ligand that functioned as a bridge attached to the metal with which it began. If the bridging ligand stabilized its original complex more than the newly formed complex, failure of its transfer would be no surprise. For example:

\[
[\text{Fe(CN)}_6]^{3-} + [\text{Co(CN)}_6]^{2-} \rightarrow [\text{Fe(CN)}_6]^{4-} + [\text{Co(CN)}_6]^{3-}
\] (13.76)

Presumably the C-bound cyanogroup stabilizes the \(d^8\) (Fe\(^{2+}\)) configuration of \([\text{Fe(CN)}_6]^{4-}\) more than the N-bound cyanogroup would stabilize a \(d^7\) (Co\(^{3+}\)) configuration in \([\text{Co(CN)}_6]^{3-}\).

If the bridging ligand contains only one atom (e.g., \(\text{Cl}^-\)), both metal atoms of the complex must be bound to it. However, if the bridging ligand contains more than one atom (e.g., \(\text{SCN}^-\)), the two metal atoms may or may not be bound to the same bridging-ligand atom (see Problem 13.30). The two conditions are called adjacent and remote attack, respectively. A remote attack may lead to both linkage isomers:

\[
\begin{align*}
[\text{(H}_2\text{N}_2\text{Co})^- + [\text{Co(NH}_3)_6\text{Cl}_3]^{2+} & \rightarrow \text{[H}_2\text{N}_2\text{Co-Cl-Cr(OH)}_2\text{Cl}]^{4+} + \text{H}_2\text{O} \\
\text{[H}_2\text{N}_2\text{Co-Cl-Cr(OH)}_2\text{Cl}]^{4+} & \rightarrow \text{[H}_2\text{N}_2\text{CoCl}^{2+}] + \text{[CrCl(OH)}_2\text{Cl}]^{3+}
\end{align*}
\] (13.77)

In the above instance the kinetically favored nitrito complex isomerizes to the thermodynamically favored nitro complex in seconds.

Tetrahedral complexes are favored by steric requirements, either simple electrostatic repulsions of charged ligands or van der Waals repulsions of large ones. A valence complex is an example of true three-coordination. Some other examples of three-coordination that have been verified by X-ray study are (a) tris(trimethylphosphine)phosphine(triphenylenephosphine)phosphine(phenyl) (Fig. 12.1a), (b) tris(triphénylphosphine)platinum(0), [Pt(PPh)3] (Fig. 12.1b), the tri(trifluoromethane)sulfonium triflate, [H2SO4]3+ (Fig. 12.1c), and the tri-n-alkylamine(triphenylenephosphine)platinum(0), [Pt(PPh3)3] (Fig. 12.1d). In all examples the geometry approximates an equilateral triangle with the metal atom at the center of the plane, as expected for sp3 hybridization. Some of the axial ligands have been omitted. (From Eller, P. G.; Corfield, P. W. R. Chem. Commun., 1971, 381-382. Reprinted with permission.)

Coordination
Number 4

Tetrahedral Complexes

This is the first coordination number to be discussed that has an important place in coordination chemistry. It is also the first for which isomerism is to be expected. The structures formed with coordination number 4 can be conveniently divided into tetrahedral and square planar forms although intermediate and distorted structures are common.

Tetrahedral complexes are favored by steric requirements, either simple electrostatic repulsions of charged ligands or van der Waals repulsions of large ones. A violence bond (VB) point of view ascribes tetrahedral structures to hybridization. Some other examples of three-coordination that have been verified by X-ray study are (a) tris(trimethylphosphine)phosphine(triphenylenephosphine)phosphine(phenyl) (Fig. 12.1a), (b) tris(triphénylphosphine)platinum(0), [Pt(PPh)3] (Fig. 12.1b), the tri(trifluoromethane)sulfonium triflate, [H2SO4]3+ (Fig. 12.1c), and the tri-n-alkylamine(triphenylenephosphine)platinum(0), [Pt(PPh3)3] (Fig. 12.1d). In all examples the geometry approximates an equilateral triangle with the metal atom at the center of the plane, as expected for sp3 hybridization. Some of the axial ligands have been omitted. (From Eller, P. G.; Corfield, P. W. R. Chem. Commun., 1971, 381-382. Reprinted with permission.)

Coordination
Number 3

This is a rare coordination number. Many compounds which might appear to be three-coordinate as judged from their stoichiometry are found upon examination to have higher coordination numbers. Examples are CsCuCl6, (infinite single chains, C≡CuCl−Cl−, C.N. = 6 at 228 and 236 pm; (two more Cl− from adjacent segments at 278 pm; note the operation of the John-Teller effect), KCuCl4, (infinite double chains, Cl−−Cu−Cu−Cl−, C.N. = 6, distorted octahedron), and NH4CuCl4 (infinite double chains, C.N. = 6, undistorted).

The KCuCl4 chain described above (C≡Cu−Cl−−Cu−Cl−−Cl−) is an example of true three-coordination. Some other examples of three-coordination that have been verified by X-ray study are (a) tris(trimethylphosphine)phosphine(triphenylenephosphine)phosphine(phenyl) (Fig. 12.1a), (b) tris(triphénylphosphine)platinum(0), [Pt(PPh)3] (Fig. 12.1b), the tri(trifluoromethane)sulfonium triflate, [H2SO4]3+ (Fig. 12.1c), and the tri-n-alkylamine(triphenylenephosphine)platinum(0), [Pt(PPh3)3] (Fig. 12.1d). In all examples the geometry approximates an equilateral triangle with the metal atom at the center of the plane, as expected for sp3 hybridization. Some of the axial ligands have been omitted. (From Eller, P. G.; Corfield, P. W. R. Chem. Commun., 1971, 381-382. Reprinted with permission.)

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The excited state cation has the potential to reduce water.

\[
2[*Ru(bpy)_3]^{2+} \rightarrow 2[Ru(bpy)_3]^{3+} + 2e^- \quad (13.65)
\]

\[
2e^- + 2H_2O \rightarrow 2OH^- + H_2 \quad (13.66)
\]

\[
2[*Ru(bpy)_3]^{2+} + 2H_2O \rightarrow 2[Ru(bpy)_3]^{3+} + 2OH^- + H_2 \quad (13.67)
\]

The \([Ru(bpy)_3]^{3+}\) generated in reaction 13.67 could then oxidize water.

\[
2[Ru(bpy)_3]^{3+} + 2e^- \rightarrow 2[Ru(bpy)_3]^{2+} \quad (13.68)
\]

\[
H_2O \rightarrow O_2 + 2H^+ + 2e^- \quad (13.69)
\]

\[
2[Ru(bpy)_3]^{3+} + H_2O \rightarrow 2[Ru(bpy)_3]^{2+} + O_2 + 2H^+ \quad (13.70)
\]

If we sum Eqs. 13.64–13.70, we obtain Eq. 13.61. The absence of a ruthenium complex in the overall equation reveals its catalytic nature.

In practice, however, the scheme fails for several reasons. First, reaction 13.67 is much slower than decay of \([*Ru(bpy)_3]^{2+}\) to its ground state. Second, the production of one mole of hydrogen requires two electrons and the production of one mole of oxygen involves four electrons, but the ruthenium complexes provide or accept only one electron at a time. This means that various intermediates arise as the reactants proceed to products and the catalyst would be required somehow to stabilize these intermediates while sufficient electrons are being provided. A variety of quenching agents, both oxidizing and reducing, have been used in attempts to circumvent these problems. The cycle presented in Fig. 13.11 is an example of reductive quenching. An electron is passed from \([*Ru(bpy)_3]^{2+}\) to methylviologen, MV\(^{2+}\).

\[
[*Ru(bpy)_3]^{2+} + CH_3N\text{C}-\text{CH}_2\text{NCH}_3 \rightarrow \quad \text{(13.71)}
\]

\[
[Ru(bpy)_3]^{3+} + CH_3\text{NCH}_2\text{NCH}_3
\]

Triethanolamine (TEOA) is added to the initial reaction mixture to reduce \([Ru(bpy)_3]^{3+}\) as it is generated; thus the back reaction producing \([Ru(bpy)_3]^{2+}\) and MV\(^{2+}\) is retarded. The reduced methylviologen MV\(^+\) reduces water to hydrogen in the presence of colloidal platinum and is oxidized back to MV\(^{2+}\), thereby completing the cycle. Many other cycles have been devised, some of which succeed in splitting water into hydrogen and oxygen with visible light, but none of which are yet of major economic potential to be studied in recent times. Another is the reported reaction of nitrogen with water to produce ammonia\(^\text{10}\) (see Chapters 15 and 19 for further discussions of nitrogen fixation):

\[
N_2 + 3H_2O \rightarrow 2NH_3 + O_2 \quad (13.72)
\]

This conversion is catalyzed by \([Ru(Hedta)(H_2O)]^{2+}\) (Hedta = trianion of ethylenediaminetetraacetic acid) at 30 \(^\circ\)C and 101 KPa in the presence of a solid semiconductor mixture (CdS/RuO\(_2\)). The photolytic production of ammonia is initiated by absorption of visible light (505 nm) by the CdS semiconductor (Fig. 13.12). Presumably, the incoming photons promote electrons from the valence band (VB) of CdS to its conducting band (CB), a process that leaves holes in the valence band. Water is photooxidized by RuO\(_2\), releasing electrons which are trapped by holes in the valence band of CdS. The electrons in the conducting band are transferred to the ruthenium complex via platinum metal. Protons from the water oxidation are attracted to the reduced ruthenium complex, interact with coordinated N\(_2\) in some unknown fashion, and are expelled as NH\(_3\). The cycle is complete when the coordination site left by NH\(_3\) becomes occupied once again by H\(_2\)O. It remains to be seen whether proposed cycles such as this one measure up to their promise.

Inner Sphere Mechanisms

---


discussion of organometallic compounds has been synthesized and characterized. A line drawing and stereoview of one of these is shown in Fig. 12.2. Note that the large C₅H₅ ring forces the other ligands back until the bond angles are essentially 90° rather than 109°. Indeed an argument could be made for considering the complex to be eight-coordinate, though little is gained by such a view. The chirality of the molecule is the important feature to be noted.

A second form of optical isomerism analogous to that shown by organic spirocyclic compounds has been demonstrated. Any molecule will be optically active if it is not superimposable on its mirror image. The two enantiomers of bis(benzoylacetonato)beryllium are illustrated in Fig. 12.3. In order for the complex to be chiral, the chelating ligand must be unsymmetric (not necessarily asymmetric or chiral, itself); [Be(acac)₂] is not chiral.

Square planar complexes are less favored sterically than tetrahedral complexes (see Table 12.1) and so are prohibitively crowded by large ligands. On the other hand, if the ligands are small enough to form a square planar complex, an octahedral complex with two additional σ bonds can usually form with little or no additional steric repulsion. Square planar complexes are thus formed by only a few metal ions. The best known are the d⁹ species such as Ni²⁺, Pd²⁺, Pt²⁺, and Au³⁺ (Chapter 11). There are also complexes of Co³⁺ (d⁶), Cu²⁺ (d⁹), and even Co⁴⁺ (d⁴) that are square planar, but such complexes are not common. The prerequisite for stability of these square planar complexes is the presence of nonbulky, strong field ligands which bond sufficiently well to compensate for the energy "lost" through four- rather than six-coordination. For Ni²⁺, for example, the cyanide ion forms a square planar complex, whereas ammonia and water form six-coordinate octahedral species, and chloride, bromide, and iodide form tetrahedral complexes. For the heavier metals the steric requirements are relaxed and the ligands are often strong enough to form the square planar geometry.

One unexpected square planar complex [Cd(OAr)₂(thf)₂] (Fig. 12.4) has recently been reported. It is the first example in this geometry for a Cd²⁺ ion. Inasmuch as a closely related complex of the smaller zinc ion, [Zn(OAr)₂(thf)₂], has distorted tetrahedral geometry, simple steric factors cannot account for the pseudo-D₂h symmetry of the cadmium complex, though to be sure, the steric relaxation of the larger metal atom and the perpendicular planes of the thf and phenoxide rings are nicely accommodated by it. Furthermore, octahedral geometry would not be unusual in a d⁶ metal ion.
Earlier we used M* to indicate a radioactive isotope. Here we use *M to indicate an excited state.

Coordination Chemistry: Reactions, Kinetics, and Mechanisms

Mechanisms of Redox Reactions

![Diagram of Reaction](image)

**Fig. 13.10** Absorption of blue light by [Ru(bpy)$_3^{2+}$] gives [Ru(bpy)$_3^{2+}$] which relaxes to [Ru(bpy)$_3^{3+}$] without emission. [Ru(bpy)$_3^{2+}$] may exist as excited state (luminescence) or undergo oxidation or reduction. Standard reduction potentials associated with individual processes are shown in the diagram. [Modified from J. A. Balzani, V. Barigelletti, F. Campagna, S. Belser, P. van Zeeuwsky, A. Coord. Chem. Rev. 1988, 82, 239-277. Used with permission.]

**Table 12.9**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log $K_{eq}$</th>
<th>$k_{	ext{lim}}$ (M$^{-1}$ s$^{-1}$)</th>
<th>$k_{	ext{lim}}$ (M$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(NH$_3$)$_5^{2+}$ + Ru(NH$_3$)$_5^{2+}$</td>
<td>4.40</td>
<td>$1.4 \times 10^4$</td>
<td>$4 \times 10^4$</td>
</tr>
<tr>
<td>Ru(NH$_3$)$_5^{2+}$ + Ru(NH$_3$)$_5^{2+}$</td>
<td>3.39</td>
<td>$1.1 \times 10^4$</td>
<td>$4 \times 10^7$</td>
</tr>
<tr>
<td>Ru(NH$_3$)$_5^{2+}$ + Co(phen)$_3^{2+}$</td>
<td>5.42</td>
<td>$1.5 \times 10^6$</td>
<td>$7 \times 10^7$</td>
</tr>
<tr>
<td>Ru(NH$_3$)$_5^{2+}$ + Co(phen)$_3^{2+}$</td>
<td>1.01</td>
<td>$2.0 \times 10^2$</td>
<td>$1 \times 10^4$</td>
</tr>
<tr>
<td>VO$_4^{3-}$ + Co(phen)$_3^{2+}$</td>
<td>0.25</td>
<td>$5.8 \times 10^{-4}$</td>
<td>$7 \times 10^{-4}$</td>
</tr>
<tr>
<td>VO$_4^{3-}$ + Ru(NH$_3$)$_5^{2+}$</td>
<td>5.19</td>
<td>$1.3 \times 10^4$</td>
<td>$1 \times 10^4$</td>
</tr>
<tr>
<td>VO$_4^{3-}$ + Fe$_3^{4+}$</td>
<td>16.50</td>
<td>$1.8 \times 10^3$</td>
<td>$2 \times 10^6$</td>
</tr>
<tr>
<td>Fe$_3^{4+}$ + Fe(phen)$_3^{2+}$</td>
<td>1.33</td>
<td>$1.4 \times 10^5$</td>
<td>$5 \times 10^5$</td>
</tr>
<tr>
<td>Fe$_3^{4+}$ + Fe(phen)$_3^{2+}$</td>
<td>3.90</td>
<td>$2.7 \times 10^7$</td>
<td>$6 \times 10^7$</td>
</tr>
<tr>
<td>Ru(NH$_3$)$_5^{2+}$ + Fe(phen)$_3^{2+}$</td>
<td>11.12</td>
<td>$3.4 \times 10^5$</td>
<td>$2 \times 10^6$</td>
</tr>
<tr>
<td>Ru(phen)$_3^{2+}$ + Fe(phen)$_3^{2+}$</td>
<td>9.40</td>
<td>$8.4 \times 10^4$</td>
<td>$4 \times 10^5$</td>
</tr>
<tr>
<td>Mo(CN)$_5^{4-}$ + IrCl$_3^{2-}$</td>
<td>2.18</td>
<td>$1.9 \times 10^4$</td>
<td>$8 \times 10^5$</td>
</tr>
<tr>
<td>Mo(CN)$_5^{4-}$ + MnO$_4^{-}$</td>
<td>$-4.07$</td>
<td>$2.7 \times 10^1$</td>
<td>$6 \times 10^4$</td>
</tr>
<tr>
<td>Mo(CN)$_5^{4-}$ + HMoO$_4^{-}$</td>
<td>8.48</td>
<td>$1.9 \times 10^4$</td>
<td>$2 \times 10^5$</td>
</tr>
<tr>
<td>FeCl$_3^{2+}$ + IrCl$_3^{2-}$</td>
<td>4.08</td>
<td>$3.8 \times 10^5$</td>
<td>$1 \times 10^6$</td>
</tr>
<tr>
<td>Fe(CN)$_3^{4+}$ + Mo(CN)$_5^{4-}$</td>
<td>2.00</td>
<td>$3.0 \times 10^4$</td>
<td>$4 \times 10^4$</td>
</tr>
<tr>
<td>Fe(CN)$_3^{4+}$ + MnO$_4^{-}$</td>
<td>3.40</td>
<td>$1.7 \times 10^5$</td>
<td>$6 \times 10^4$</td>
</tr>
</tbody>
</table>


When this cation absorbs light at 452 nm, the excited state species that initially forms, [Ru(bpy)$_3^{2+}$], relaxes to a relatively long-lived one, [Ru(bpy)$_3^{2+}$].

The electronic transition involved in the absorption is an example of a metal-to-ligand charge transfer in which a 4 electron of ruthenium is promoted to a 4 antibonding orbital of one of the bipyridine ligands. Thus the excited state complex, [Ru(bpy)$_3^{2+}$], may be formulated as [Ru(bpy)$_3^{2+}$],. The availability of an electron in a ligand antibonding orbital allows this excited state cation a much better reducing agent than the ground state cation. Furthermore, the "hole" created at the ruthenium center enhances its electron-seeking power and as a result, the excited cation is also a much better oxidizing agent than it was in its ground state. A comparison of the redox properties of the ground state with those of the excited state is shown in Fig. 13.10. Here we see that [Ru(bpy)$_3^{2+}$] is a better oxidizing agent than [Ru(bpy)$_3^{2+}$] by 2.12 volts (1.84 V + 1.28 V) and a better reducing agent by 2.12 volts (+0.86 V + 1.26 V). These are large voltages from which one can easily see the potential for a wide range of redox chemistry.

**Fig. 13.10** Absorption of blue light by [Ru(bpy)$_3^{2+}$] gives [Ru(bpy)$_3^{2+}$] which relaxes to [Ru(bpy)$_3^{3+}$] without emission. [Ru(bpy)$_3^{2+}$] may exist as excited state (luminescence) or undergo oxidation or reduction. Standard reduction potentials associated with individual processes are shown in the diagram. [Modified from J. A. Balzani, V. Barigelletti, F. Campagna, S. Belser, P. van Zeeuwsky, A. Coord. Chem. Rev. 1988, 82, 239-277. Used with permission.]

The suggestion led to the speculation that solar energy could be used to make hydrogen gas which could then be used as fuel. At pH 7 and 10 Pa. potentials for the reactions.

$$2e^- + 2H_2O \rightarrow 2H_2 + O_2 \quad \Delta G^\circ = -238 \text{ kJ mol}^{-1}$$

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$$2e^- + 2H_2O \rightarrow 2H_2 + O_2 \quad \Delta G^\circ = -238 \text{ kJ mol}^{-1}$$

Water does not absorb visible light, but one could envision a sequence of reactions that utilizes [Ru(bpy)$_3^{2+}$] as a photosensitizer for the decomposition. The first step would be absorption of solar energy by [Ru(bpy)$_3^{2+}$]:

$$[\text{Ru(bpy)}_3^{2+}] \rightarrow [\text{Ru(bpy)}_3^{3+}]$$

$$[\text{Ru(bpy)}_3^{2+}] \rightarrow [\text{Ru(bpy)}_3^{3+}]$$

species, but the 2,6-di-t-butyl groups may prevent coordination of a fifth and sixth ligand. From an electronic viewpoint, it may be that the stronger cadmium-phenoxide bonds dominate the bonding picture, leaving the weakly basic thf molecules to bind as best they can.\footnote{If so, this would be an example of Bent's rule (the maximization of s character towards the strongest bonding ligand) acting in a complex ion. See Problem 12.38.}

Square planar complexes rarely show optical isomerism. The plane formed by the four ligating atoms and the metal ion will ordinarily be a mirror plane and prevent the possibility of chirality. An unusual exception to this general rule was used in an ingenious experiment to prove that platinum(II) complexes were not five-coordinate species, but on warming slightly it converts to a five-coordinate complex. Since covalent bonding is obviously of great importance in coordination compounds, it is possible to have stable five-coordinate complexes, but it is true that there is a delicate balance of forces in these complexes, and their stability with respect to other possible structures is not great. For example, the compound \([\text{Co} \text{(dien)} \text{Cl}]_2\) (where \text{dien} = \text{EtNHCH2CH2NHCH2CH}_2\text{H}) and \([\text{Ni}(\text{dien})\text{Cl}]_2\), which contains both square planar and tetrahedral species. An other example is the pair of compounds of empirical formula \([\text{CoCl}_2\text{dien}]\) and \([\text{NiCl}_2\text{dien}]\), containing octahedral cations and tetrahedral anions.

If electrostatic forces were the only forces operating in bonding, five-coordinate compounds would always disproportionate into four- and six-coordinate species (as does the \([\text{Co}(\text{dien})\text{Cl}]_2\) complex above). Since covalent bonding is obviously of great importance in coordination compounds, it is possible to have stable five-coordinate complexes, but it is true that there is a delicate balance of forces in these complexes, and their stability with respect to other possible structures is not great. For example, the compound \([\text{Ni}(\text{PNP})\text{Cl}]_2\) (where \text{PNP} = \text{Cl}_{2}\text{P(\text{C}_6\text{H}_5)}\text{P(\text{C}_6\text{H}_5)}\text{P}) is a true five-coordinate species, but on warming slightly it converts to \([\text{Ni}(\text{PNP})\text{Cl}]_2\text{N}_2\text{Cl}_2\), which contains both square planar and tetrahedral species. Another example is the pair of compounds of empirical formula \([M\text{Cl}_2\text{dien}]\) and \([N\text{Cl}_2\text{dien}]\), containing octahedral cations and tetrahedral anions.

In the past a coordination number of 5 was considered almost as rare as a coordination number of 3. Again, many of the compounds which might appear to be five-coordinate on the basis of stoichiometry are found upon close examination to have other coordination numbers. Thus \([\text{C}_6\text{H}_5\text{CoCl}_3]\) and \([\text{Ni(H}_2\text{O})_2\text{ZnCl}_3]\) contain discrete tetrahedral \(\text{MCl}_4^2\) 's and free chloride ions. Thallium fluorodichloride, \(\text{TlFCl}_2\), is composed of infinite chains, \(\text{F}-\text{AlF}_2-F\), in which the coordination number of the aluminum is 6. The complex of cobalt(II) chloride and diethylenetriamine, \(\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_3\), of empirical formula \([\text{CoCl}_2\text{dien}]\) is not a five-coordinate molecule but a salt, \([\text{Co}((\text{dien})_2\text{CoCl}_2]\) containing octahedral cations and tetrahedral anions.
Co(III)–N bond is necessary before electron transfer reactions can occur. In contrast, the self-exchange rate constant for the \( \text{[Ru(NH}_3]_3^{2+}/[\text{Ru(NH}_3]_3^{2+} \) couple is \( 8.2 \times 10^7 \text{ M}^{-1} \text{s}^{-1} \) and the \( \text{Fe}--\text{N} \) bond length difference is 0.04 Å. This much faster rate for the ruthenium exchange is consistent with a small bond length adjustment prior to electron transfer. The cobalt and ruthenium systems are not entirely analogous, however, since cobalt goes from a low spin \( d^9 \) complex to a high spin \( d^7 \) complex while ruthenium remains low spin in both the oxidized and reduced forms. It has been argued that the cobalt reaction is anomalously slow because it is spin forbidden; however, recent work does not support this hypothesis.\(^{44}\)

It should be noted that not all self-exchange reactions between Co(III) and Co(II) are slow. The nature of the bound ligand has a significant influence on the reaction rate. In particular, ligands with \( \pi \) systems provide easy passage of electrons. For \( \text{[Co(phen)]}^{3+}/[\text{Co(phen)]}^{3+} \) exchange, for example, \( k \) is \( 4 \times 10^{10} \text{ M}^{-1} \text{s}^{-1} \), many orders of magnitude faster than for the cobalt ammine system.\(^{42}\)

Marcus has derived a relationship from first principles that enables one to calculate rate constants for outer sphere reactions:\(^{43}\)

\[
k_{22} = k_{21}k_{12}k_{12}^{-1}\]

(13.55)

To illustrate the application of this equation and the definitions of all of its terms, we will calculate the rate constant, \( k_{22} \), for the reaction of Eq. 13.47 (called a cross reaction as compared to a self-exchange reaction). For this reaction, \( k_{12} \) is the rate constant for the self-exchange process involving the hexacyanoferrate complexes:

\[
\text{[Fe(CN)}_6]^{3+} + \text{[Fe*(CN)]}^{3+} \rightarrow \text{[Fe(CN)}_6]^{3+} + \text{[Fe*(CN)]}^{3+}
\]

\( k_{12} = \frac{7.4 \times 10^2 \text{ M}^{-1} \text{s}^{-1}}{s^{-1}} \)

\( k_{12} \) is the rate constant for the similar reaction involving the octacyanoanthylenediamine complexes:

\[
\text{[Mo(CN)}_6]^{3+} + \text{[Mo*(CN)]}^{3+} \rightarrow \text{[Mo(CN)}_6]^{3+} + \text{[Mo*(CN)]}^{3+}
\]

\( k_{12} = 3 \times 10^4 \text{ M}^{-1} \text{s}^{-1} \)

\( K_{22} \) is the equilibrium constant for the overall reaction (Eq. 13.47):

\[
\text{[Fe(CN)}_6]^{3+} + \text{[Mo*(CN)]}^{3+} \rightarrow \text{[Fe*(CN)]}^{3+} + \text{[Mo(CN)}_6]^{3+}
\]

\( K_{22} = 1.0 \times 10^4 \)

and \( \log f_2 = (48 K_{22}/1000 k_{22}/2 \sigma^2) \). This last term consists of \( z \), which is the collision frequency of two uncharged particles in solution and is taken as \( 10^4 \text{ M}^{-1} \text{s}^{-1} \). The factor \( f_2 \) has been described as a correction for the difference in free energies of the two reactions and is often close to unity (in this case it is 0.85).\(^{44}\) When all of the appropriate values are substituted into Eq. 13.55, \( K_{22} \) is calculated to be \( 4 \times 10^4 \text{ M}^{-1} \text{s}^{-1} \), which compares quite well with the experimental value of \( 3.0 \times 10^4 \text{ M}^{-1} \text{s}^{-1} \). This Table 13.8 summarizes results for a number of outer sphere cross reactions. Confidence in the Marcus equation is high enough that, if it leads to a calculated rate constant that is in strong disagreement with an experimental value, a mechanism other than outer sphere should be considered.

The Marcus equation (13.55) connects thermodynamics and kinetics, as shown by the dependence of \( k_{22} \) on \( K_{22} \): As \( K_{22} \) increases, the reaction rate increases. Thus outer sphere reactions which are thermodynamically more favorable tend to proceed faster than those which are less favorable. These observations may be surprising to you since most elementary treatments of reaction dynamics keep thermodynamics (how far) and kinetics (how fast) separate. Here we see that how fast a reaction occurs can depend to some degree on how far it goes, or the driving force, \( \Delta G \). The simplified Marcus equation we have presented here, however, breaks down when \( K_{22} \) becomes large. The complete theory reveals that rate increases rapidly with increasing spontaneity, reaching a maximum when the change in free energy is equal to the sum of reorganization energies, and then decreases as the driving force increases further.

The redox properties of a transition metal complex may change dramatically if it has absorbed energy and exists in an excited state. One of the most famous and widely studied complexes in this area is the \( \text{[Fe(2,2'-bipyridine)}_3]^3+ \) cation.
Although five-coordinate compounds are still less common than those of either coordination number 4 or 6, recently there has been considerable interest in them, and the number of compounds with known structures has increased rapidly. The complexes can be described as "regular" or "distorted" trigonal bipyramidal (TPB; Fig. 12.6), "regular" or "distorted" square pyramidal (SP; Fig. 12.7), or as "highly distorted structures," i.e., something between TPB and SP. As we have seen, however, every intermediate structure between "perfectly TPB" and "perfectly SP" is possible (Chapter 6), and it serves little purpose to try to fit them into neat "pigeonholes." The differences between the various structures are often slight and the energy barriers tending to prevent interconversion are also small.

Of particular interest in regard to the delicate balance between the forces favoring TPB versus SP structures are two pentacyanonickelate(II) salts with different but very similar cations. Tris(1,3-diaminopropane)chromium(III) pentacyanonickelate(II), \([\text{Cr(tn)}_3][\text{Ni(CN)}_5]\), contains square pyramidal anions. In contrast, crystalline tris(ethylenediamine)chromium(III) pentacyanonickelate(II) sesquihydrate, \([\text{Cr(en)}_3][\text{Ni(CN)}_5] \cdot 1.5\text{H}_2\text{O}\), contains both square pyramidal anions (Fig. 12.7) and slightly distorted trigonal bipyramidal anions. The IR and Raman spectra of this solid exhibit two sets of bands, one of which (the TPB set) disappears when the sesquihydrate is dehydrated. In aqueous solution the structure is apparently also square pyramidal. It would appear that the SP structure is inherently more stable but by such a slight margin that forces arising in the hydrated crystal can stabilize a TPB structure. The forces favoring each of the limiting structures are not completely understood, but the following generalizations can be made. On the basis of ligand repulsions alone, whether they be considered naively as purely electrostatic or as Pauli repulsions from the bonding pairs, since effects arising from incompletely filled \(d\) orbitals are not present. Likewise, we should expect \(d^5\) and \(d^{10}\) to favor the TPB structure. Comparison of the relative energies of the orbitals in TPB (\(D_{5h}\)) versus SP (\(C_{4v}\)) geometry (Fig. 12.8) shows that \(d^5, d^4, d^3\), and \(d^2\) configurations should also favor TPB versus SP as much or more since the \(e''\) orbitals of \(C_{4v}\) and \(d''\) are lower in energy than the \(e''\) orbitals of a TPB complex. \(^{18}\) For \(d^6\) the order of stability again switches back to favor TPB (\(e''\) is lower in energy than \(a_1\)) and this continues through \(d^7\) and \(d^8\). Unfortunately, there are few data available to test these predcitions. The low spin \(d^6\) complex \([\text{Co(dpe)}_2\text{Cl}]^+\) [dpe = 1,2-bis(diphenylphosphino)ethane] crystallizes in two forms: a red solid that contains SP ions and a green form that contains TPB ions (Fig. 12.9). \(^{19}\) Apparently, the slight ligand field stabilization energy favoring the SP arrangement...
In this type of reaction bonds are neither made nor broken. Consider the reaction:

\[
[Fe(CN)_{6}]^{3-} + [Co(NH_3)_6]^{3+} \rightarrow [Fe(CN)_{6}]^{3-} + [Co(NH_3)_6]^{3+}
\]  
(13.47)

Such a reaction may be considered to approximate a simple collision model. The rate of the reaction is faster than cyanide exchange for either reactant so we consider the process to consist of electron transfer from one stable complex to another with no breaking of Fe—CN or Mo—CN bonds.

An outer sphere electron transfer may be represented as follows:

\[
O + R \rightarrow [O—R] \quad (13.48)
\]

\[
[O—R] \rightarrow [O—R]^* \quad (13.49)
\]

\[
[O—R]^* \rightarrow O^- + R^* \quad (13.50)
\]

First the oxidant (O) and reductant (R) come together to form a precursor complex. Activation of the precursor complex, which includes reorganization of solvent molecules and changes in metal-ligand bond lengths, must occur before electron transfer can take place. The final step is the dissociation of the ion pair into product ions.

A specific example further clarifies the activation and electron transfer steps. The exchange reaction between solvated Fe(III) and Fe(II) has been studied with radioactive isotopes of iron.  

\[
[Fe(H_2O)_6]^{3+} + [Fe(H_2O)_6]^{2+} \rightarrow [Fe(H_2O)_6]^{2+} + [Fe(H_2O)_6]^{3+}
\]  
(13.52)

The energy of activation, \( \Delta G^* \), for this reaction is 33 kJ mol\(^{-1}\). One might ask why it is not zero since the reactants and products are the same. In order for electron transfer to occur, the energies of the participating electronic orbitals must be the same, as required by the Franck-Condon principle. In this reaction an electron is transferred from the \( s_z \) orbital of Fe(III) to a \( s_z \) orbital of Fe(III). The bond lengths in Fe(II) and Fe(III) complexes are unequal (see Table 4.4), which tells us that the energies of the orbitals are not equivalent. If the electron transfer could take place without an input of energy, we would obtain as products the Fe(II) complex with bond lengths typical of Fe and the Fe(III) complex with bond lengths typical of Fe(III). Both could then relax with the release of energy. This would clearly violate the first law of thermodynamics. In fact, there must be an input of energy in order for electron transfer to take place. The actual process occurs with shortening of the bonds in the Fe(II) complex and lengthening of the bonds in the Fe(III) complex until the participating orbitals are of the same energy (Fig. 13.9). Vibrational stretching and compression along the metal—ligand bonds allow the required configuration to be achieved.

The energy of activation may be expressed as the sum of three terms:

\[
\Delta G^* = \Delta G_1^* + \Delta G_2^* + \Delta G_3^*
\]  
(13.53)

\[ \Delta G_1^* \] is the energy required to bring the oxidant and reductant into a configuration in which they are separated by the required distance (for charged reactants this includes work to overcome Coulombic repulsion). \( \Delta G_2^* \) is the energy required for bond compression and stretching to achieve orbitals of equal energy, and \( \Delta G_3^* \) is the energy needed for solvent reorganization outside of the first coordination sphere.

Potential energy diagrams further clarify the connection between molecular motion and electron transfer. The potential energy of all reactant and associated solvent nuclei before electron transfer can be approximated as a harmonic potential well; the potential energy of all product and solvent nuclei after electron transfer can be approximated as a harmonic potential well. The extent of this interaction is related to \( \Delta G^* \) shown in the figure. If the coupling interaction is strong, which is the condition when bond distortions are small, electron transfer is favorable. If the interaction is very weak, associated with large bond distortions, \( \Delta G^* \) will be large and the reaction will be slow. These considerations are equally applicable to heteronuclear reactions as depicted in Fig. 13.9b.

The importance of bond distortion magnitudes is revealed in the self-exchange reaction of hexamminecobalt complexes:

\[
[Co(NH_3)_6]^{3+} + [Co(NH_3)_6]^{3+} \rightarrow [Co(NH_3)_6]^{2+} + [Co(NH_3)_6]^{3+}
\]  
(13.54)

The second-order rate constant for this slow reaction is \( 10^{-8} \) M\(^{-1}\) s\(^{-1}\). The Co—N bond length in Co(III) is 1.931(15) Å while in Co(II) it is 2.144(9) Å, a difference of 0.213 Å. Considerable elongation of the Co(III)—N bond and compression of the

---

balances the inherent superiority of the TBP arrangement and allows the isolation of both isomers. In solution, the two forms interconvert readily, either by a Berry pseudorotation or through dissociation and recombination (see Chapter 6).

Finally, polydentate ligands can affect the geometry of a complex merely as a result of their own steric requirements. For example, we find some tetradentate ligands such as tris(2-dimethylaminoethyl)amine, \( \text{Me}_6 \text{tren} = ((\text{CH}_3)_2 \text{NCH}_2 \text{CH}_2)_3 \text{N} \), form only five-coordinate complexes (Fig. 12.10), apparently because the polydentate ligand cannot span a four-coordinate tetrahedral or square planar complex and cannot conform ("fold") to fit a portion of an octahedral coordination sphere.

We have seen that with nonmetallic central atoms such as phosphorus \((d^0)\), more electronegative elements prefer the axial positions of a TBP structure. A molecular orbital analysis of metal complexes\(^{20}\) indicates that most \(d^5\) configurations follow this same pattern. A notable exception is \(d^5\), which favors electropositive substituents at apical sites and electronegative substituents at equatorial sites. In the same way, the normally weak bonding of axial substituents is reversed with the \(d^5\) configuration. Thus we find the methyl group in the axial position in the \(d^5\) iridium(I) complex shown in Fig. 12.11a in contrast to its universal equatorial position in phosphoranes. Also, in contrast to the phosphoranes, the axial bonds are shorter in \(\text{Fe(CO)}_5\) than are the equatorial bonds (Fig. 12.11b); however, it must be stressed that there are exceptions to this behavior (Table 12.2). The same type of analysis\(^{21}\) predicts that in \(d^5\) complexes good \(\pi\)-accepting ligands will prefer the equatorial position. The compounds shown in Figs. 12.11 and 12.12 allow us to test this. Note that most of the ligands occur in both axial and equatorial positions depending upon what other ligands are present.

Table 12.2

<table>
<thead>
<tr>
<th>Complex</th>
<th>(M-L) (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Fe(CO)}_5)</td>
<td>181 183</td>
</tr>
<tr>
<td>([\text{Co(CNCH}_3)_5]^+)</td>
<td>184 188</td>
</tr>
<tr>
<td>([\text{Pt(SnCl}_3)_5]^+)</td>
<td>254 254</td>
</tr>
<tr>
<td>([\text{Mn(CO)}_5]^+)</td>
<td>182 180</td>
</tr>
</tbody>
</table>


\(^{21}\) There is insufficient space here to go through the complete derivation, but it may be noted that the method is not unlike that given previously for octahedral complexes (Chapter 11). For the complete method, see Footnote 20.

![Fig. 12.9 The structures of the red, square pyramidal isomer (a) and the green trigonal bipyramidal isomer (b) of the chlorobis[l,2-bis(diphenylphosphino)ethane]cobalt(II) cation. Phenyl groups and other substituents have been removed for clarity. (From Stalick, J. K.; Corfield, P. W. R.; Meek, D. W. \(\text{Inorg. Chem.}\) \textbf{1973}, \textit{12}, \textit{1668-1675}. Reproduced with permission.)](image)

![Fig. 12.10 Molecular structure of bromotris(2-dimethylaminoethyl)aminecobalt(II) cation in \(\text{[CoBr(Me}_6 \text{tren)}\text{JBr}\). (From Di Vaira, M.; and Orioli, P. L. \(\text{Inorg. Chem.}\) \textbf{1967}, \textit{6}, \textit{955}. Reproduced with permission.)](image)

![Fig. 12.11 Complexes showing apparent exceptions to the rules for trigonal bipyramidal bonding. (a) The methyl ligand seeks the axial position and allows the strong \(\pi\)-acceptors to occupy equatorial positions. Substituent groups on the phosphine ligands omitted for clarity. (From Rossi, A. R.; Hoffmann, R. \(\text{Inorg. Chem.}\) \textbf{1975}, \textit{14}, \textit{365-374}. Reproduced with permission.) (b) The equatorial bonds in \(\text{Fe(CO)}_5\) are slightly longer than the axial bonds.](image)
The dissymmetry would thus be lost, and when the chelate ring reforms, it would have a 50-50 chance of producing either the A or A isomer (Chapter 12). Since the rate-determining step in this mechanism is the dissociation of the ligand, the rate of racemization \( k_r \) would have to equal the rate of dissociation \( k_d \). For example, tris(phenanthroline)nickel(II) racemizes at the same rate \( k_r = 5.3 \times 10^{-4} \text{ s}^{-1} \) as it dissociates \( k_d = 1.6 \times 10^{-4} \text{ s}^{-1} \), which implies dissociation is part of the racemization mechanism. If racemization takes place faster than dissociation (as it does, e.g., for tris(phenanthroline)iron(II)): \( k_r = 6.7 \times 10^{-4} \text{ s}^{-1} \) and \( k_d = 0.70 \times 10^{-4} \text{ s}^{-1} \), this mechanism can be eliminated.

For cases that involve dissociation, it is probable that only one of the chelate detaches with formation of a five-coordinate complex. This complex could have either trigonal bipyramidal or square pyramidal geometry and either of these would underlie Berry pseudorotation (see Chapter 6) with scrambling of ligand sites. Reattachment of the dangling end of the bidentate ligand to reform the chelate ring would give a racemic mixture of \( A \) and \( A \) isomers.

For many complexes, \( k_r > k_d \), which means that racemization occurs without bond rupture; for these, an intramolecular pathway must beoperative. Four symmetry allowed intramolecular pathways have been identified (Fig. 13.7). 29 The "push through" (six coplanar ligands) and the "crossover" (four coplanar ligands) mechanisms both require large metal-ligand bond stretches to relieve steric hindrance and are energetically unfavorable. "Twist" mechanisms require more modest bond stretches and are believed to account for the racemization. The earliest twist mechanism, proposed by Rüy and Dutt, 30 is known as the rhombic twist. Some years later, Bailar suggested a trigonal twist mechanism. 31 The Bailar-Rüy twist involves rotating a trigonal face that is not associated with a threefold axis of the complex through a trigonal prismatic transition state into its mirror image. The Bailar twist can be seen as twisting the complex about a threefold axis through a trigonal prismatic transition state into its mirror image. It is in order to avoid the experimental difficulties encountered so that many years have passed with little firm experimental evidence in support of one or the other of the mechanisms. It appears that rigid chelates and those with small bite angles favor a trigonal twist. 32 Small bite angles are known to stabilize trigonal prismatic geometries (Chapter 12) and thus might be expected to reduce energy barriers to such a twist. Calculations suggest that the trigonal twist is favored when the bite \( b \), defined as the distance between donor atoms in the same chelate ligand, is substantially smaller than \( l \), the distance between donor atoms on neighboring chelate ligands (see Fig. 13.7). 33 On the other hand, for a rhombic twist to be favored, \( b \) must be much greater than \( l \). It would appear that both mechanisms are rather common because many complexes belong to each geometrical class. In cases where \( b \) and \( l \) are not significantly different, both twist mechanisms may operate simultaneously. Intramolecular isomerization of cis and trans octahedral complexes, \( \text{MCOCO}_3 \), is also well established for some complexes and probably proceeds through a trigonal twist mechanism. 29

35 Mechanisms of Redox Reactions

It might be assumed that there would be little to study in the mechanism of electron transfer—that the reducing agent and the oxidizing agent would simply bump into each other and electron transfer would take place. Reactions in solution are complicated, however, by the fact that the oxidized and reduced species are often metal ions surrounded by shields of ligands and solvating molecules. Electron transfer reactions
Since CN" and SnCl5 do not occur in the same complex in this series, the inequality shown for them is uncertain.

In SP geometry the central atom may be in the plane of the basal ligands or above it to varying degrees. The following discussion assumes that the metal atom is lying somewhat above the basal plane, as is commonly found. Under these conditions the "normal" situation (d°-d", and d°-d") is for the apical bond to be the strongest with weaker basal bonds. As in the TBP case, the d° configuration is reversed with stronger basal bonds and a weak apical bond. Likewise, good donors usually seek weaker basal bonds. As in the TBP case, the configuration is reversed with stronger "normal" situation (d°-d", and d°-d") and d°-d°) somewhat above the basal plane, as is commonly found. Under these conditions the interelectron repulsions can be neglected to a first approximation and the spectrum interpreted solely on the basis of the simple one-electron energy level diagrams (Fig. 12.13). In the more general case, however, these electron-electron effects must be treated in a manner analogous to that given in Chapter 11 for octahedral complexes.

The magnetic susceptibilities of the low spin five-coordinate complexes thus differ significantly from corresponding low spin octahedral complexes. The unavailability of the fifth d orbital can be rationalized in terms of dsp hybrid bonding. The TBP structure results from d°-d° hybridization and SP from d°-d° hybridization. In this sense valence bond theory is in qualitative agreement with simple crystal field theory or more elaborate molecular orbital schemes. The latter two methods, however, also account for the energy levels of the other d orbitals as well as assign the difference between high and low spin complexes to the relative energies of the d° and d° hybrid orbitals (see Fig. 12.8). The placement of these energy levels can be reasonably interpreted by means of spectral measurements. In some low spin complexes the interelectron repulsions can be neglected to a first approximation and the spectrum interpreted solely on the basis of the simple one-electron energy level diagrams (Fig. 12.13). In the more general case, however, these electron-electron effects must be treated in a manner analogous to that given in Chapter 11 for octahedral complexes.

Five-coordinate complexes with d°, d°, d°, and d° may be either high or low spin. The magnetic susceptibility of the low spin complexes is that expected if one of the d orbitals is unavailable for occupancy by the metal d electrons. Thus 3 equals 0 (d°), 4 (d°), 5 (d°), and 6 (d°). The magnetic susceptibilities of the low spin five-coordinate complexes thus differ significantly from corresponding low spin octahedral complexes. The unavailability of the fifth d orbital can be rationalized in terms of dsp hybrid bonding. The TBP structure results from d°-d° hybridization and SP from d°-d° hybridization. In this sense valence bond theory is in qualitative agreement with simple crystal field theory or more elaborate molecular orbital schemes. The latter two methods, however, also account for the energy levels of the other d orbitals as well as assign the difference between high and low spin complexes to the relative energies of the d° and d° hybrid orbitals (see Fig. 12.8). The placement of these energy levels can be reasonably interpreted by means of spectral measurements. In some low spin complexes the interelectron repulsions can be neglected to a first approximation and the spectrum interpreted solely on the basis of the simple one-electron energy level diagrams (Fig. 12.13). In the more general case, however, these electron-electron effects must be treated in a manner analogous to that given in Chapter 11 for octahedral complexes.

Table 12.3

<table>
<thead>
<tr>
<th>Complex</th>
<th>Apical</th>
<th>Basal</th>
<th>dsp</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mn(NH3)6]+</td>
<td>198</td>
<td>294</td>
<td>d°</td>
</tr>
<tr>
<td>[NiCl4]2-</td>
<td>238</td>
<td>230</td>
<td>d°</td>
</tr>
<tr>
<td>[Ni(CN)4]2-</td>
<td>220</td>
<td>216</td>
<td>d°</td>
</tr>
<tr>
<td>[CoCl4]2-</td>
<td>242</td>
<td>246</td>
<td>d°</td>
</tr>
<tr>
<td>[Sn(C2H5)5]2-</td>
<td>224</td>
<td>222</td>
<td>d°</td>
</tr>
</tbody>
</table>

* Reproduced with permission. 


Since CN" and SnCl5 do not occur in the same complex in this series, the inequality shown for them is uncertain.

Fig. 12.13 Spectra of (a) bromo(cis-methylmercapto-o-phenyl)phosphinodimine(II) and (b) bromo(cis-dimethylarsino-o-phenyl)arsinodimine(II) cations. [From Furlani, C. Coord. Chem. Rev. 1968, 3, 141. Reproduced with permission.]

These are the simplest hybridizations to visualize. It is possible to substitute more d character for p character and arrive at the same symmetry. For example, d°-p° also form TBP, and d°-p° also form SP. The actual percentages of p, d°, and d° character will depend upon energetic factors such as promotion energy and quality of overlap of the resulting hybrids.
ammonia, which possesses no free lone pairs when it is bound to a metal, is the leaving group, no acceleration is observed.

Hydroxide ion also may have an appreciable effect on the rate of hydrolysis of octahedral complexes. The rate constant for hydrolysis of \([\text{Co(NH}_3\text{Cl}_4\text{]}^{2-}\) in basic solution is a million times that found for acidic solutions. Furthermore, the reaction is found to be second order and dependent on the hydroxide ion concentration:

\[
\text{rate} = k[\text{Co(NH}_3\text{Cl}_4\text{]}^{2-}][\text{OH}^-] \tag{13.38}
\]

Although an associative mechanism is consistent with these results, the prevailing opinion is that the reaction takes place via proton abstraction:

\[
\begin{align*}
\text{[Co(NH}_3\text{Cl}_4\text{]}^{2-} + \text{OH}^- & \rightarrow \text{[Co(NH}_3\text{Cl}_4\text{]}^{2-} + \text{H}_2\text{O} \quad \text{(13.39)} \\
\text{[Co(NH}_3\text{Cl}_4\text{]}^{2-} + \text{Cl}^- & \rightarrow \text{[Co(NH}_3\text{Cl}_4\text{]}^{2-} \quad \text{(13.40)} \\
\text{[Co(NH}_3\text{Cl}_4\text{]}^{2-} + \text{H}_2\text{O} & \rightarrow \text{[Co(NH}_3\text{Cl}_4\text{]}^{2-} \quad \text{(13.41)}
\end{align*}
\]

According to this viewpoint, the hydroxide ion rapidly sets up an equilibrium with the amido-cobalt complex. The rate-determining step is the dissociation of this complex (Eq. 13.40), but since its concentration depends on the hydroxide ion concentration through equilibrium, the reaction rate is proportional to the hydroxide ion concentration.

This mechanism, assigned the symbol \(S_{\text{A,CP}}\) for a first-order reaction involving the conjugate base of the complex, is supported by a number of observations. It rationalizes the fact that the hydroxide ion is unique in its millionfold increase in rate over acid hydrolysis; other anions which are incapable of abstracting protons from the complex, but which would otherwise be expected to be good nucleophiles, do not show this increase. Furthermore, the \(S_{\text{A,CP}}\) mechanism can apply only to complexes in which one or more ligands have ionizable hydrogen atoms. Thus complexes such as \([\text{Co(NH}_3\text{Cl}_4\text{]}^{2-}\) and \([\text{Co(CN}_3\text{Cl}_4\text{]}^{2-}\) would not be expected to exhibit typical base hydrolysis and indeed they do not. In these cases, the hydrolysis proceeds slowly and without dependence on hydroxide ion.

If the hydroxide ion accelerates reactions by proton abstraction rather than by direct attack, it might be supposed that it would be possible to trap the five-coordinate intermediate by addition of large amounts of anion other than hydroxide. One system for which this is possible is the base hydrolysis of \([\text{Co(NH}_3\text{R}_2\text{]}^{2+}\) (\(X = \text{OSO}_2\text{CF}_3\)) with \(\text{N}_2^*\) as the trapping agent:

\[
\text{[Co(NH}_3\text{R}_2\text{]}^{2+} + \text{OH}^- \rightarrow \text{[Co(NH}_3\text{R}_2\text{]}^{2+} + \text{H}_2\text{O} \quad \text{(13.42)}
\]

\[
\text{[Co(NH}_3\text{R}_2\text{]}^{2+} + \text{X}^- \rightarrow \text{[Co(NH}_3\text{R}_2\text{]}^{2+} + \text{X}^- \quad \text{(13.43)}
\]

\[
\begin{align*}
\text{[Co(NH}_3\text{R}_2\text{]}^{2+} & \rightarrow \text{[Co(NH}_3\text{R}_2\text{]}^{2+} \\
\text{[Co(NH}_3\text{R}_2\text{]}^{2+} & \rightarrow \text{[Co(NH}_3\text{R}_2\text{]}^{2+}
\end{align*}
\]

There are several mechanisms that are possible for such an inversion, some of which can be eliminated by appropriate experiments. For example, one mechanism would involve complete dissociation of one chelating ligand with formation of a square planar or a trans diaqua complex as a first step:

\[
\begin{align*}
\text{[Co(NH}_3\text{R}_2\text{]}^{2+} & \rightarrow \text{[Co(NH}_3\text{R}_2\text{]}^{2+} \\
\text{[Co(NH}_3\text{R}_2\text{]}^{2+} & \rightarrow \text{[Co(NH}_3\text{R}_2\text{]}^{2+}
\end{align*}
\]

When this reaction was carried out in 0.10 M hydroxide and 1.0 M azide, both the hydroxo (90.3%) and azido (9.7%) complexes were formed. Keep in mind that without base, azide substitution would not be observed within the experimental time period. Furthermore, the rate of hydrolysis is not much different when azide is replaced with perchlorate or acetate. It becomes clear that these anions are spectators of the five-coordinate activated complex and are not involved in the loss of \(X^-\).

The preceding discussion of substitution mechanisms barely scratches the surface of a field that has occupied the attention of many of the world's best coordination chemists. It is an area which seems to have an infinity of problems as well as methods of attack. It is unfortunate that it is not possible here to present a more comprehensive theory of substitution mechanisms. The discussion presented errs on the side of omission of fine points and controversial interpretations. For every experiment designed to confirm a mechanism, an alternative explanation can usually be found. As one noted researcher once said: "The members of the other school of thought are extremely ingenious at coming up with alternative explanations for all of the conclusive experiments that we seem to do." This should serve to remind us of the truism that it is not possible to prove that a particular mechanism is the correct one: it is only possible sometimes to prove that an alternative mechanism is not correct. To this might be added a corollary: Often it is extremely difficult to prove that the alternative is impossible.

Another set of reactions that has received considerable attention is that in which optically active complexes, especially tris(chelate) compounds racemize:

\[
\begin{align*}
\text{[Co(NH}_3\text{R}_2\text{]}^{2+} & \rightarrow \text{[Co(NH}_3\text{R}_2\text{]}^{2+} \\
\text{[Co(NH}_3\text{R}_2\text{]}^{2+} & \rightarrow \text{[Co(NH}_3\text{R}_2\text{]}^{2+} \\
\text{[Co(NH}_3\text{R}_2\text{]}^{2+} & \rightarrow \text{[Co(NH}_3\text{R}_2\text{]}^{2+}
\end{align*}
\]

\[
\begin{align*}
\text{[Co(NH}_3\text{R}_2\text{]}^{2+} & \rightarrow \text{[Co(NH}_3\text{R}_2\text{]}^{2+} \\
\text{[Co(NH}_3\text{R}_2\text{]}^{2+} & \rightarrow \text{[Co(NH}_3\text{R}_2\text{]}^{2+} \\
\text{[Co(NH}_3\text{R}_2\text{]}^{2+} & \rightarrow \text{[Co(NH}_3\text{R}_2\text{]}^{2+}
\end{align*}
\]

Isomerism in Five-Coordinate Complexes

Although it has long been known that various geometric and optical isomers are possible for coordination number 5, examples have been few. We have already seen examples of TBP-SP isomerism in an Ni(II) complex (page 480) and a Co(II) complex (page 481). Another example is \([(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Ru}(\text{CO})((\text{CF}_3)_2\text{C}_2\text{S})_2\text{J}\). It forms two isomers, one orange and one violet, which coexist in solution. Recrystallization from most solvents (e.g., acetonitrile) yields only the orange isomer, but dichloromethane/hexane as solvent yields a mixture of orange crystals and violet crystals. Both isomers are square pyramidal, but the orange isomer has the carbon monoxide ligand in the apical position, and the violet isomer has a basal carbon monoxide with one of the phosphine ligands at the apex of the pyramid (Fig. 12.14). A related type of geometric isomerism is found in the organometallic complex dibromodicarbonylcyclopentadienylrhenium(III). Both isomers have the cyclopentadienyl ring at the apex of a square pyramid with the basal ligands in either a cis or a trans arrangement.25

Finally, optical isomerism is even more rare. The first example of the determination of the absolute configuration of such a chiral complex is shown in Fig. 12.15.26

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Fig. 12.14 Stereoviews of the inner coordination spheres about the central ruthenium atom in the orange (top) and violet (bottom) isomers of \([(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Ru}(\text{CO})((\text{CF}_3)_2\text{C}_2\text{S})_2\text{J}\). [From Bernal, I.; Clearfield, A.; Ricci, J. S., Jr., J. Cryst. Mol. Struct. 1974, 4, 43-54. Reproduced with permission.]

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Fig. 12.15 A Schiff base complex of dicarbonylcyclopentadienylmolybdenum(II) cation. [From Bernal, I.; LaPlaca, S. J.; Korp, J.; Brunner, H.; Herrmann, W. A. Inorg. Chem. 1978, 17, 382-388. Reproduced with permission.]

Note that these compounds are not enantiomers, but true diastereomers with different properties, and they may be separated by fractional crystallization. The asymmetric carbon atom has an $S$ configuration in both diastereomers, but the chirality about the molybdenum atom is different. Thus the asymmetric carbon aids in the resolution of the molybdenum center, but its presence is not necessary for the complex to be chiral. It is merely necessary for the Schiff base to be asymmetric, i.e., have one pyridine nitrogen and one imino nitrogen. If the bidentate ligand had been ethylenediamine, bipyridine, or the oxalate ion, there would have been a mirror plane and no chirality at the molybdenum.
This expression simplifies to Eq. 13.36 with $k_{obs} = k_{d} \cdot S_{1}I_{2}$ under pseudo first-order conditions. Furthermore, the form of the rate law does not change if bond making becomes more important than bond breaking ($k_{d}$). Since rate laws for $D_{aq}$ and $A_{aq}$ cannot be distinguished with certainty (knowledge of rate and equilibrium constants for individual reaction steps may provide clarification), it is not surprising that there have been considerable debate and controversy over the mechanistic details of many octahedral substitution reactions. Few reactions appear to fit into the limiting $D$ and $A$ categories; thus most discussion centers around the $I_{d}$ and $I_{a}$ mechanisms.

Because of the inertness of $C_{III}$ and $C_{II}$ complexes, their substitution reactions were the first among those of octahedral complexes to be extensively studied. Most evidence supports the $I_{d}$ mechanism for substitution in $C_{III}$ complexes. First, there is little dependence of reaction rate on the nature of the incoming ligand. If bond making were of significant importance, the opposite would be expected.

Data are presented in Table 13.4. The rate expression for pentaaquocobalt(III)

$$\text{[Co(NH}_{3}]^{2+} \cdot H_{2}O \rightarrow \text{[Co(NH}_{3}]^{2+} \cdot H_{2}O}$$

(13.36)

We see only a small variation in rate constants for a variety of monodentate ligands. It is instructive to also consider the reverse reaction of Eq. 13.35, the reaction of the $C_{III}$ complex. If this is an $I_{d}$ reaction, $M$—$X$ bond strength should correlate with reaction rate since most of the activation energy would be associated with bond breaking. Table 13.5 satisfies our expectation that the reaction rate depends on the kind of $M$—$X$ bond being broken. The entering group and leaving group data provide convincing evidence for a dissociative mechanism and this view is further supported by steric arguments. The reaction in which water replaces $C_{I}$ in $[\text{Co(NH}_{3}]^{2+} \cdot H_{2}O]$ takes place 22 times faster than the same reaction for $[\text{Co(NH}_{3}]^{3+} \cdot H_{2}O]$. The greater steric requirements of methylamine encourage dissociation of the $C_{I}$ ligand. If the reaction proceeded by an $I_{d}$ or $A$ pathway, the order of rates would be the opposite because increased steric repulsion of the incoming ligand would be expected to slow the reaction. Finally, it should be noted that the absence of a trans effect (so important in square planar substitution) for $C_{III}$ complexes is consistent with a dissociative mechanism.

There is growing evidence that substitution reactions in $C_{III}$ complexes may not be typical of octahedral transition metal complexes. Early studies of substitution reactions for $C_{II}$ complexes revealed a rather strong dependence of reaction rate on the nature of the entering group, which supported the $I_{d}$ mechanism. More recently, high pressure oxygen-NMR spectroscopy has come to widespread use for obtaining mechanistic details about fast reactions and, as a result, many water-stable transition metal complexes have been investigated. The parameter of interest that is yielded by these experiments is volume of activation, $\Delta V^*$, which is a measure of the change in compressibility that occurs as the reaction proceeds from the ground state to the transition state (see page 542). The data in Table 13.6, obtained for solvent exchange with $[\text{M(NH}_{3}]^{2+} \cdot H_{2}O]$ complexes, show a positive $\Delta V^*$ for $C_{III}$ but negative values for $C_{I}$, $C_{II}$, and $C_{III}$, suggesting an $I_{d}$ mechanism for the cobalt ion but $I_{d}$ for chromium, rhodium, and iridium ions. Data for water exchange reactions of first-row hexagonal tripodal ions are shown in Table 13.7. We see a general increase in volatiles of activation as we move across the periodic table from $C_{III}$ to $C_{II}$. In fact the value for $C_{II}$ approaches that predicted for an $A$ mechanism. The trend may be viewed as a gradual change from strongly associative to more strongly dissociative. Similar NMR studies of solvent exchange reactions also have been carried out for divalent transition metal ions, $[\text{M(NH}_{3}]^{2+} \cdot H_{2}O]$. In these experiments, volumes of activation indicate a change from $I_{d}$ to $I_{a}$ across the first row; i.e., the dissociative mechanism is more important for $C_{III}$ than for $C_{II}$. Since volumes of activation also include volume changes in solvents and reactants, interpretation is not always straightforward, and some believe that the power of the method has been overstated. For example, Langford and Swaddle have presented opposing views on this matter. Undoubtedly, the $I_{d}$ pathway is more common for octahedral substitution than once thought.

Substitution reactions taking place in water solution can often be accelerated by the presence of an acid or base. If the coordinated leaving group (X) has lone pairs which can interact with $H^+$ or metal ions such as $Ag^+$ or $Hg^+$, the $M$—$X$ bond will be weakened and loss of $X$ facilitated. This effect is seen in the reaction of $[\text{Cr(H}_{2}O)_{6}]^{3+}$:

$$\text{[Cr(H}_{2}O)_{6}]^{3+} + H^+ = \text{[Cr(H}_{2}O)_{5}F]^{2+} + \text{H}_{2}O}$$

(13.37)

Available lone pairs of the bound fluorine group are attracted to the hydrogen ion, leading to the formation of a weak acid. The rate constant for the overall reaction is $6.2 \times 10^{-10}$ s$^{-1}$ in neutral solution, but $1.4 \times 10^{-8}$ s$^{-1}$ in acid solution. When
Another interesting example that combines both geometric isomerism and chirality consists of complexes of the type:

![Complexes](image)

Note that the cis isomer lacks an improper axis of rotation and is therefore chiral, but that the trans isomer has a plane of symmetry and will be achiral in the absence of an asymmetric carbon in the phosphine ligand. 

This is by far the most common coordination number. With certain ions six-coordinate complexes are predominant. For example, chromium(III) and cobalt(III) are almost exclusively octahedral in their complexes. It was this large series of octahedral complexes which led Werner to formulate his theories of coordination chemistry and which, with square planar platinum(II) complexes, formed the basis for almost all of the classic work on complex compounds. Before discussing the various isomeric possibilities for octahedral complexes, it is convenient to dispose of the few nonoctahedral geometries.

### Coordination Number 6

This is by far the most common coordination number. With certain ions six-coordinate complexes are predominant. For example, chromium(III) and cobalt(III) are almost exclusively octahedral in their complexes. It was this large series of octahedral complexes which led Werner to formulate his theories of coordination chemistry and which, with square planar platinum(II) complexes, formed the basis for almost all of the classic work on complex compounds. Before discussing the various isomeric possibilities for octahedral complexes, it is convenient to dispose of the few nonoctahedral geometries.

### Distortions from Perfect Octahedral Symmetry

Two forms of distortion of octahedral complexes are of some importance. The first is tetragonal distortion, either elongation or compression along one of the fourfold rotational axes of the octahedron. This type of distortion has been discussed previously in connection with the Jahn-Teller effect. Another possibility is elongation or compression along one of the four threefold rotational axes of the octahedron that pass through the centers of the faces, resulting in a trigonal antiprism. Another configuration that is not really a distortion but involves a reduction of symmetry may be mentioned here. It consists of the replacement of six unidentate ligands in a complex such as [Co(NH$_3$)$_6$]**3+** with chelate rings such as

RPh$_3$P

The difference of two electrons can be represented formally as:

$$\text{S}_2\text{C} \quad \rightarrow \quad \text{S}_2\text{C}^2-$$

Another interesting example that combines both geometric isomerism and chirality consists of complexes of the type:  

![Complex](image)

Although by far the greatest number of six-coordinate complexes may be derived from the octahedron, a few interesting complexes have the geometry of the trigonal prism. For many years the only examples of trigonal prismatic coordination were in crystal lattices such as the sulfides of heavy metals (MoS$_2$ and WS$_2$, for example). The first example of this geometry in a discrete molecular complex was tris(m-1,2-di-phenylethene-1,2-dithiolato)rhenium Re[S$_2$C(C$_2$H$_4$)$_3$]$_3$ (Fig. 12.17). Following that, a significant series of trigonal prismatic complexes of ligands of the type R$_2$C=S$_2$ was fully characterized with rhenium, molybdenum, tungsten, vanadium, zirconium, and niobium, and suggested for other metals.

There is considerable ambiguity concerning the charge on this type of ligand. This is because it may be formulated either as a neutral dithioketone or the dianion of an unsaturated dithiol. The difference of two electrons can be represented formally as:

$$\text{S}_2\text{C} \quad \rightarrow \quad \text{S}_2\text{C}^2-$$

Since the electrons involved are delocalized over molecular orbitals not only of the ligand but of the metal as well, it is impossible to assign a formal charge to the ligand or the metal. Nevertheless, the actual distribution of electron density may be quite important in determining how a reaction proceeds, as suggested for molybdenum enzymes (see also Chapter 19).

**Fig. 12.16** (a) Tetragonal and (b) trigonal distortion of an octahedral complex. Either may occur via elongation or compression.

**Trigonal Prism**

![Diagram](image)
As mentioned above, the $k_2$ term of the rate law shown in Eq. 13.10 could also arise from dissociation (D) of X to give a three-coordinate complex which then reacts with Y:

$$ML_2TX \rightarrow ML_2(TY) \rightarrow ML_2TY$$  \hspace{1cm} (13.15)

In other words, the form of the rate law does not help one distinguish between an A or D mechanism for the $k_2$ pathway. The ambiguity in the interpretation of the $k_2$ term has caused much discussion and experimentation. It is found that reactions take place faster in more nucleophilic solvents, suggesting that solvent attack plays an important role.

Also, dissociative reactions should be accelerated by the presence of sterically demanding ligands; just the opposite is observed, in keeping with an $A$ or $D$ mechanism.

Further insight into the question of an associative versus a dissociative mechanism can be provided by thermodynamic data such as that shown in Table 13.1 for the substitution of bromide by iodide or thiocyanate in the reaction:

$$\text{PE}_3 + \text{R} - \text{Br} + X \rightarrow \text{R} - \text{Pt} - X + \text{Br}^-$$  \hspace{1cm} (13.16)

The reaction rate is primarily determined by the enthalpy of activation ($\Delta H^*$), which is usually the case in square planar nucleophilic substitution reactions. Of greater importance, so far as a dissociative versus an associative mechanism is concerned, are the entropies and volumes of activation, $\Delta S^*$ and $\Delta V^*$, respectively. Note that the values are negative for both the $k_1$ and the $k_2$ steps. The observed decrease in entropy is what we would expect for a mechanism in which two particles come together to give an activated complex. The volume of activation is determined by doing the reaction under high pressure:

$$\Delta V^* = RT \ln \left( \frac{k_1}{k_2} \right)$$  \hspace{1cm} (13.17)

An activated complex with a smaller volume than the reacting species will give rise to a negative $\Delta V^*$ and is characteristic of association (see page 533 for further discussion).

### Table 13.1

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Activation parameters for the substitution of THF by NH$_3$</th>
<th>SC(NH$_2$)$_2$</th>
<th>Cl NH$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$</td>
<td>$k_2$</td>
<td>$\Delta H^*$</td>
<td>$\Delta S^*$</td>
</tr>
<tr>
<td>PE$_3$</td>
<td>R</td>
<td>60</td>
<td>59</td>
</tr>
<tr>
<td>$k_3$</td>
<td>$k_4$</td>
<td>$\Delta H^*$</td>
<td>$\Delta S^*$</td>
</tr>
<tr>
<td>Cl NH$_2$</td>
<td>R</td>
<td>16</td>
<td>16</td>
</tr>
</tbody>
</table>

**The Trans Effect**

None of the above factors has been studied more exhaustively than the effect of the ligand trans to the leaving group. By varying the nature of this ligand, it is possible to cause rate changes of many orders of magnitude. Furthermore, the effect can be used to advantage in designing syntheses.

Many experiments have been carried out to gain a clearer understanding of the trans effect. None of the above factors has been studied more exhaustively than the effect of the ligand trans to the leaving group. By varying the nature of this ligand, it is possible to cause rate changes of many orders of magnitude. Furthermore, the effect can be used to advantage in designing syntheses.

Evidence for a dissociative mechanism has been reported: Lanza, S.; Menelli, D.; Moio, P.; Sacschihi, J.; Romeo, R.; Torc, M. L. Inorg. Chem. 1984, 23, 4428-4433. The reaction, which involves substitution of dpe in Pt(dpe)$_2$, proceeds by loss of one dpe ligand. However, it is possible that the dpe ligand that remains coordinated can function in a catalytic capacity, it can be divided into those workers acknowledge, whether this reaction can be called a true dissociation.

Negative values for $\Delta S^*$ and $\Delta V^*$ do not prove that a reaction is associative. Solvent reorganization can lead to unexpected entropy changes and contribute to overall volume changes. However, large negative values, such as those in Table 13.1, are generally accepted as indicating an associative mechanism. See Inorganic High Pressure Chemistry, Kinetics and Mechanisms; van Eldik, R., Ed.; Elsevier: Amsterdam, 1986; van Eldik, R.; Asano, T.; Lehnke, W. J. Chem. Rev. 1989, 89, 295-608.
In addition to the neutral complexes, it is possible to add one, two, or three electrons to form reduced species of the type \([\text{M(S}_2\text{C}_2\text{R}_2)_3]^-\). Present evidence is that the reduced species tend to retain the trigonal prismatic coordination with some distortion towards a regular octahedron with increasing addition of electrons (see Table 12.4).

One of the most interesting features of the 1,2-ethenedithiolate or 1,2-dithiolene complexes is the short distance between the two sulfur atoms within a chelate ring. This distance is remarkably constant at about 305 pm, some 60 pm less than the sum of the van der Waals radii (Table 8.1), indicating the strong possibility of some S—S bonding that may stabilize the trigonal structure. One way in which this might come about is by pulling the sulfur atoms towards each other, reducing the bite angle (it is about 81° in the complex in Fig. 12.17). Perfect octahedral coordination requires 90°. Another way to look at it is to imagine the molecule in Fig. 12.17 undergoing a 60° twist of one of the \(S_3\) triangles to form an octahedron. If the other dimensions remain the same, the sulfur atoms would have to move away from each other, and this would be inhibited if there is any S—S bonding.

There are few trigonal prismatic complexes with unidentate ligands, but both \([\text{Zr(CH}_3)_6]^{2-}\) and \([\text{W(CH}_3)_6]^{2-}\) have \(D_3h\) symmetry, as shown in the margin. \(^{36}\) The factors favoring \(O_h\) symmetry and inhibiting trigonal distortion are not difficult to see: steric effects of bulky ligands, large partial charges on the six ligands, and relatively small metal size. To be sure, these are absent in these hexamethyl compounds and in the hypothetical \(\text{CrH}_6\) studied by ab initio calculations. \(^{37}\) The factors favoring \(D_3d\) symmetry are more subtle: for example, the relative stabilization of formally nonbonding orbitals similar to that in the MO analysis of \(\text{BeH}_2\) and \(\text{H}_2\text{O}\) in Chapter 5. \(^{37}\)

<table>
<thead>
<tr>
<th>Table 12.4</th>
<th>Map of twist angles [θ] in (dithiolato)metal complexes, ([\text{ML}_3]^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group VII (4)</td>
<td>Group VII (5)</td>
</tr>
<tr>
<td>ZrL(_3)(^{-}) (θ = 19.6°)</td>
<td>NbL(_3)(^{-}) (θ = 0.6°)</td>
</tr>
<tr>
<td>VIL(_3) (θ = 0°)</td>
<td>TaL(_3) (θ = 10°)</td>
</tr>
</tbody>
</table>

\(^{*}\) Trigonal prism, \(θ = 0°\); octahedron, \(θ = 60°\)

\(^{35}\) For reviews of complexes containing these ligands, see references in Footnote 29.


The Rate Law for Nucleophilic Substitution in a Square Planar Complex

A step in elucidating a mechanism for a reaction is to determine the rate law experimentally. The reaction of interest here may be represented as

\[ T \rightarrow M - X + Y \rightarrow T \rightarrow M - Y + X \] (13.9)

in which \( Y \) is the entering nucleophilic ligand, \( X \) is the leaving ligand, and \( T \) is the ligand trans to \( X \). Kineticists try to simplify their experiments as much as possible, and one way to do that in this case is to run the reaction under pseudo first-order conditions. Practically, this means that the concentration of \( Y \) is made large compared to that of the starting complex so that changes in \([Y]\) will be insignificant during the course of the reaction \([Y] = \text{constant}\). For reactions in which reverse processes are insignificant, the observed pseudo first-order rate law for square planar substitution is:

\[
\text{rate} = -\frac{d[ML_2TX]}{dt} = k_1[ML_2TX] + k_2[ML_2TX][Y] (13.10)
\]

This expression may be rearranged to give:

\[
\text{rate} = (k_1 + k_2[Y])[ML_2TX] = k_{obs}[ML_2TX] (13.11)
\]

and

\[
k_{\text{obs}} = k_1 + k_2[Y] (13.12)
\]

From Eq. 13.12 we can see that by repeating the reaction at various concentrations of \( Y \), we can obtain both \( k_1 \) and \( k_2 \) because a plot of \( k_{\text{obs}} \) against \([Y]\) will give a straight line with \( k_1 \) as the intercept and \( k_2 \) as the slope (Fig. 13.1). What does the rate law tell us about the nature of the reaction? Substitution reactions in inorganic chemistry have been divided into four classes based on the relative importance of bond making and bond breaking in the rate-determining step:

1. **Associative, A.** The \( M - Y \) bond is fully formed before \( M - X \) begins to break.
2. **Interchange associative, I_{\text{a}}.** The \( M - X \) bond begins to break before the \( M - Y \) bond is fully formed, but bond making is more important than bond breaking.
3. **Dissociative, D.** The \( M - X \) bond is fully broken before the \( M - Y \) bond begins to form.
4. **Interchange dissociative, I_{\text{d}}.** The \( M - Y \) bond begins to form before the \( M - X \) bond is fully broken, but bond breaking is more important than bond making.

Nonzero values for both \( k_1 \) and \( k_2 \) in Eqs. 13.10-13.12 indicate that \( ML_2TX \) is reacting by two different pathways. The \( k_1 \) term, first order with respect to both complex and \( Y \), indicates an associative pathway, \( A \), similar to the \( S_{\text{N}}2 \) reaction of organic chemistry. The term arises from the nucleophilic attack of \( ML_2TX \) by \( Y \). As

Fig. 13.1 Rate constants \((k_{\text{obs}}, \text{s}^{-1})\) as a function of nucleophile concentration \([Y]\) for reaction of \( \text{Pt(py)}_2\text{Cl}_2 \) with various nucleophiles in methanol at 30 °C. [Pura Belluco, U.; Cataldi, L.; Bartoli, F.; Pencan, R. G.; Turco, A. J. Am. Chem. Soc. 1965, 87, 241-246. Used with permission.]
Optical Isomerism in Octahedral Complexes

It was mentioned above that tris[chelate] complexes of the type $[\text{Co(en)}_3]^3+$ lack an improper axis of rotation. As a result, such complexes can exist in either of two enantiomeric forms (or a racemic mixture of the two). Figure 12.20 illustrates the complex ions ($\text{Co(en)}_3)^3+$ and ($\text{Cr}(\text{ox})_3)^3+$, each of which is chiral with $D_3$ symmetry. It is not necessary to have three chelate rings present. The cation dichloro-bis(ethylenediamine)cobalt(III) exists as two geometric isomers, cis and trans. The trans isomer has approximate $D_3a$ symmetry (Fig. 12.21b). Because it has three internal mirror planes, it is achiral. 40 The cis isomer has $C_2$ symmetry and is chiral (Fig. 12.21a). Since the two chloride ions replace two nitrogen atoms from an ethylenediamine ring without disturbing the remaining geometry, the optical activity is preserved. 41 For purposes of dissymmetry, the change of two nitrogen atoms to two chlorides is insignificant. Further replacement of chelate rings by paired univalent ligands can take place as in cis-cis-cis-$[\text{Co}(\text{H}_2\text{O})_3\text{Cl}_2]^2+$, which is chiral, 42 but in ordinary practice the resolution of enantiomers is limited to complexes containing chelate rings. The chelate rings provide the complex with additional stability (see "The Chelate Effect," page 522). In addition, the nonchelate complexes are difficult to synthesize, and it is also difficult to separate the large number of geometric isomers.

Werner synthesized and resolved optical isomers as strong corroborative evidence for his theory of octahedral coordination. Although he did not discuss the subject in his first paper, the idea appears to have come to him about four or five years later, 43 and he was able to resolve amminechlorobis(ethylenediamine)cobalt(III) cation (cf. Fig. 12.21 with one chloro group replaced by ammonia) about fourteen years after he first became interested in this aspect. 44 Werner realized that the presence of enantiomers in the cis but not the trans compound was incompatible with alternative formulations of these complexes. He succeeded in resolving a large series of complexes including Co(III), Cr(III), Fe(II), and Rh(III) as metal ions, and ethylenediamine, oxalate, and bipyridine as chelating ligands. Nevertheless, a few of his critics pointed out that all his ligands contained carbon. By associating optical activity somehow with "organic" versus "inorganic" compounds and ignoring all symmetry arguments, they proceeded to discount his results. In order to silence these specious arguments, Werner synthesized and resolved a polynuclear complex containing no carbon atoms, tris[triammine-$\mu$-dihydroxocobalt(III)]cobalt(III) (Fig. 12.22). 45 This

40 These are also sometimes called cis-trans isomers, but the former nomenclature is unwieldy. However, the IUPAC recommendations are moving away from the use of terms like facial and meridional.

41 This assumes that the ethylenediamine-metal rings are strictly planar, which they are not. We shall see that these rings are skewed. However, since the two skew forms interconvert rapidly, for purposes of optical activity, the compound behaves as though it were achiral.


Complexes with $d^9$ electronic configurations usually are four-coordinate and have square planar geometries (see Chapter 12). These include complexes of Pt(II), Pd(II), Ni(II) (also sometimes called tetrahedral, often octahedral), Fe(II), Rh(II), Co(II), and Au(I). Among the $d^9$ losses, Pt(II) was a particular favorite of early kineticians. Complexes of Pt(II) have been attractive for rate studies because they are stable, relatively easy to synthesize, and undergo ligand exchange reactions at rates that are slow enough to allow easy monitoring. Reaction rate ratios for Pt(II):Pd(II):Ni(II) are approximately $10^3 : 10^7$. Furthermore, because isomerization of less stable Pt(II) precursors to thermodynamically more stable ones is a slow process, scrambling of ligands is not generally a problem.

There are several pathways by which one ligand may replace another in a square planar complex, including nucleophilic substitution, electrophilic substitution, and oxidative addition followed by reductive elimination. The first two of these are probably familiar from courses in organic chemistry. Nucleophilic addition and reductive elimination reactions will be covered in detail in Chapter 15. All three of these classes have been effectively illustrated by Cross for reactions of PtMeCl(PMe$_2$Ph)$_2$:

$$\text{PtMeCl(PMe$_2$Ph)$_2$} + \text{MeCl} \rightarrow \text{PtMeCl(PMe$_2$Ph)$_2$} + \text{Cl}^- \quad (13.4)$$

$$\begin{align*}
\text{PtCl}_2(P\text{Me$_2$Ph})_2 &= \text{MeHgCl} \\
\text{PdCl}_2(P\text{Me$_2$Ph})_2 &= \text{MeHgCl} \\
\text{NiCl}_2(P\text{Me$_2$Ph})_2 &= \text{MeHgCl}
\end{align*} \quad (13.5)$$

$$\text{PdMeCl}\text{PMe$_2$Ph)$_2$} \rightarrow \text{PdMeClPMe$_2$Ph)$_2$} + \text{MeCl} \quad (13.6)$$

The reaction in Eq. 13.5 can be thought of as an electrophilic attack by HgI$_2$ on the platinum-carbon bond. The oxidative addition reaction shows oxidation of Pt(II) to Pt(IV) with simultaneous expansion of the coordination number of Pt from 4 to 6.

For the remainder of this section on square planar substitution reactions, we will confine our attention to those proceeding by a nucleophilic path. We turn now to consideration of the mechanistic details of these reactions.


Elimination of methyl chloride returns the oxidation state to +2 and the coordination number to 4 with a net substitution of chloride for methoxide.

Much of what is currently known about substitution reactions of square planar complexes came from a large number of careful studies executed in the 1960s and 1970s. You should not conclude, however, that details of the mechanisms of these reactions are of historical interest only. Work in this area continues unabated as studies focus on elucidation of specific mechanistic details, biological effects, and homogeneous catalysis. For example, the mechanism for the Wacker process (Chapter 15), which utilizes square planar PtCl$_2$F$_2$ as a homogeneous catalyst for the industrial conversion of ethylene to acetaldehyde, is still a subject of investigation. The overall reaction for the process is:

$$\text{CH}_2=\text{CH}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CHO} \quad (13.7)$$

Knowledge of the mechanism may suggest changes in reaction conditions (solvent, temperature, pressure, etc.) that could improve the efficiency of the overall process. As another example, early studies of the hydrolysis of cis-[Pt(NH$_3$)$_2$Cl$_2$] are still of interest because of the ability of this complex to inhibit the growth of malignant tumors (Chapter 19). The biological activity of this compound is believed to involve coordination of DNA to the Pt, and the details of this interaction are under intense investigation. However, it is generally agreed that prior to DNA complexation, chloro groups of Pt(NH$_3$)$_2$Cl$_2$ are reversibly replaced by water, thereby assisting in the transfer of the drug from the blood to the tumor cells, where the water or chloride ligands can be displaced by donor groups of DNA.

$$\text{Cl}^- + \text{NH}_3 \rightarrow \text{Cl}^- + \text{H}_2\text{O}$$

For the remainder of this section on square planar substitution reactions, we will confine our attention to those proceeding by a nucleophilic path. We turn now to consideration of the mechanistic details of these reactions.

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Resolution of Optically Active Complexes

Few inorganic chemists have been as lucky as Pasteur in having their optically active compounds crystalize as recognizable, hemi-crystals of the two enantiomers which may be separated by visual inspection. Various chemical methods have been devised to effect the resolution of coordination compounds. They all involve interaction of the enantiomeric pair of the racemic mixture with some other chiral species. For optically active cations, interaction with one enantiomer of a chiral tertiary amine or camphor-sulfonic acid, or one enantiomer of a metal complex anion will result in differentially soluble diastereomers, the shifting of equilibria in solution, or various other changes in physical properties that allow the separation to be effected. For the resolution of an anion, chiral bases such as strychnine or brucine (protonated to form cations) may be used. Neutral complexes present difficulties since it is generally impossible to form salts. Differential physical properties toward dissymmetric substrates may be employed such as preferential extraction into a dissymmetric solvent or preferential adsorption chromatographically upon quartz, sugar (both consisting of a chiral substrate), or other chiral substrate.

Fig. 12.23 One enantiomer of the cis-dihydroxo(dithionite)(III) rhodium(III) salt

The determination of the absolute spatial relationship (the chirality or "handedness") of the atoms in a dissymmetric coordination compound is a problem that has intrigued inorganic chemists from the days of Werner. The latter had noted none of the physical methods now available for such determinations. Note that it is not possible to assign the absolute configuration simply on the basis of the direction of rotation of the plane of polarized light, although we shall see that, through analysis of the rotatory properties of enantiomers, strong clues can be provided as to the configuration.

Before discussing the methods of experimentally determining absolute configurations, let us briefly discuss means of denoting such configurations. As was the case in organic chemistry, these rules grew up before much was known about the absolute configurations, so they leave much to be desired in terms of logical interrelationships. The simplest method, already mentioned, is notation of the experimen-tal direction of rotation of polarized light (d or l), or of (+) or (-). Thus one may speak of (+)-[Co(en)₃]³⁺, which is dextrorotatory with respect to light of wavelength equal to 589 nm. This label identifies enantiomers with respect to each other, but serves little purpose otherwise, although we shall see that by using certain techniques and assumptions, strong clues can be provided with regard to configuration.

Next, as in Emil Fischer's system for D-glyceraldehyde and sugars, we can arbitrarily assign the D configuration to (+)-[Co(en)₃]³⁺ and compare all known configurations with it. This now immediately tells us the configuration of a d-isomer (by comparing it with a figure of D-[Co(en)₃]³⁺), but the d symbol is an arbitrary one that could have as readily been xz or www. Furthermore, it can even seduce the unwary into thinking that a has something to do with being "dextrorotatory" or having "right-handedness."

A systematic basis can be gained by viewing a tri(chelate) complex, the most common species of chiral coordination compounds, down the threefold rotation axis. If the helix thus viewed is right-handed, the isomer is the A-isomer, and its mirror image is the B-isomer. The A, B, D, and L and A-isomers may be thus portrayed as shown in the margin. Note that it is a result of these systems that A ≠ L and A ≠ D, furthering possible confusion.

In ordinary X-ray diffraction work both enantiomers give exactly the same diffraction pattern, and thus this method gives no information on the absolute configuration about the metal atom. However, absolute configurations of coordination compounds can be directly determined by means of the anomalous dispersion of X rays, called Bijvoet analysis. The method has not been widely applied, but as is the related problem in organic chemistry of the absolute configuration of d-glyceraldehyde, once one absolute configuration is known, there are methods to correlate others. The absolute configuration of d-[Co(en)₃]³⁺ has been determined as the chloride and bromo-

47 Although, some relatively simple chiral complexes such as cis-bis(hydroxamato)dithionite-cobalt(III) salt exhibit this behavior. Some of these were prepared by Werner and were, unknown to him, resolving themselves spontaneously as he recrystallized them. This occurred at the very time that he was spending 14 years pursuing the resolution of enantiomeric complexes. Sec Bernal, L. Kaufman, G. B. J. Chem. Educ. 1987, 64, 904-918.
Chapter 13

Coordination Chemistry:
Reactions, Kinetics,
and Mechanisms

Despite extensive study, inorganic chemistry has yet to achieve the understanding of reaction mechanisms enjoyed by organic chemistry. This situation, to which we alluded previously in Chapter 6, can be attributed to the inherent difficulties involved in trying to systematize the reactions of more than one hundred elements. Even attempts to predict from one element to another in the same group are not always successful. The classical synthetic schemes developed for the hexaaaminecobalt(III) and hexaaaminorhodium(III) cations illustrate this lack of generality. The preparation of the cobalt complex involves a combination of ligand displacement and redox chemistry. To the starting material, a stable and common cobalt(II) salt (such as the nitrate or chloride), the desired ligand (ammonia) is added in high concentrations to displace two chloride ligands (13.1). An oxidizing agent (air or hydrogen peroxide with a charcoal catalyst) is used to effect the change in oxidation state:

\[ \text{[CoCl}_4]^{2-} + 2\text{NH}_3 \rightarrow \text{[Co(NH}_3)_6]^{2+} + 4\text{Cl}^- \]  

Simple rhodium(III) salts, unlike their cobalt counterparts, are stable in water. Thus the hexaaaminorhodium(III) cation can be prepared from reactions that are already in the +3 oxidation state:

\[ \text{RhCl}_3 + \text{H}_2\text{O} \rightarrow \text{[Rh(NH}_3)_6]^{3+} \]  

Because forcing conditions are required in order to remove the last chloro ligand from rhodium and displace it with \( \text{NH}_3 \), the reaction is often carried out in a sealed tube at elevated temperature and pressure.

The hexaaamine preparations described above were both devised in the 19th century, long before reaction mechanisms were investigated. Mechanistic insight acquired in the latter half of the 20th century has led to the development of more systematic syntheses for many complexes of cobalt and rhodium. For example, the hexaaamine complexes may be readily prepared by simple substitution of \( \text{NH}_3 \) for the \( \text{CF}_3\text{SO}_4^- \) (trifluoromethanesulfonate or triflate) ligand in [M(NH_3)6OSO_3CF_3]^2-(M = Co, Rh), a starting material that can easily be obtained from the pentaaamine chloro complex.1

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Fig. 12.25 The Cotton effect: (a) positive Cotton effect; (b) negative Cotton effect. The absorption band is not shown; it would be a positive Gaussian curve centered on $\lambda_{max}$, but off scale. The dashed line represents the ORD curve (and relates to the refractive index scale on left). The solid line represents the CD curve ($e_d - e_l$, scale on right). The maximum absorption, zero values of ORD, and maxima and minima of CD values occur at $\lambda_{max}$. The two figures, (a) and (b), represent two enantiomers. These are ideal curves for an absorption peak well separated from other absorptions. [Modified from Gillard, R. D. Prog. Inorg. Chem. 1966, 7, 215-276. Reproduced with permission.]

Although ORD was used extensively at one time because of simpler instrumentation, circular dichroism is currently much more useful. The CD effect arises because there is differential absorption of left and right circularly polarized light associated with transitions such as $1 \epsilon \rightarrow 1 \epsilon$ and $1 \alpha \rightarrow 1 \beta$. The circular dichroism is the difference between the molar absorptivities of the left and right polarized light, $e_d - e_l$ (solid curves in Fig. 12.25).\textsuperscript{34} Complexes having the same sign of CD for a given absorption band will have the same absolute configuration.

Some typical values are listed in Table 12.5.

### Table 12.5

<table>
<thead>
<tr>
<th>Formula of complex\textsuperscript{b}</th>
<th>$v$ (cm$^{-1}$)</th>
<th>$e_d - e_l$</th>
<th>Absolute configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>(+)$_{3}$[Co(III)en$_3$$]^3+\textsuperscript{c}\textsuperscript{a}$</td>
<td>20,280</td>
<td>2.18</td>
<td>A</td>
</tr>
<tr>
<td>(−)$_{3}$[Co(III)en$_3$$]^3+\textsuperscript{c}\textsuperscript{a}$</td>
<td>23,310</td>
<td>−0.20</td>
<td>A</td>
</tr>
<tr>
<td>(+)$_{3}$[Co(S-$\text{ala}$)$_3$$]^3+\textsuperscript{c}\textsuperscript{a}$</td>
<td>20,280</td>
<td>1.95</td>
<td>A</td>
</tr>
<tr>
<td>(−)$_{3}$[Co(S-$\text{ala}$)$_3$$]^3+\textsuperscript{c}\textsuperscript{a}$</td>
<td>22,780</td>
<td>−0.58</td>
<td>A</td>
</tr>
<tr>
<td>(+)$_{3}$[Co(S-$\text{glu}$)$_3$$]^3+\textsuperscript{c}\textsuperscript{a}$</td>
<td>21,000</td>
<td>2.47</td>
<td>A</td>
</tr>
<tr>
<td>(+)$_{3}$[Co(S-$\text{ala}$)$_3$$]^3+\textsuperscript{c}\textsuperscript{a}$</td>
<td>18,500</td>
<td>1.3</td>
<td>A</td>
</tr>
<tr>
<td>(−)$_{3}$[Co(S-$\text{ala}$)$_3$$]^3+\textsuperscript{c}\textsuperscript{a}$</td>
<td>21,600</td>
<td>−0.2</td>
<td>A</td>
</tr>
<tr>
<td>(+)$_{3}$[Co(S-$\text{glu}$)$_3$$]^3+\textsuperscript{c}\textsuperscript{a}$</td>
<td>19,600</td>
<td>2.5</td>
<td>A</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Saito, Y. Inorganic Molecular Dissymmetry; Springer-Verlag: Berlin, 1979, p 136. Note that the tris(ala) complex has a different chromophore (CoN$_6$O$_4$) than the tris(diamine) complexes (CoN$_6$), and so the resemblance is only approximate.

\textsuperscript{b} en = ethylenediamine; pn = propylenediamine; ala = alaninate; glu = glutamate.

\textsuperscript{c} Since in each case the A isomer will have the same value with opposite sign for its specific rotation, the same value for the absorption maximum, and the same value(s) with opposite sign for the circular dichroism compared to the A isomer, these values are not all listed here.

In addition to the dissymmetry generated by the tris(chelate) structure of octahedral complexes, it is possible to have dissymmetry in the ligand as well. For example, the gauche conformation of ethylenediamine is dissymmetric (Fig. 12.27) and could be resolved were it not for the almost complete absence of an energy barrier preventing

\textsuperscript{34} Sometimes the value of $e_d - e_l$ is given as $\Delta e$. If $\Delta e$ is positive ($e_d > e_l$), it is called a positive Cotton effect, etc.
12.25 It is well and good to say that macrocyclic polyethers "stabilize metals, such as sodium, that might otherwise react ..., to form [Dinuclear complex]"* but specifically, in terms of a Born-Haber cycle, what part does the macrocyclic ligand play in the reaction described on page 526?

12.26 Assuming that Pullin was at least a reasonably careful worker, how was it possible for him to get "identical" spectra from solutions of the nitro and nitrito isomers discussed on page 533?

12.27 Read the section on point groups in Chapter 3 again and identify the symmetry elements and operations in the molecules and ions shown in the figures listed below. Determine the appropriate point group for each molecule and ion.

a. 12.1e b. 12.10 c. 12.25a, b d. 12.39
b. 12.2a

c. 12.4 d. 13.18a, b e. 12.22 f. 12.40

c. 12.4 d. 13.18a, b e. 12.22 f. 12.40

d. 12.5a, b

12.28 Occasionally, in the preparation of the artwork for a research article or a textbook, the photographic negative taken from the original line drawing of the artist is inverted "upside-down" (or reverse, front-to-back) and the resulting image is reversed. Does this make any difference? Discuss. Are there any exceptions to the general rule? Illustrate your argument with sketches.

12.29 Consider the shapes (i.e., bond angles $\theta$, and bond lengths $d$) of T-shaped ($\theta > \theta_t = d_t$) and Y-shaped ($\theta < \theta_t = d_t$) molecules (Fig. 12.1d).

a. What causes these molecules to be T-shaped or Y-shaped rather than equivalent?

b. For one of these shapes, $d > d_t = d_t$; for the other, $d < d_t = d_t$. Which is which?

c. What is the point group symmetry of these molecules?

12.30 The circular dichroism spectral data for the dextrorotatory enantiomer of tris(2,2'-diaminocyclohexane)cobalt(III) cation, $(+\text{Co(R,R-chxn)}$,$^2$+, can be solved to give a spectrum $(\pm \text{Co(R,R-chxn)}$,$^2$+, if listed in Table 12.5, would appear as follows:

<table>
<thead>
<tr>
<th>$\nu$ (cm$^{-1}$)</th>
<th>$\epsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20,000</td>
<td>2.28</td>
</tr>
<tr>
<td>22,500</td>
<td>0.69</td>
</tr>
</tbody>
</table>

Assign the correct $A$ or $\bar{A}$ configuration to the metal. Do you get the same answer as in Problem 12.31? Discuss.

12.31 The X-ray crystal structure of the dextrorotatory enantiomer of tris(2,2'-diaminocyclohexane)cobalt(III) cation, $(+\text{Co(R,R-chxn)}$,$^2$+, may be solved to give Fig. 12.53 as one of the two possible enantiomeric solutions.

a. Is Fig. 12.53 a $\bar{A}$ or an $A$ enantiomer?

b. Does $(+\text{Co(R,R-chxn)}$,$^2$+ have a $\bar{A}$ or $A$ configuration about the metal? Is your answer the same as in Problem 12.30? Explain.

c. Is the lattice $\bar{R}$ or $R$?

d. Are the chelate rings $\bar{R}$ or $R$?

12.32 If either pure A or pure B from Equation 12.4 is heated at 75 °C in dimethylformamide, the isomers interconvert until there is a mixture of 40% A and 60% B. Why is this not a 50-50 mixture? Is this a racemization?

12.33 Which of the following is the most likely structure for pentacyanocobalt(III)-$\mu$-cyanopentamethinecobalt(III) cation: $(\pm\text{Co[R,R-chxn]}$,$^2$+ or $(\pm\text{Co[R,R-chxn]}$,$^2$+?

12.34 Metallothionein is found in humans and other animals. It appears to remove toxic cadmium ion from the kidneys. This protein has 27 sulfhydryl groups and can function as a protective chelating agent. Each metal ion is thought to be bound to three sulfhydryl groups. Show the probable geometry around the cadmium ion when bound to this chelating agent.

12.35 Urea ligands usually bond through the oxygen atom, although there are two potential nitrogen donor atoms available as well. Recently unambiguously behavior of a substituted urea has been demonstrated. Pyridylmethylurea forms $N,N'$-bident chelate platform complexes with $\text{Ni}^{2+}$ and $\text{Cu}^{2+}$ (Fig. 12.53a) but $N,O$-bidentate complexes with $\text{Zn}^{2+}$ (Fig. 12.54d).

a. Suggest a reason for this behavior.

b. If you did not have the X-ray crystal structure, what other experimental evidence might you use to differentiate between $O$-bonding and $N$-bonding in ureas? (Hint: Compare the analogous problem with proton-binding sites. Chapter 9.)

c. What might you use to differentiate between $O$-bonding and $N$-bonding in ureas? (Hint: Compare the analogous problem with proton-binding sites. Chapter 9.)

12.36 Twelve-coordination is certainly rare, as discussed on pages 510-511, yet there is another discrete complex discussed in this chapter with $C_N=12$, though not so identified. Can you find it?

12.37 Which of the following is the most likely structure for pentacyanocobalt(III)-$\mu$-cyanopentamethinecobalt(III) cation: $(\pm\text{Co[R,R-chxn]}$,$^2$+ or $(\pm\text{Co[R,R-chxn]}$,$^2$+?

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12.36 Twelve-coordination is certainly rare, as discussed on pages 510-511, yet there is another discrete complex discussed in this chapter with $C_N=12$, though not so identified. Can you find it?
racediation. Attachment of the chelate ligand to a metal retains the chirality of the
gaucho form, but the two enantiomers can still interconvert through a planar con-
formation at a very low energy, similar to the interconversions of organic rings
systems. Thus, although it is possible in principle to describe two enantiomers of a complex
such as [Co(NH₃)₆]³⁺, in practice it proves to be impossible to isolate them
because of the rapid interconversion of the ring conformers.⁵⁷

If two or more rings are present in one complex, they can interact with each other
and certain conformations might be expected to be stabilized as a result of possible
reductions in interatomic repulsions. For example, consider a square planar complex
containing two chelated rings of ethylenediamine. From a purely statistical point of
view we might expect to find three structures, which may be formulated M₆₆, M₆₈, and
M₈₆ (which is identical to M₈₈). The first two molecules lack a plane of symmetry,
but M₈₆ is a mono form. Corey and Bailar⁵⁸ were the first to show that the M₆₈
and M₆₆ should predominate over the mono form since the latter has unfavorable
H—H interactions of the axial-axial and equatorial-equatorial type between the two
rings (Fig. 12.26). The enantiomeric M₆₆ and M₆₆ forms are expected to be about 4 kJ
mol⁻¹ more stable than the meso isomer, other factors being equal.

More important consequences result for octahedral tris(chelate) complexes.
Again, from purely statistical arguments, we might expect to find M₆₈₈, M₆₈₆, M₈₆₆,
and M₈₈₈ forms. In addition, these will all be optically active from the tris(chelate)
structure as well, so there are expected to be eight distinct isomers formed. In general,
a much smaller number is found, usually only two. This stereoselectivity is most easily
followed by using a chiral ligand such as propylenediamine, CH₃(CH₂)⁺CH₂NH₂.

The five-membered chelate ring will give rise to two types of substituent positions,
propensity, /β(-)-propylenediamine bonds preferentially as a A chelate and
those that are essentially axial and those that are essentially equatorial. All substi-
tuents followed by using a chiral ligand such as propylenediamine, CH₃(CH₂)
(NH₂)₂CH(NH₂)₂.) are much smaller is found, usually only two. This stereoselectivity is most easily
followed by using a chiral ligand such as propylenediamine, CH₃(CH₂)
(NH₂)₂CH(NH₂)₂.

The difference in stability between the various isomers has been related to
preferred packing arrangements of chelate rings about the central metal atom. Thus,
for S-propylenediamine forming a 5 chelate ring, the most efficient method of fitting
around a metal will be in the form of a left-handed helix. This arrangement minimizes
the various repulsions. It has been termed the heli isomer since the C—C bonds are
parallel to the threefold axis of the complex (Fig. 12.29). The alternative isomer, in
which the ligands form a right-handed helix about the metal, is known as the ab isomer
since the C—C bonds are obtuse to the threefold axis (Fig. 12.30).⁵⁹

⁵⁷ Note that in this case the chirality is not due to the arrangement about the metal atom, but results
from the S or A chirality of the ethylenediamine-metal ring. See Shimura, Y. Bull. Chem. Soc.
(Japan) 1959, 32, 371.

⁵⁸ Corey, E. J.; Bailar, J. C., Jr. J. Am. Chem. Soc. 1959, 81, 2620–2629. This is the classic paper in
the field upon which all of the subsequent work has been based. See also Suizu, Y. "Molecular

⁵⁹ Specifically since there are three chelate rings, each of which can potentially be either hel or ab,
these two isomers should be labeled as hel, and only since it is possible to have mixed hel-hel complex.

Fig. 12.27 Enantiomeric conformations of gauche ethylenediamine (L-2-
chelate); Note that S represents a right-handed helix and A a left-handed helix.

Fig. 12.28 Conformational interactions in bis(chelate) square planar complexes: (a) AA form; (b) AB form. All hydrogen atoms except four have been omitted for greater clarity. Dashed
lines represent inter-ring H—H repulsions. [Modified from Corey, E. J.; Bailar, J. C., Jr.
J. Am. Chem. Soc. 1959, 81, 2620-2629. Reproduced with permission.]

Δ-M₆₆₈₈ (= l-M₆₆₈₈) where Δ, A, d, and L refer to the absolute configuration about
the metal related to A-(+)-Co(en)₃³⁺ (= the D enantiomer; see Fig. 12.26). In a
typical reaction such as the oxidation of cobalt(II) chloride in the presence of racemic
R,S-propylenediamine, only two isomers were isolated:

[Co(H₂O)₆]³⁺ + R-pn + S-pn ↔ Δ-[Co(S-pn)]³⁺ + Δ-[Co(R-pn)]³⁺ (12.7)

Fig. 12.29 The heli conformer of the A or d enantiomer of tri(diamine)
metal complexes. The hatched circles represent the positions of the methyl
groups in the propylene-
diamine complex. For propylene diamine, this represents the A₆₆₈ or S₆₆₈
isomer. [Modified from
Reproduced with permission.]

Fig. 12.29 The heli conformer of the A or d enantiomer of tri(diamine)
metal complexes. The hatched circles represent the positions of the methyl
groups in the propylene-
diamine complex. For propylene diamine, this represents the A₆₆₈ or S₆₆₈
isomer. [Modified from
Reproduced with permission.]

Note that in this case the chirality is not due to the arrangement about the metal atom, but results
from the S or A chirality of the ethylenediamine-metal ring. See Shimura, Y. Bull. Chem. Soc.
(Japan) 1959, 32, 371.
12.10 Draw the most likely structure of pentamminecobalt(III)-thiocyanato- pentacyano-cobalt(II).

12.11 Which of the two isomers, Co(Hdmg)$_2$(SCN)py or Co(Hdmg)$_2$(NCS)py, would you predict to be thermodynamically the most stable? Hiding represents the monoanion dimethylglyoximate, HON=C(CH$_3$)C(CH$_3$)=NO$^-$.

12.12 Draw the molecular structure of the following complexes:
   a. cis-dichlorotetracyanochromate(III)
   b. trans-dichlorotetracyanochromate(III)
   c. trans-dichlorobis(trimethylphosphine)palladium(II)
   d. trans-dinitrocobalt(III)

12.13 Why does iron(II) hexacyanoferrate(III) spontaneously isomerize to Prussian blue?

12.14 With the aid of the table of ligand abbreviations given in Appendix I find the names of each of the ligands listed below. Sketch the structure of each ligand and classify it as unidentate, bidentate, tridentate, etc. Sketch the mode of attachment of the ligand to a metal ion.
   a. acac  c. dtp  e. dien  g. dtp  i. fod  k. ox  m. phen  n. pn  p. tap  q. tn  r. trien
   b. bpy  d. chxn  f. dmf  h. edta  j. Hedta  l. pc  o. py

12.15 Arrange the following six ligands in order of increasing ability to form stable complexes and account for your order.

12.16 A recent review of steric effects in coordination compounds includes the following statements concerning stability:
   a. Tetrahedral geometry should be more stable than square planar for C.N. = 4.
   b. Octahedral geometry should be more stable than trigonal prismatic for C.N. = 6.
   c. Square antiprismatic geometry should be slightly more stable than dodecahedral, which is considerably more stable than cubic for C.N. = 8.
   Discuss these statements in terms of Table 12.1.

12.17 The macrocyclic ligand enterobactin (Fig. 19.27c) has an extraordinarily high affinity for Fe$^{3+}$ with a stability constant of $10^{53}$, the largest known stability constant for Fe$^{3+}$ with a naturally occurring substance.$^{67}$

   a. Suggest a structure for the Fe(III)-enterobactin complex that explains its high stability.
   b. If the concentration of the Fe(III)-enterobactin complex within the microorganism is $10^{-7}$ mol L$^-1$, how many liters of bacteria would have to be searched to find a single free Fe$^{3+}$ ion?

12.18 In Chapter 6 it was pointed out that X rays are diffracted by electrons. Yet on page 528 it is stated that the atomic electrons of complexed cesium electride "do not show" in the structure determination. Discuss this apparent paradox. (Hint: Why is it hard to locate hydrogen atoms in an X-ray crystallographic determination?)

12.19 A few years ago other cationic cryptates have been known for a number of years. More recently, anionic cryptates have been characterized. Suggest a structure for [CN(CH$_3$)$_2$CH$_2$CH$_2$NH$_2$][CN(CH$_3$)$_2$CH$_2$CH$_2$NH$_2$]. (See Footnote 112.)

12.20 There is a complex (C.N. = 6) with a chiral metal center illustrated in this chapter that is not so labeled. Find it and determine if the isomer shown is $A$ or $A'$.

12.21 Figure 12.52 illustrates two forms of the pentacyano-cuprate(II) ion, [Cu(NO$_3$)$_5$]$^-$. Discuss all of the types of isomerism exhibited in these ions.

12.22 The molecules shown in Fig. 12.1a, c appear to be "left-handed." Do these molecules have chirality? Explain.

12.23 If you learned the Cahn-Ingold-Prelog rules in organic chemistry, test your recall by assigning the appropriate $R$,$S$ notation to the molecule shown in Fig. 12.2. Assume that the C$_5$H$_5$ ligand is a "single atom" of mass 65 (5 x 13).


Fig. 12.52 Two forms of the [Cu(NO$_3$)$_5$]$^-$. All bond distances in angstroms. [From Klanderman, K. A.; Hamilton, W. C.; Bernal, I. Inorg. Chem. Acta 1977, 23, 117-129. Reproduced with permission.]

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Asymmetric Syntheses Catalyzed by Coordination Compounds

There has been considerable interest in the stereospecific synthesis of organic compounds using optically active coordination compounds. Chiral catalysts are sought for the production of drugs, pesticides, pheromones, and fragrances. Quite recently a significant advance was made with the discovery that asymmetric epoxidation can be achieved with manganese(III) complexes containing chiral chelating agents. One of the catalysts used is generated from manganese(II) acetate, (R,R')- or (S,S')-1,2-diamino-1,2-diphenylethane, a substituted salicylaldehyde, and lithium chloride. In the presence of this catalyst and sodium hypochlorite, alkenes are converted to epoxides:

\[ R_1, R_2, R_3 = \text{H, alkyl, aryl} \]
\[ R = \text{Ph} \]
\[ X = \text{H, OMe, Me, Cl, NO}_2 \]

Some cis substituted alkenes can be converted to chiral epoxides in greater than 90% enantiomeric excess by this process.\(^{40}\)

Hydrogenation of double bonds using a rhodium(I) catalyst (see Chapter 15) may be carried out stereospecifically using a chiral diphosphine such as "diop" or "binap" (Fig. 12.31). The chirality of the diphosphine makes the two possible transition states (leading to the two enantiomeric products) diastereomers and therefore subject to differences in equilibrium concentrations, energies of activations, and reaction rates—one enantiomeric product may thus form to the exclusion of the other. The (diop)Rh(I)-catalyzed enantioselective hydrogenation is used commercially to make S-(l)-DOPA, a drug used to treat Parkinson's disease, and aspartame [S-(l,1)-phenylalanyl-N-(l,1)-aspartic acid], an artificial sweetener. The (binap)Ru(II) catalysis may become even more useful.\(^{61}\)

Coordination Number 7

Coordination number 7 cannot be considered at all common. The relative instability of these species can be attributed to the fact that the additional energy of the seventh bond is offset by (1) increased ligand-ligand repulsion, (2) weaker bonds, and (3) generally reduced ligand field stabilization energy as a result of non-octahedral geometry. There are five geometries known: (1) a pentagonal bipyramid (Fig. 12.32), which is also found in the main-group compound IF, (Fig. 6.12); (2) a capped octahedron in which a seventh ligand has been added to a triangular face (Fig. 12.33); and (3) a capped icosahedron in which a seventh ligand has been added to a triangular face (Fig. 12.33) and (3) a

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called sodium pump necessary for the proper $\text{Na}^+$/K$^+$ ionic balance responsible for electrical gradients and potentials in muscle action.\(^{11}\)

The ultimate in encirclement of metal ions by the ligand is shown by encapsulation reactions in which the ligand forms a three-dimensional cage about the metal. The resulting cage (Fig. 12.51) is called a 

\[ \text{cryptate} \]

One class of cryptate-forming ligands are the so-called "football ligands," because the polyether bridges between the two nitrogen atoms resemble the seams of a football. Ligands of this type form exceptionally stable complexes with alkali metals and show high selectivity when the size of the "football" is adjusted to fit the desired cation.\(^{12}\)

Closely related to the football ligands are the so-called "sepolchrate ligands." One can be formed by the condensation of formaldehyde and ammonia onto the nitrogen atoms of tris(ethylenediamine)cobalt(III). This results in tris(methylene)amino caps on opposite faces of the coordination octahedron. If the synthesis utilizes one of the (A or B)-enantiomers, the chirality of the complex is retained. Furthermore, the complex may be reduced to the corresponding cobalt(II) cation and reoxidized to cobalt(III) without loss of chirality. This is particularly unusual in that, as we shall see in the following chapter, cobalt(II) complexes are quite labile in contrast to the stability of cobalt(III) complexes. Once again the extra stability of polydentate complexes is demonstrated.

In contrast, Bernal has isolated a self-resolving complex whose chirality depends only on the conformation of an acyl bridge:

![Acyl Bridge Chirality](image)

Single crystals consist of only a single enantiomer, and so in the solid state the enantiomers do not racemize despite the seeming lack of barriers to rotation of the rings (see Chapter 13). Presumably crystal-packing forces "lock in" the chirality. Immediately upon solution, the complex racemizes, indicating the fragility of the forces stabilizing it.

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\(^{12}\) Bernal, L., personal communication.
capped trigonal prism in which a seventh ligand has been added to a rectangular face (Fig. 12.34). They are of comparable stability and easily interconvertible. Therefore there are also many intermediate cases, and the situation is reminiscent of five-coordinate geometries.

In many of these complexes, the requirements of polydentate ligands favor coordination number 7. Thus it is not difficult to see the effects of five macrocyclic and coplanar nitrogen atoms in Fig. 12.32 on the resulting pentagonal bipyramidal structure. In some cases, even unfavorable interactions may be forced by the ligand geometry. For example, in one type of seven-coordinate complex, it appears as though the seventh coordination, forced by the geometry of the other six coordinating atoms, might in some cases better be considered as an "antibond" rather than a bond. This effect is seen in the series of \([\text{M(pyjtren)}]^{2+}\) complexes (M = Mn, Fe, Co, Ni, Cu, Zn; pyjtren = \([\text{C}_5\text{H}_4\text{NCH} = \text{NCH}_2\text{CH}_3\text{N}]\) in which the three imine nitrogen atoms are at the vertices of one equilateral triangle and the three pyridine nitrogen atoms are at the vertices of another.\(^\text{63}\) One could refer to this arrangement as an approximate octahedron, but since the metal ion is closer to the imine nitrogens than to the pyridine nitrogens, it is best to refer to it as a trigonal antiprism (Fig. 12.35).\(^\text{64}\)

Even that is not a perfect description because there is some trigonal distortion (rotation of opposing triangular faces tending toward a trigonal prism) in each com-

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\(\text{64}\) Note that an octahedron is a special case of trigonal antiprism in which all edges have the same length. However, in contrast to the usual choice of coordinates \((x, y, z)\) on the fourfold axes for an octahedron, the highest fold axis in a trigonal antiprism is the threefold axis which is assigned to the \(z\) axis. Note that (except for the choice of coordinates and corresponding labels) the trigonal splitting closely resembles a pseudooctahedral splitting (Chapter 11): three lower orbitals, \(a_1\) and \(e\), and \(t_2\) (in \(D_3\)) and two higher orbitals, \(e^*\) and \(t_2^*\). The effect of trigonal antiprismatic distortion on the relative energy of the \(a_1\) orbital with respect to the \(e\) and \(t_2\) orbitals will depend upon the interaction of the \(e^*\) orbital with the \(N_7\) lone pair orbital. It is shown above as lower than \(t_2\) but has been suggested that in some of these complexes it may lie between \(t_2\) and \(e^*\). As in the octahedral case, \(\pi\) bonding can be added to the \(\sigma\) only system.
differing stability constants of the \([M\text{ligand}]^+\) complexes, it is possible to form mixed metal compounds:

\[
\text{Na} + K + 18\text{-crown-6} \rightarrow [K(18\text{-crown-6})]^+ + \text{Na}^-
\]

(12.42)

As expected, all of these systems are strongly reducing and tend to decompose on exposure to air and moisture, so very careful work is necessary to study them. In a few cases, single crystals have been grown and structures determined crystallographically.\(^ {108} \) Thus crystalline \([Na\text{macrocycle}]^-\) \(Na^-\) consists approximately of closest packed, large, complex cations with sodide anions in the octahedral holes (Fig. 12.50a). The alkalide ions can be found and measured; as expected they are considerably larger than the alkali metal cations. In fact, the \(Cs^-\) anion is the largest known monatomic ion with a radius of about 310-350 pm. In one salt there is anion-anion contact giving an effective radius of 319 pm. In addition to the usual difficulties of assigning an exact radius to an ion, the ceside anion has the added property that it is not only the largest ion, but also the most polarizable.

The structure of \([Cs(18\text{-crown-6})]^-\) \(e^-\) has been determined.\(^ {109} \) Because the electrode anions are extremely poor scatterers compared to the large cesium cation (and to a lesser extent the C and O atoms of the crown ether), the structure has the odd appearance of complexed metal cations with no corresponding anions (Fig. 12.50b). However, the most likely position of the electrons can be inferred from the presence of cavities of 240-pm radius; presumably the electrons are located in these cavities.

One final example of macrocyclic complexation will be given: From the arguments presented in Chapter 9, the fluoride ion, \(F^-\), should be a strong base and nucleophile. Normally, however, it does not show these expected properties because its very basicity attracts it to its counterion so strongly that it is tie-paired in solution and not free to react. However, addition of, for example, crown-6 to a solution of potassium fluoride in benzene increases the solubility tenfold and also increases the nucleophilicity of the fluoride ion. We shall encounter this phenomenon again in Chapter 15, which covers organometallic chemistry.

Earlier we saw that chelating ligands form complexes of greater stability than those of unidentate ligands. This greater stability was attributed primarily to entropy effects but enthalpy effects are of some importance. Macrocyclic ligands are even more stable than open-chain chelating ligands. A thermodynamic comparison of 18-crown-6 complexes of \(Na^+, K^+, \) and \(Ba^{2+}\) with those of pentaglyme, \(CH_3(OCH_2CH_2)_3OCH_2\), is shown in Table 12.7. The additional stability is primarily an enthalpy effect due to preorganization of the macrocycle. This is not to say that the conformation of 18-crown-6 is the same as that found in the complex.

![Fig. 12.50](image)

Nevertheless, the energy required to rearrange the macrocyclic ligands for complex formation is less than the energy required to rearrange pentaglyme into a suitable conformation.\(^ {110} \) In addition to their direct structural relationship to biological molecules, macrocycles such as the polyethers may provide clues to the discrimination shown by biological tissues toward various ions. This selectivity provides the so-

<table>
<thead>
<tr>
<th>Table 12.7</th>
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<tr>
<td>Thermodynamic contributions to the macrocyclic effect in complexes of 18-crown-6 and pentaglyme, (CH_3(OCH_2CH_2)_3OCH_2), in methanol*</td>
</tr>
<tr>
<td></td>
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<tr>
<td>(\log K_i)</td>
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<td>(\Delta H)</td>
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<td>(\Delta S)</td>
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</table>

\* Modified from Hancock, R. D.; Martell, A. E. "Comments Inorg. Chem. 1988, 6, 237-284. Free energy and enthalpy changes are expressed in kJ mol\(^{-1}\) and \(\Delta S\) difference are expressed in J K\(^{-1}\) mol\(^{-1}\).

other six M—N bond distances (201–223 pm) are considerably shorter than the van der Waals radii (on X–Y distance less than the van der Waals sum is often the accepted criterion for bonding). In spite of constraints that would be expected to restrict the movement of N2 away from the metal, it appears that for most of these complexes, the M—N2 distance is too long to be a true bond. For Mn(II) and Co(II), the M—N2 distances are shorter than the van der Waals interactions, implying a weak bond. This is not an unexpected result for high spin Mn(II) because the a1 orbital is only half-filled. In the case of Co(II), it has been argued that the a1 and e levels have been interchanged, resulting in just one electron in the a1 orbital in this complex as well.

At the same time, the bond angles (C—N—C) at the N2 position vary from 112° (as expected for an amine ligand) in the manganese complex (where repulsion is least) up to a maximum value of 120° in the iron complex with maximum repulsions. The tertiary amine nitrogen atom (N3) corresponds to a three-ribbed umbrella that has been inverted by the wind (the handle is the lone pair directed at the metal). As the N1 and e levels fill, the repulsions increase, the metal–nitrogen distance increases, and the umbrella begins to flatten:

$$\text{C} \quad \text{N} \quad \text{C}$$

$\text{N}(7)$

Although both geometrical and optical isomerism are in principle possible in seven-coordinate complexes, no examples are known. Note, for example, that the pyrrole complexes must be optically active (see Fig. 12.35b), subject of course to kinetic stability with respect to racemization.

### Coordination Number 8

Although coordination number 8 cannot be regarded as common, the number of known compounds has increased rapidly in recent years, so that it is now exceeded only by four- and six-coordination. The factors important in this increase can be traced largely to improved three-dimensional X-ray techniques and to increased interest in the coordination chemistry of lanthanide and actinide elements (see Chapter 14).

Two factors are important in favoring eight-coordination. One is the size of the metal cation. It must be sufficiently large to accommodate eight ligands without undue crowding. Relatively few eight-coordinate complexes are known for the first transition series. The largest numbers of this type of complex are found for the lanthanides and actinides, and it is fairly common for zirconium, hafnium, niobium, tantalum, molybdenum, and tungsten. A corollary is the requirement that the ligands be relatively small and electronegative. The commonest ligating atoms are carbon, nitrogen, oxygen, and fluorine. The second factor is the oxidation state of the metal, a high formal charge raises the probability of a high coordination number. This is not unexpected for lanthanides and actinides, for their high formal charges usually lead to high coordination numbers.

The a-only ligand field splitting pattern for a trigonal antiprism (D3h) consists of three levels: the a1 (dxy, dzy, dxz), and the 2e (dx2−y2, dxy).

- - 2e (dx2−y2, dxy)
- - 1e (dxy, dxz)
- - a1 (dzy)
- - a2 (dzy)

The lone pair of the tertiary amine nitrogen atom (N3) capping the trigonal antiprism is directed at the center of a trigonal antiprismatic face and thus interacts directly with the a1 orbital.

Figure 12.36 illustrates the metal–nitrogen distances in this series of complexes. The upper trace represents the M—N2 distance. An increase in electrons in orbitals directed at any of the seven nitrogen atoms causes an increase in bond length. Specifically, in the case of the Fe2Cl9 complex, the only low spin complex in the series, there is a dramatic decrease in one distance and concomitant increase in the other. The low spin (a1) configuration maximizes electron density toward the axial nitrogen while minimizing it in the direction of the trigonal antiprismatic nitrogen atoms.

The M—N2 distances for the nickel, copper, and zinc complexes (323, 311, and 301 pm, respectively) are about 10 pm longer than the sum of the van der Waals radii (r(MV) + r(N2)), which are 315, 295, and 295 pm, respectively (see Table 8.1). The

Fig. 12.36 Effect of orbital occupancy on metal–nitrogen distances. Upper part of diagram gives the M—N2 distances (shown as solid line). The long pair of the tertiary amine nitrogen (N3) is directed at the N2 orbitals on the metal ion. The lower part of the diagram gives the M—N2 distances (shown as dotted line). The distances (shown as solid line) for nitrate nitrogen atoms. N2, are slightly shorter and thus are located just below the values (shown as dot) for pyridine nitrogen atoms. N3. Dashed line (---) represents a constant electron configuration, while the dotted line (---) represents an increasing number of electrons in a given type of orbital on the metal ion. The orbital occupancy, (a1)2(1e)2(2e)2, is given under each metal ion.
Coordination Chemistry: Structure

A combination of these techniques with physical methods such as nonaqueous electrochemistry and those showing the anomalously low ESCA binding energy and the Mössbauer chemical shift were used to characterize the \(-\mathrm{I}\) gold. Unfortunately Sir Ronald did not live to see his prediction verified: he died in an automobile accident in 1971.

In a similar manner the so-called Zintl salts composed of alkali metal cations and clusters of metals as anions (see Chapter 16) were known in liquid ammonia solution but proved to be impossible to isolate. Upon removal of the solvent they reverted to alloys. Stabilization of the cations by complexation with macrocyclic ligands allowed the isolation and determination of the structures of these compounds.

This general trait of crown ethers and cryptands (to be discussed later) to stabilize alkali metal salts has been extended to even more improbable compounds, the alkalides and electrides, which exist as complexed alkali metal cations and alkalide or electride anions. For example, we saw in Chapter 10 that alkali metals dissolve in liquid ammonia (and some amines and ethers) to give solutions of alkali electrides:

\[
M^{\mathrm{III}} + e^- \longrightarrow M^{+} \tag{12.38}
\]

However, the situation is somewhat more complicated than Eq. 12.38 would indicate, because the electrons can react further with the metal to form alkalide ions:

\[
M + e^- \longrightarrow M^- \tag{12.39}
\]

Thus, in general, there are alkali metal cations, alkalide anions, and electride anions (and perhaps other minor species) in an equilibrium mixture dictated by various energetic factors. Note, for example, that because of the excellent solvating of the electride ion by liquid ammonia, the alkalide ions are not favored in these solutions, and they are somewhat atypical. By using methylamine and other solvents, even adding solvents of low polarity such as \(\text{CH}_2\text{Cl}_2\), the equilibria can be shifted and crystals sometimes grown. The affinity of alkali metal ions for crown ethers and cryptands causes cationic complexes to form readily in solution. (See Eq. 12.37 above.) This, too, will affect the equilibrium, with Eq. 12.38 being shifted to the right and, therefore, Eq. 12.39 being shifted to the left, by the addition of non-solvents. A rough generalization can be made that excess ligand will favor the formation of the electride much as all of the metal may be complexed as the cation.

\[
\text{Cs} + \text{excess 18-crown-6} \longrightarrow [\text{Cs}(18\text{-crown-6})^+] + e^- \tag{12.40}
\]

On the other hand, a mole ratio of 2:1, metal:crown, tends to favor the alkalide:

\[
2\text{Na} + 18\text{-crown-6} \longrightarrow [\text{Na}(18\text{-crown-6})^+] + \text{Na}^+ \tag{12.41}
\]

Aside from the effects of ligand stoichiometry and the nature of the solvent, there are also differences in stability of the alkalide ions. The sodide anion is the most stable, and the ceside ion the least. Because of differential stabilities of the alkalide ions and the ceside ion the least. Because of differential stabilities of the alkalide ions and

\[
d^2 \text{Nil*, or more simply as Na*. so also }
\]

\[
\text{water Na(H}^+\text{) as in liquid ammonia the solvation may be indicated by the subscript "am", e.g., or omitted altogether.}
\]

\[
2\text{Na} + \text{excess 18-crown-6} \longrightarrow [\text{Na}(18\text{-crown-6})^+] + \text{Na}^+ \tag{12.41}
\]

The Chelate Effect 527

For a shorter, more recent review, see Dye, J. L. Inorg. Chem. 1985, 24, 2727-441. For an extensive review of this chemistry, see Dye, J. L. Acc. Chem. Res. 1981, 14, 2727-441.
Coordination Chemistry: Structure

oxidation state favoring eight-coordination. This requirement arises out of the electroneutrality principle. The formation of eight dative bonds to a metal in a low oxidation state would result in excess electron density on the metal. The common oxidation states are thus $\pm 3$ or greater, resulting in electron configurations with few remaining $d$ electrons such as $d^0$, $d^1$, $d^2$.

There are several coordination polyhedra available for eight-coordination. The most regular, the cube, is almost never found in discrete complexes but occurs in lattices such as CsCl. The two common structures are the trigonal dodecahedron (Fig. 12.37a) and the square antiprism (Fig. 12.37b). Both may be considered to be distortions of the simple cube resulting in reduced ligand-ligand repulsions. The square antiprism has slightly less ligand-ligand repulsion than the dodecahedron. Other geometries are known, but these two are the most important.

From a valence bond point of view, the formation of both the dodecahedron and the square antiprism can arise from $sp^d$ hybridization. The necessity of using four $d$

Fig. 12.37 Distortions of the cube to form: (a) the trigonal dodecahedron; (b) the square antiprism. Note the similarity of the dodecahedron, viewed down the puckered CDHG face (C2 axis) and the antiprism, viewed down the ABCD face (5*-axis). [From Lippard, S. J. Prog. Inorg. Chem. 1968, 6, 109-193. Reproduced with permission.]

The picture of the formation of, for example, $[\text{Mn(CN)}_6]^{3-}$, as a combination of Mn$^2+$($d^7$) + $3\text{CN}^-$ has little physical meaning and is merely a bookkeeping device, but hardly more so than Ca$^{2+}$ + $6\text{NH}_3$, discussed extensively earlier.

There appears to be at least one exception to the general rule: $[\text{Et}_4\text{N}]_4[\text{U(NCS)}_4]_2$ has cubic anions in the solid, but the structure is not triclinic (Countryman, R. J.; McDonald, R. S. J. Inorg. Nucl. Chem. 1971, 33, 2713-2720). Note that the cube is a special case of the square prism, and like the trigonal prism with respect to the octahedron, the ligand-ligand interactions are greater compared to the square antiprism.

Higher Coordination Numbers

There are few structures known with coordination numbers larger than 8. The existence of coordination number 12 in some crystal lattices was mentioned above. Discrete nine-coordinate structures are known for complexes such as $[\text{Ln(H}_2\text{O})_9]^{3+}$ and for the hydride complexes $[\text{MH}_5]^-$ (where $\text{M} = \text{Tc}$ or Re). These structures are formed by adding a ligand to each of the rectangular faces of a trigonal prism (Fig. 12.40).
With trivalent metals, acetylacetonate thus forms neutral tris complexes such as [Al(acac)_3], [Tl(acac)_3], [Cr(acac)_3], and [Co(acac)_3]. As a result of resonance, the two M—O bonds in each of these complexes are equal in length, as are the two C—O and the two C—C bonds, giving a symmetric structure (only one ring shown):

$$\begin{align*}
\text{H}_2\text{C} & \quad \text{CH} & \quad \text{CH}_2 \\
\text{M} & \quad \text{O} & \quad \text{O} \\
\text{H}_2\text{C} & \quad \text{CH} & \quad \text{CH}_2 \\
\end{align*}$$

(12.36)

Ligand-metal π bonding enhances the delocalization of electrons compared to that in the free enolate, producing some resonance stabilization.

An interesting example of at least partial destruction of resonance from Jahn-Teller distortion is given by bipyridinebis(hexafluoroacetylacetonato)copper(II)

the two ring C—C bonds, giving a symmetric structure (only one ring shown):

$$\begin{align*}
\text{H}_2\text{C} & \quad \text{CH} & \quad \text{CH}_2 \\
\text{M} & \quad \text{O} & \quad \text{O} \\
\text{H}_2\text{C} & \quad \text{CH} & \quad \text{CH}_2 \\
\end{align*}$$

(12.36)

An area of particular research interest in recent years has been the construction of planar, macrocyclic ligands. These are special types of polynuclear ligands in which the linking atoms are constrained in a large ring encircling the metal atom. Examples are polyethers in which the ether oxygen atoms, separated by two methylene groups each, lie in a nearly planar arrangement about the central metal atom (Fig. 12.49) and the remainder of the molecule lies in a "crown" arrangement, hence the name "crown ethers." All of the oxygen atoms "point" toward the metal atom, and these macrocycles have the unusual property of forming stable complexes with alkali metals. This exceptional stability has been attributed to the close fitting of the alkali metal ion into the hole in the center of the ligand. However, some data seem to contradict this simple model. Although calculations indicate that the Li⁺ should preferentially fit crown-4, in solution crown-4, crown-5, crown-6, and crown-7 all prefer K⁺. Hancock has suggested that this may arise because the five-membered ring formed when any of the above crown ethers binds to an alkali metal cation best fits the size of K⁺.

Gas-phase studies show that crown-5 prefers Li⁺ more than the other alkali metal cations:

crown-3: Li⁺ > Na⁺ > K⁺ > Cs⁺

crown-6: Na⁺ > Li⁺ > Rb⁺ > Cs⁺

crown-7: K⁺ > Na⁺ > Rb⁺ > Li⁺ > Cs⁺

The difference in affinities shown in gas and solution phases suggests that solvent effects are quite important. These ligands have the unusual ability to promote the solubility of alkali ions in organic solvents as a result of the large hydrophobic organic ring. For example, alkali metals do not normally dissolve in ethers as they do in ammonia (see Chapter 10). However, some data seem to contradict this simple model. Although calculations indicate that the Li⁺ should preferentially fit crown-4, in solution crown-4, crown-5, crown-6, and crown-7 all prefer K⁺. Hancock has suggested that this may arise because the five-membered ring formed when any of the above crown ethers binds to an alkali metal cation best fits the size of K⁺.

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crown-7: K⁺ > Na⁺ > Rb⁺ > Li⁺ > Cs⁺

The difference in affinities shown in gas and solution phases suggests that solvent effects are quite important. These ligands have the unusual ability to promote the solubility of alkali ions in organic solvents as a result of the large hydrophobic organic ring. For example, alkali metals do not normally dissolve in ethers as they do in ammonia (see Chapter 10), but they will do so if crown ligands are present:

$$K = \text{crown-6} \cdot \frac{\text{D}_1}{\text{D}_2} \cdot [\text{K(crown-6)}]$$

(12.37)

The ability to complex and stabilize alkali metal ions has been exploited several times to effect syntheses that might otherwise be difficult or impossible. Consider the
No compounds are known with ten or more distinct ligands (i.e., nonchelate structures); however, a few ten-coordinate chelate structures have been described. One possible structure is a "double trigonal bipyramid" with bidentate nitrate or carbonate ions at each of the TBP sites (Fig. 12.41a). Coordination numbers as high as 12 are also known with six bidentate nitrate ligands along the edges of a dodecahedron, but these complexes are rare (Fig. 12.41b).

What generalizations can be made concerning high and low coordination numbers? All generalizations have exceptions, but we can list the following trends. The factors favoring low coordination number are:

1. Soft ligands and metals in low oxidation states. Electronically, these will favor low coordination numbers because extensive \(\pi\) bonding will compensate in part for the absence of additional (potential) \(\sigma\) bonding. Metals in low oxidation states are electron rich and do not seek additional contributions of electron density from additional ligands.

2. Large, bulky ligands. If the complex is coordinatively unsaturated (in an electronic sense), then steric hindrance may prevent additional ligands from coordinating to the metal.

3. Counterions of low basicity. Any cationic complex with a low coordination number is a Lewis acid potentially susceptible to attack and coordination by its anionic counterion. For this reason, anions of low basicity and coordinating ability are chosen for counterions. Among the oxyanions, nitrate and perchlorate have a long history of use. Both show some coordinating ability (cf. the nitrate complexes discussed in the preceding section), and as strong oxidizers their presence with organic ligands can be potentially hazardous. The triflate anion, \(CF_3SO_3^-\), obviates the explosive hazard and also reduces the tendency toward rotational disorder in crystals. Fluoride adducts of strong Lewis fluoroacids such as \(BF_3\), \(PF_5\), and \(SnF_6^{2-}\) are frequently chosen as counterions be-
The Chelate Effect

Reference has been made previously to the enhanced stability of complexes containing chelate rings. This extra stability is termed the chelate effect. It is chiefly an entropy effect common to all chelate systems, but often additional stabilization results from enthalpy changes. Entropy changes associated with chelation are complex. With regard to translational entropy there are two points of view which are essentially equivalent in that they are both statistical and probabilistic in nature. They therefore relate to the entropy of the system but they look at the problem from somewhat different aspects. One is to consider the difference in dissociation between ethylenediamine complexes and ammonia complexes, for example, in terms of the effect of the ethylenediamine ring (the electronic effects of the nitrogen atoms in ethylenediamine complexes and ammonia complexes, for example, in terms of the electronic effects of the ethylenediamine ring (the electronic effects of the nitrogen atoms in ethylenediamine complexes and ammonia complexes, for example, in terms of the electronic effects of the nitrogen atoms in ethylenediamine complexes and ammonia complexes, for example). The isomers in question are represented by compounds such as 

\[ \text{[Co(NH}_3]_6\text{NO}_3\text{]} \quad \text{[Co(NH}_3]_4\text{NO}_2\text{]} \quad \text{[Co(NH}_3]_2\text{NO}_2\text{]} \quad \text{[Co(NH}_3]_2\text{NH}_2\text{]} \quad \text{[Co(NH}_3]_2\text{N}_2\text{]} \quad \text{[Co(NH}_3]_2\text{N}_2\text{]} \]

These all have the empirical formulas 

\[ \text{Co(NH}_3]_2\text{N}_2\text{]} \quad \text{[Co(NH}_3]_2\text{N}_2\text{]} \]

but they have formula weights that are 2, 2, 3, 4, 4, and 5 times this, respectively.

A special case of coordination isomerism is sometimes given the name "polymerization isomerism" since the various isomers differ in formula weight from one another. However, the term is unfortunate since polymerization is normally used to refer to the reaction in which a monomeric unit builds a larger structure consisting of repeating units. The isomers in question are represented by compounds such as 

\[ \text{[Co(NH}_3]_6\text{NO}_3\text{]} \quad \text{[Co(NH}_3]_4\text{NO}_2\text{]} \quad \text{[Co(NH}_3]_2\text{NO}_2\text{]} \quad \text{[Co(NH}_3]_2\text{NH}_2\text{]} \quad \text{[Co(NH}_3]_2\text{N}_2\text{]} \quad \text{[Co(NH}_3]_2\text{N}_2\text{]} \]

There are also decided enthalpy effects present. These may be most simply calculated from the number of chelate rings formed. As seen in Table 12.6, the calculated entropy values (33.4 kJ mol\(^{-1}\)) are in reasonable agreement with the observed values. Given the complexity of the thermodynamics involved in chelation, it is somewhat fortuitous that this simple approach is as successful as it is.

There are also decided entropy effects present. These may be most simply viewed in terms of the chelate being "preformed." In other words, certain energy costs that have to be paid to form complexes, such as steric interference between two adjacent ligands, repulsion between the dipoles of two adjacent ligands, etc., may have been paid, in part, when the potentially bidentate ligand was originally attached to the metal. The nitrogen atom can move only a few hundred picometers away and can swing back and attach to the metal again. The complex has a smaller probability of dissociating and is therefore experimentally found to be more stable toward dissociation.

A more sophisticated approach would be to consider the reaction:

\[ \text{[Ni(NH}_3]_2\text{H}_2\text{O}(\text{H}_2\text{O})\text{]} \quad \text{[Ni(NH}_3]_2\text{H}_2\text{O}(\text{H}_2\text{O})\text{]} \]

in terms of the enthalpy and entropy. Since the bonding characteristics of ammonia and ethylenediamine are very similar, we expect \( \Delta H \) for this reaction to be small. To a first approximation the change in entropy would be expected to be proportional to the number of chelate rings present at the beginning and end of the reaction. The reaction proceeds to the right with an increase in number of particles, and hence translational entropy favors the production of the chelate system instead of the hexaammine complex.\(^\text{100}\)

in the replacement of water molecules by chelates, the increase in number of molecules in solution causes an increase of entropy given by \( \Delta S = \Delta G \) at 53.5 \( = 3.4 \text{ kJ mol}^{-1} \) for the free-energy stabilization of the complex at constant. For each chelate ring formed, as seen in Table 12.6, the calculated entropy values (33.4 kJ mol\(^{-1}\)) are in reasonable agreement with the observed values. Given the complexity of the thermodynamics involved in chelation, it is somewhat fortuitous that this simple approach is as successful as it is.

Finally, chelating ligands such as acetylacetonate enjoy resonance stabilization as a result of forming six-membered rings having some aromatic character. Acetylacetonate (4,4'-pentanebione) coordinates as an anionic enolate ligand:

\[ \text{CH}_3\text{C}^\text{O}\text{CH}==\text{C}^\text{O}\text{CH}_3 \quad \text{CH}_3\text{C}^\text{O}\text{CH}==\text{C}^\text{O}\text{CH}_3 \quad \text{CH}_3\text{C}^\text{O}\text{CH}==\text{C}^\text{O}\text{CH}_3 \]

In comparison, the driving force for this reaction (\( \Delta G = -19 \text{ kJ mol}^{-1} \)) comes predominantly from the \( \Delta G \) term.

Table 12.6

Thermodynamic contributions to the chelate effect in complexes of nickel(ll) and copper(ll)

<table>
<thead>
<tr>
<th>Ammonia complexes</th>
<th>( \Delta G )</th>
<th>( \Delta S )</th>
<th>Ethylenediamine complexes</th>
<th>( \Delta G )</th>
<th>( \Delta S )</th>
<th>Chelate effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{[Ni(NH}_3]_2\text{H}_2\text{O}(\text{H}_2\text{O})\text{]} )</td>
<td>-74.2</td>
<td>-46.3</td>
<td>( \text{[Ni(NH}_3]_2\text{H}_2\text{O}(\text{H}_2\text{O})\text{]} )</td>
<td>-29.0</td>
<td>-33.2</td>
<td>-32.9</td>
</tr>
<tr>
<td>( \text{[Co(NH}_3]_2\text{H}_2\text{O}(\text{H}_2\text{O})\text{]} )</td>
<td>-44.7</td>
<td>-46.3</td>
<td>( \text{[Co(NH}_3]_2\text{H}_2\text{O}(\text{H}_2\text{O})\text{]} )</td>
<td>-41.9</td>
<td>-38.2</td>
<td>-38.7</td>
</tr>
<tr>
<td>( \text{[Ni(NH}_3]_2\text{H}_2\text{O}(\text{H}_2\text{O})\text{]} )</td>
<td>-84.2</td>
<td>-51.8</td>
<td>( \text{[Ni(NH}_3]_2\text{H}_2\text{O}(\text{H}_2\text{O})\text{]} )</td>
<td>-101.8</td>
<td>-117.8</td>
<td>-117.8</td>
</tr>
</tbody>
</table>


\(^\text{99}\) Entropy changes associated with solvation and rotational differences are also important. The driving force for this reaction (\( \Delta G = -18 \text{ kJ mol}^{-1} \)) comes predominantly from the \( \Delta H \) term.

\(^\text{100}\) Hancock, R. D.; Martell, A. E. Comments Inorg. Chem. 1988, 6, 237-238.
cause they have a low tendency to transfer fluoride ions to the acidic cation, though such transfer can occur if the cation is sufficiently acidic. For example, a successful way of abstracting a chloride ion from the coordination sphere of a metal is to allow the complex to react with silver tetrafluoroborate. Silver chloride is precipitated, and the low-basicity and (one hopes) noncoordinating $\text{BF}_4^-$ is introduced as a co-ion. Thus, potentially, the [tris(3-ethylpyrazolyl)hydroborato]chlorocobalt(II) could react with silver tetrafluoroborate to give the very stable silver chloride and the tetrafluoroborate salt of a three-coordinate cation. However, when this reaction was attempted, fluoride abstraction (from $\text{BF}_4^-$) was found instead (Fig. 12.42). Similar three-coordinate "tripod" ligands are known of the type $\text{[CIR}_3\text{PY}]^-$ (where Y can be O, S, or a pair of electrons on the phosphorus atom). These tripod ligands strongly determine three coordination positions in a pyramidal arrangement, leading to a fourth coordination by a halide. Bridging by fluorides may also occur. For example, $\text{SnF}_6^{2-}$ can coordinate to the very strong Lewis acid $\text{SbF}_5$ to form $\text{[F}_5\text{Sn}—\text{SbF}_5]^-$. It is very difficult to abstract a fluoride ion from $\text{SbF}_5^-$.

It has been suggested that $\text{SnF}_6^{2-}$ should be the anion of choice in the synthesis of reactive yet potentially isolable cationic Lewis acids.

These will serve to maximize the electron contribution to stabilizing the complexes. Because of their high electronegativity, fluoride and oxygen-containing ligands can stabilize high oxidation states.

1. **High oxidation states and hard ligands.** These will serve to maximize the electronic contribution to stabilizing the complexes. Because of their high electronegativity, fluoride and oxygen-containing ligands can stabilize high oxidation states.

Fig. 12.42 Reactions of tris(3-ethylpyrazolyl)hydroboratochlorocobalt(II) with silver tetrafluoroborate. A fluoride ion has been abstracted from the $\text{BF}_4^-$ anion to give tris(3-ethylpyrazolyl)hydroboratochlorocobalt(II). All of the unlabeled atoms are carbons and the hydrogen atoms are not shown. (Modified from Gorrell, I. B.; Parkin, G. Inorg. Chem. 1990, 29, 2452-2456. Reproduced with permission.)


Fig. 12.47 Portion of the crystal structure of Prussian blue showing the bridging by
tridentate cyanide ions. Circles represent iron(II) (O), iron(III) (C), and oxygen in water
(•). The remaining interstitial or “zeolitic” water in the cubic sites has been omitted for
clarity, as have most of the cyanide ions. In addition, some of the cyanide ions are
replaced by water molecules coordinated to iron(IU), and there are also vacancies in the structure.

This has been interpreted in terms of linkage isomers of the type:

\[ \text{Fe}^{II} - \text{CN} - \text{Fe}^{III} - \text{CN} - \text{Fe}^{II} - \text{CN} \]

in which the linear arrays shown in Eq. 12.23 represent portions of the cubic arrays
shown in Fig. 12.47. The initial product is C-coordinated to the chromium(III) since
that was the arrangement in the original hexacyanochromate(III). The iron(II) coordi-
nates to the available nitrogen atoms to form the Prussian-blue-type structure. As in
the case of Prussian blue discussed above, however, there will be preferential LFSE
favoring the coordination of the strong field C-linkage to the potential low spin \( \Delta_{2g} \)
configuration of iron(II), approximately twice as great as that of the \( \Delta_{2g} \) configuration
of chromium(III) (see Table 11.3).

Other Types of Isomerism
In general the other types of isomerism for coordination compounds are less interest-
ing than those discussed previously, but will be listed briefly to show the variety of
possibilities.

Ligand Isomerism
Since many ligands are organic compounds which have possibilities for isomerism, the
resulting complexes can show isomerism from this source. Examples of isomeric
ligands are 1,2-diaminopropane ("propylene diamine," \( \text{pda} \)) and 1,3-diaminopropane
("trimethylene diamine," \( \text{tn} \)) or ortho-, meta-, and para-toluidine (\( \text{CH}_2\text{C}_6\text{H}_4\text{NH}_2 \)).

Ionization Isomerism
The ionization isomers \( [\text{Co(NH}_3]_3\text{Br}][\text{SO}_4] \) and \( [\text{Co(NH}_3]_5\text{Br}_3][\text{SO}_4] \) dissolve in water to
yield different ions and thus react differently to various reagents:

\[ [\text{Co(NH}_3]_3\text{Br}][\text{SO}_4] + \text{Ba}^{2+} \rightarrow \text{BaSO}_4(s) \quad (12.24) \]

\[ [\text{Co(NH}_3]_5\text{Br}_3][\text{SO}_4] + \text{Ba}^{2+} \rightarrow \text{No reaction} \quad (12.25) \]

\[ [\text{Co(NH}_3]_3\text{Br}][\text{SO}_4] + \text{Ag}^+ \rightarrow \text{No reaction} \quad (12.26) \]

\[ [\text{Co(NH}_3]_5\text{Br}_3][\text{SO}_4] + \text{Ag}^+ \rightarrow \text{AgBr(s)} \quad (12.27) \]

Solvate Isomerism
This is a somewhat special case of the above interchange of ligands involving neutral
solvate molecules. The best known example involves isomers of "chromic chloride
hydrates," of which three are known: \( [\text{Cr(H}_2\text{O}_2]_3\text{Cl}_3 \), \( [\text{Cr(H}_2\text{O}_2]_5\text{Cl}_2\text{H}_2\text{O} \), and
\( [\text{Cr(H}_2\text{O}_2]_5\text{Cl}_4\text{H}_2\text{O} \). These differ in their reactions:

\[ [\text{Cr(H}_2\text{O}_2]_3\text{Cl}_3 \rightarrow \text{CrCl}_3 + 3\text{H}_2\text{O} \quad (12.28) \]

\[ [\text{Cr(H}_2\text{O}_2]_5\text{Cl}_2\text{H}_2\text{O} \rightarrow \text{CrCl}_3 + 2\text{H}_2\text{O} \quad (12.29) \]

\[ [\text{Cr(H}_2\text{O}_2]_5\text{Cl}_4\text{H}_2\text{O} \rightarrow \text{CrCl}_3 + 3\text{H}_2\text{O} \quad (12.30) \]

\[ [\text{Cr(H}_2\text{O}_2]_3\text{Cl}_3 + 3\text{AgCl} \rightarrow \text{No reaction} \quad (12.31) \]

\[ [\text{Cr(H}_2\text{O}_2]_5\text{Cl}_2\text{H}_2\text{O} + 2\text{AgCl} \rightarrow \text{AgCl}_2 \quad (12.32) \]

\[ [\text{Cr(H}_2\text{O}_2]_5\text{Cl}_4\text{H}_2\text{O} + \text{AgCl} \rightarrow \text{AgCl}_3 \quad (12.33) \]


Coordination Isomerism
Salts that contain complex cations and anions may exhibit isomerism through the
interchange of ligands between cation and anion. For example, both hexaam-
This was disputed by Shimizu,27 who claimed that they had quite different spectra. Lecompte and Davol compared the X-ray powder patterns of the two forms and found that they were "rigorously identical."28 They suggested that the red color in the supposed nitrito complex was a result of some unreacted starting material, namely [Co(NH₃)₅Cl]Cl₂, in the product.

Adell29 measured the rate of conversion of the red form to the yellow form photometrically and found it to be a first-order reaction. This is to be expected if the conversion is an intramolecular rearrangement involving no other species (with the possible exception of the solvent). On the other hand, if the red isomer is actually unreacted starting material in the form of [Co(NH₃)₅Cl]Cl₂, the reaction might be expected to be second order:

\[
\frac{d\left[\text{Co(NH}_3\text{)}_5\text{Cl}^2+\right]}{dt} = f\left[\text{Co(NH}_3\text{)}_5\text{Cl}^2+\right] \left[\text{NO}_3^-\right]
\]  
(12.14)

Murmann and Taube,30 showed that the formation of the nitrito complex occurs without the rupture of the Co-O bond. They used ¹⁸O-labeled [(NH₃)₅Co(OH)]²⁺ as a starting material and found that all of the ¹⁸O remained in the complex. This argues in favor of reaction 12.15 in preference to 12.16:

\[
\begin{align*}
\text{[(NH}_3\text{)}_5\text{Co(OH)}^2+] & + \text{N}_2\text{O}_5^- \rightarrow \left[\text{NH}_3\text{Co}^2+\text{O}^-\text{H}^-\right] \left[\text{NO}_3^-\right] \\
\text{[(NH}_3\text{)}_5\text{Co(NO}_3\text{)}_2^2+\text{HONO}^2-] & + \text{N}_2\text{O}_5^- \\
\text{[(NH}_3\text{)}_5\text{Co(NO}_3\text{)}_2^2+\text{HONO}^2-] & + \text{N}_2\text{O}_5^- \\
\end{align*}
\]  
(12.15)

The labeled nitrito complex may be caused to rearrange by heating. In this process no loss of ¹⁸O is found even in the presence of excess nitrite, confirming Adell’s hypothesis that the reaction is an intramolecular rearrangement:

\[
\left[\text{NH}_3\text{Co}^2+\text{O}^-\text{H}^-\text{ON}_3^-\right] \rightarrow \left[\text{NH}_3\text{Co}^2+\text{O}^-\text{H}^-\text{ON}_3^-\right]
\]  
(12.16)

Finally, the ¹⁸O can be quantitatively removed by the basic hydrolysis of the nitrito isomer:

\[
\text{[(NH}_3\text{)}_5\text{Co(NO}_3\text{)}_2^2+] + \text{OH}^- \rightarrow \left[\text{NH}_3\text{Co(OH)}^2+\text{ON}_3^-\right] + \text{H}_2\text{O}
\]  
(12.18)

All these experiments are consistent with the original hypothesis of Jorgensen and Werner of linkage isomerism. It is difficult to rationalize the "rigorous" contrary evidence of some of the early workers except by the general phenomenon that it is deceptively easy to obtain the experimental results that one expects and desires.

Werner knew of two other examples of linkage isomerism, both nitro-nitrito isomers, and they underwent the same period of skepticism and confirmation as the compounds discussed above although considerably less work was done with them. A period of more than 50 years passed before Basolo and coworkers attacked the problem with rather amazing results.32 Linkage isomerism, once relegated to a few lines as an "exceptional" situation in discussions of isomerism, now boasts an extensive chemistry which continues to develop. The first new linkage isomers prepared were nitro-nitrito isomers of Cr(III), Rh(III), Ir(III), and Pt(IV). In all cases except Cr(III), the nitrito isomer converts readily to the more stable nitro isomer.

The first thiocyanate linkage isomers were isolated after it was noted that the structures of cis complexes containing thiocyanate and either ammonia or phosphine were S- or N-linked, respectively (Fig. 12.43). The hypothesis provided was that these isomers were more stable than the alternatives (i.e., S-bonded in the phosphine complex, N-bonded in the ammine complex) because of the competition for π bonding orbitals on the metal. The phosphine forms the best π bonds and hence tends to monopolize the σ bonding orbitals of the platinum, reducing the stability of the weaker sulfur π bond, hence the thiocyanate ion bonds through the nitrogen atom. In the absence of competition for π orbitals (ammonia cannot form a π bond), the sulfur atom is preferentially bonded. Using this hypothesis as a basis, Basolo and coworkers33 attempted to find complexes in which the π bonding tendencies were balanced,

![Fig. 12.43 Structures of [Pt(SCN)₂(NH₃)₂]⁺ and [Pt(NCS)₂(PPh₃)]²⁻ illustrating the competition for π bonding of orbitals of the metal. One set of σ bonds has been omitted for clarity. The "d orbital" left-right symmetry has been lost due to polarization. Compare with Fig. 11.30. In addition to empty d orbitals, sulfur has filled p orbitals. See Table 11.11 and accompanying discussion.](image)

28 Lecompte, J.; Davol, C. Bull. Soc. Chim. 1945, 32, 676. Powder patterns are determined by the type of crystal lattice and by the spacings in the lattice. They are useful as "fingerprints" devices for the identification of crystals.
30 First-order kinetics is to be expected for an intramolecular reaction, but its presence is not proof of such a mechanism. The brackets in this equation represent the concentrations of the various species (in mol L⁻¹) rather than indications of structural isomers.
32 The differences in these reactions of N₂O₅ versus NO₃⁻, the presence or absence of OH⁻ as a product, etc., were more apparent than real since these species will interact with each other or form an equilibrium mixture. The general argument does not depend upon the exact nature of the reactants and products.
Symbiosis

Jorgensen proposed the principle of **symbiosis** with respect to hard and soft acid-base behavior. This rule of thumb states that hard species will tend to increase the hardness of the atom to which they are bound and thus increase its tendency to attract more hard species. Conversely, the presence of some soft ligands enhances the ability of the central atom to accept other soft ligands. In terms of the electronic versus covalent picture of Pearson's hard and soft or Drago's $E$ and $C$ parameters (see Chapter 9), the best "strategy" of a complex is to "put all its eggs in one basket." i.e., form all hard ("electrostatic") or all soft ("covalent") bonds to ligands. There are many examples that could be given to illustrate this tendency in metal complexes:

<table>
<thead>
<tr>
<th>All ligands hard</th>
<th>All ligands soft</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(NH$_3$)$_5$NCS]$^{2-}$</td>
<td>[Co(NH$_3$)$_5$SCN]$^{2-}$</td>
</tr>
<tr>
<td>[Rh(NH$_3$)$_5$I]$^{2-}$</td>
<td>[Rh(NH$_3$)$_5$Cl]$^{2-}$</td>
</tr>
<tr>
<td>[Fe(NCS)$_3$]$^{2-}$</td>
<td>[Fe(CN)$_3$]$^{2-}$</td>
</tr>
</tbody>
</table>

In the first example the hard ammonia ligands tend to harden the cobalt, and so the thiocyanate ligands soften the cobalt, making it bond to the soft end of the thiocyanate (the sulfur atom). Similarly, in the case of Rh(III) five ammonia ligands result in preference for nitrogen at the sixth position; if all six soft sulfur atoms can ligate, they will. Iron(II) appears to prefer the hard nitrogen atom unless softened by the presence of carbonyl groups.

The symbiotic theory adequately covers most of the linkage preferences observed for octahedral complexes. Unfortunately, it contradicts exactly the $\sigma$ bonding theory applied above to square planar complexes. $\pi$ bonding can be equated with softness. Conversely, the presence of some soft ligands can also increase the $\sigma$ bonding with hardness. In the case of octahedral complexes we say that the presence of soft, $\sigma$ bonding ligands favors the addition of more soft, $\pi$ bonding ligands (symmetric theory), but in the case of square planar complexes we say that soft, $\pi$ bonding ligands discourage the presence of other $\pi$ bonds and favor the addition of hard, $\sigma$ only ligands (symmetry competition theory).

Pearson, in elaborating upon these ideas, distilled the essence of the $\pi$ competition theory to two soft ligands in metal trans positions will have a destabilizing influence on each other when attached to class (b) (soft) metal atoms. He also provided additional examples of the rule that symbiosis prevails in octahedral complexes, antisymbiosis in square planar complexes. Tetrahedral complexes are expected to show antisymbiosis but on a much reduced scale compared with the square planar complexes.

**Related Structures**

**Prussian Blue** and Related Structures

Prussian blue is a special case of ambidentate behavior in ligands. The cyanide ion provides good examples of such behavior. In discrete complexes it almost always bonds through the carbon atom because of the stronger $\sigma$ bonding in that mode. It has also been reported to form a few linkage isomers such as cis-[Co(NCN)(CN)$_5$]$^{2-}$ and cis-[Co(CN)$_5$SCN]$^{2-}$.

A large number of polymeric complexes is known containing ambidentate cyanide bridging groups. These are related to "Prussian blue," which is formed by the addition of ferric salts to ferrocyanides:

\[
\text{Fe}^{3+} + [\text{Fe}_{x}^{2+}(\text{CN})_{y}]^{2-x} \rightarrow \text{Fe}_{x}^{3+}[(\text{FeCN})_{y}]^{2-x}
\]

(12.19)

Addition of ferrous salts to ferricyanides produces "Turnbull's blue":

\[
\text{Fe}^{2+} + [\text{Fe}_{x}^{2+}(\text{CN})_{y}]^{2-x} \rightarrow \text{Fe}_{x}^{2+}[(\text{FeCN})_{y}]^{2-x}
\]

(12.20)

It has been shown that the iron-cyanide framework is the same in Prussian blue, Turnbull's blue, and other related polymeric cyanide complexes [Fig. 12.47], differing only in the number of ions necessary to maintain electrical neutrality. Various quantities of water molecules may also be present in the large cubic holes. Prussian blue has a structure with hexacoordinate, low spin Fe(II) bonded through the carbon atoms and hexacoordinate, high spin Fe(III) bonded through the nitrogen atoms of the cyanide. To achieve the stoichiometry, one-fourth of the Fe(III) sites are occupied by water molecules. This reduces the number of bridging cyanide groups (Fe$^{2+}$-$\text{CN}$-$\text{N}$-$Fe$^{3+}$) somewhat, and water molecules occupy the otherwise empty ligand positions thus created. There is also one water molecule in each cubic site.$^{93}$

Although prepared from different starting materials, Turnbull's blue is identical. Although X-ray and magnetic data support this identity, the best evidence comes from the fact that the Mössbauer spectra of Prussian blue and Turnbull's blue are the same.$^{94}$ Since Mössbauer spectra are extremely sensitive to the electron density and serve to emphasize that there are many factors involved, both electronic and steric, in determining which of the possible isomers will be preferred.$^{95}$

For further discussion of this problem, see DeSilva, N. J.; Burmeister, J. L.; Ivery, Chem. 1971, 10, 1904-1907. It should also be noted that although the phenomenon of symbiosis is very real, the choice of the word symbiosis to describe it is unfortunate, as DeSilva and Burmeister point out, symbiosis in biology refers to the "building together" of different species, rather than the same species, in intimate association. Nevertheless, inorganic chemists will undoubtedly continue to use the term in its current sense.

---

84 See Chapter 13 for a discussion of the electronic factors operative in the trans influence.

85 Note the differences in the electronic factors operative in the trans influence.


allowing the isolation of both isomers. Examples of the complexes thus isolated are \([\text{Ph}_3\text{As})_2\text{Pd(SCN)}_2J\), \([\text{Ph}_3\text{As})_2\text{Pd(NCS)}_2J\), and \([\text{bpy})\text{Pd(SCN)}_2J\), \([\text{bpy})\text{Pd(NCS)}_2J\). In both cases, on warming, the S-bonded isomer is converted to the N-bonded isomer, which is presumably slightly more stable.

The competition for \(\pi\) bonding is indicated in the behavior of the selenocyanate group, \(\text{SeCN}^-\). This group readily bonds to the heavier group VIIIB (8) metals via the selenium atom to form complexes such as \([\text{Pd(SeCN)}_4]^{2-}\) and trans-\([\text{Rh(PPh}_3)_2(\text{SeCN)})_2^-\). However, in a closely related complex, \([\text{Rh(PPh}_3)_2(\text{CO})(\text{NCS})_2^-\), the presence of a trans carbonyl group apparently favors coordination via the non-\(\pi\)-bonding nitrogen atom.\(^{85}\)

Another example of apparent electronic (i.e., \(\pi\) bonding) control of linkage isomerism comes from bidentate chelates having one strong and one weak donor atom (Fig. 12.44). The presence of an S-bonded thiocyanato group trans to the non-\(\pi\)-bonding nitrogen atom, but an N-bonded thiocyanato group trans to the \(\pi\) bonding phosphine donor is indicative of \(\pi\) competition in this complex.\(^{86}\)

Steric Effects

Steric factors may play an important role in stabilizing one or the other of a pair of linkage isomers. Thus nitro-nitrito, thiocyanato-isothiocyanato, and selenocyanato-isoselenocyanato pairs differ in steric requirements (Fig. 12.45).

One or more factors may be operating simultaneously to provide a delicate balance of counterpoising effects. An interesting series of compounds illustrates the competing effects in linkage isomers of square planar palladium(II) complexes (Fig. 12.46a-d).\(^{87}\) The six-membered chelate ring in Figure 12.46c allows an essentially unstrained angle of 89.1° at the palladium atom. The aryl-aryl-substituted phosphines are only weakly \(\pi\) bonding, but the expected N-bonded isomer obtains. As the chelate ring is contracted to five atoms (Fig. 12.46b), and then to four atoms (Fig. 12.46a), the electronic environment on the phosphorus is essentially constant, but the steric constraints are relaxed as shown by the decreasing P–Pd–P bond angle. First one (Fig. 12.46b), then both (Fig. 12.46a) thiocyanate groups rearrange as the large sulfur atom is allowed more room around the palladium atom. However, the same effect can be accomplished by holding the geometry essentially constant (Fig. 12.46d), if one of the phosphorus atoms is replaced by a smaller, non-\(\pi\)-bonding

Configuration also exhibited by the posttransition metals in their highest oxidation states (Ga(III)). The d⁰ configuration is limited to Cu(I) and Zn(II), but it is otherwise unimportant. This configuration is found in copper(II) compounds but is otherwise unimportant. It occurs in copper(I) complexes as the most stable species but is otherwise unimportant. It has not the closed subshell stability of d⁰ nor the LFSE possible for d⁰. Copper(II) may be fairly easily reduced to copper(I) (see Eqs. 14.10 and 14.11).

Six-coordinate complexes are expected to be distorted from pure octahedral symmetry by the Jahn-Teller effect and this distortion is generally observed (Chapter 11). A number of five-coordinate complexes are known, both square pyramidal and trigonal bipyramidal. Four-coordination is exemplified by square planar and tetrahedral species as well as intermediate configurations.

For the first transition series this configuration is limited to Cu(I) and Zn(II), but it is also exhibited by the posttransition metals in their highest oxidation states (Ga(III), Ge(IV)). The copper(I) complexes are good reducing agents, being oxidized to Cu(II). They may be stabilized by precipitation with appropriate counterions to the extent that Cu(I) may form to the exclusion of Cu(II):

\[
\text{Cu}^{2+} (+aq) + 2\text{I}^{-} (+aq) \rightarrow \text{CuI}_{2}(s) \quad (14.10)
\]

\[
\text{Cu}^{2+} (+aq) + 2\text{CN}^{-} (+aq) \rightarrow \text{CuCN}_{2}(s) + \text{CN}^{-} (+aq) \quad (14.11)
\]

Zinc(II), gallium(III), and germanium(IV) are the most stable oxidation states for these elements, but the latter two are paramagnetic, and zinc(III) exhibits a reluctance to assume their highest possible oxidation state. The spherical symmetry of the d⁰ configuration affords no LFSE, so the preferred coordination is determined by other factors. For Cu(I), the preferred coordination is linear (sp²), two-coordination, although three-coordination is also exhibited by several tetrahedral complexes. Zinc(II) is typically either tetrahedral (e.g., [ZnCl₄]²⁻) or octahedral (e.g., [Zn(H₂O)₆]²⁺), but both trigonal bipyramidal and square pyramidal five-coordinate complexes are known (see Chapter 12). The post-transition metals form tetrahedral (e.g., [GaCl₄]⁻) and octahedral (e.g., [Ge(acac)₄]²⁻, [GeCl₆]⁻, and [AsF₆]³⁻) complexes.
often appear as intermediates in substitution reactions of square planar complexes (see Chapter 13). More recently it has been shown that this geometry can be stabilized with a ligand combination of chelating amine and W accepting ligands. The effect of ligand field strength on the instability of the d orbital is pronounced. The splitting of the 3d orbitals in a d5 Au(II) complex, for example, is about 80% greater than that found in analogous Cu(II) complexes (see Chapter 11). The ninth electron of the gold complex would have to reside in the highly unfavorable 3d orbital and this could lead to an extreme tetragonal distortion. Thus the odd electron of Au(II) is easily ionized and disproportionation to Au(I) and Au(III) results.

The effect of the 3d electron configuration and the properties of the light versus heavier metals, but the emf data to make such an evaluation will be presented in the form of a Latimer diagram.

Having computed in general terms the properties of transition metals both on the basis of the d-electron configuration and the properties of the light versus heavier metals, we shall now look more specifically at the stabilities of the various oxidation states of each element in aqueous solution. Every oxidation state will not be examined in detail, but the emf data to make such an evaluation will be presented in the form of a Latimer diagram.

If you are not thoroughly familiar with the principles of electrochemistry, you should review Chapter 10 and the Latimer diagram derived there (below) before considering the following discussion for determining the stability of oxidation states:

$$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$$

A table of emf values appears in Appendix F.

There are two sources of thermodynamic instability for a particular oxidation state of an element in aqueous solution: (1) The element may reduce the hydrogen in water or hydronium ions; (2) it may oxidize the oxygen in water or hydroxide ions; or (3) it may disproportionate.

The emf values for reduction of hydrogen in water are given in Eqs. 10.116 to 10.119. They determine the minimum reduction emf necessary for a species to effect reduction of the oxygen in water. For example, MnO$_2$ would be predicted to react with neutral water but no reaction is observed. In some cases reactions are extremely slow and are not observed for kinetic reasons. In others, products of the reaction, such as oxide coatings, protect the reactant surfaces. Furthermore, reactions are usually not run at standard conditions and then E° values do not reflect the true spontaneity of the reaction.

**Oxidation States and EMFs of Groups 1–12**

<table>
<thead>
<tr>
<th>Species</th>
<th>Reduction Reaction</th>
<th>Reduction EMF (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO$_2$(aq) + 8H$^+$ + 5e$^-$ → Mn$^{2+}$ + 4H$_2$O</td>
<td>E° = -1.23 V</td>
<td>(14.19)</td>
</tr>
<tr>
<td>2MnO$_4^-$ + 10H$^+$ + 8e$^-$ → 2MnO$_2$(aq) + 4H$_2$O</td>
<td>E° = -0.33 V</td>
<td>(14.20)</td>
</tr>
<tr>
<td>2MnO$_4^-$ + 10H$^+$ + 8e$^-$ → 2MnO$_2$(aq) + 4H$_2$O</td>
<td>E° = 1.70 V</td>
<td>(14.21)</td>
</tr>
<tr>
<td>2MnO$_4^-$ + 2H$^+$ + 2e$^-$ → 2MnO$_2$(aq)</td>
<td>E° = +0.47 V</td>
<td>(14.23)</td>
</tr>
</tbody>
</table>

24 Predictions based on emf values are not always borne out in the laboratory. For example, pure MnO$_2$ would be predicted to react with neutral water but no reaction is observed. In some cases reactions are extremely slow and are not observed for kinetic reasons. In others, products of the reaction, such as oxide coatings, protect the reactant surfaces. Furthermore, reactions are usually not run at standard conditions and then E° values do not reflect the true spontaneity of the reaction.
Disproportionation occurs when a species is both a good reducing agent and a good oxidizing agent. In basic solution, for example, \( \text{Cl}_2 \) disproportionate to \( \text{Cl}^- \) and \( \text{ClO}_3^- \) ions:

\[
\begin{align*}
\text{Cl}_2(g) + e^- & \rightarrow \text{Cl}^- (aq) & E^0 = +1.40 \text{ V} \\
\text{Cl}_2(g) + 2\text{OH}^-(aq) & \rightarrow \text{ClO}_3^-(aq) + \text{H}_2\text{O} + e^- & E^0 = -0.89 \text{ V} \\
\text{Cl}_2(g) + 2\text{OH}^-(aq) & \rightarrow \text{Cl}^- (aq) + \text{ClO}_3^-(aq) + \text{H}_2\text{O} & E^0 = +0.51 \text{ V}
\end{align*}
\]

Species susceptible to disproportionation are readily picked out from an emf diagram such as that given for manganese. The "normal" behavior of an element (i.e., when uncomplicated by disproportionation) is for the emf values to decrease steadily from left to right. Good reducing agents are on the right, good oxidizing agents are on the left, and stable species are toward the middle. Whenever this gradual change from more positive to more negative is broken, disproportionation can occur. For manganese in acid solution such breaks occur at two species: \( \text{Mn}^{2+} \) and \( \text{HMnO}_4^- \). As it turns out, both ions are also unstable because they are reduced by water, but even if they were stable in this regard they would be unstable as a result of disproportionation reactions:

\[
\begin{align*}
\text{Mn}^{2+}(aq) + e^- & \rightarrow \text{Mn}^{3+}(aq) & E^0 = 1.56 \text{ V} \\
\text{Mn}^{2+}(aq) + 2\text{H}_2\text{O} & \rightarrow \text{MnO}_4^{2-}(aq) + 4\text{H}^+(aq) + e^- & E^0 = -0.90 \text{ V} \\
2\text{Mn}^{2+}(aq) + 2\text{H}_2\text{O} & \rightarrow \text{Mn}^{3+}(aq) + \text{MnO}_4^{2-}(aq) + 4\text{H}^+(aq) & E^0 = +0.66 \text{ V}
\end{align*}
\]

Other applications of emfs include the prediction of thermodynamically possible redox reactions (e.g., will \( \text{Sn}^{4+} \) oxidize \( \text{Fe}^{2+} \) to \( \text{Fe}^{3+} \)) and the stabilization of oxidation states through the formation of complexes. The former is a straightforward application of thermodynamics and will not be discussed further here. The second is of great importance. It was introduced in Chapter 11 and will be discussed further below.

The Nernst equation was given before (Eq. 10.115), and in this chapter the effect of pH on the reduction potential of the hydrogen ion has been mentioned, but the effect in general should be emphasized. There are several types of reactions in which concentration of the reactants and products affect the stability of various oxidation states. This can be understood through application of the Nernst equation. The reduction potential of hydrogen will vary with the concentration of the hydrogen ion, hence the commonly known fact that many reasonably active metals dissolve in acid but not in base. Perhaps even more important is the effect of hydrogen ion concentration on the emf of a half-reaction of a particular species. Consider the permanganate ion as an oxidizing agent in acid solution (as it often is). From the Latimer diagram above we can readily see that the reduction emf is 1.51 V when all species have unit activity, whereas it is not shown in the complete equation: \( \text{MnO}_4^{2-}(aq) + 8\text{H}^+(aq) + 5e^- \rightarrow \text{Mn}^{2+}(aq) + 4\text{H}_2\text{O} \) (14.30) which makes it clear that the concentration of the hydrogen ion enters the Nernst equation to the eighth power—the oxidizing power of the permanganate ion is strongly pH dependent. If the hydrogen ion concentration is reduced to \( 10^{-14} \text{ M} \) (1 M OH\(^-\)), a different set of values is obtained:

\[
\begin{align*}
\text{MnO}_4^{2-} & \rightarrow \text{MnO}_4^{-} + \text{e}^- & E = 0.59 \\
\text{MnO}_4^{-} & \rightarrow \text{MnO}_4^{2-} + \text{H}_2\text{O} + 2\text{e}^- & E = 0.51 \\
\text{MnO}_4^{2-} & \rightarrow \text{Mn}^{2+} + 4\text{OH}^- + 2\text{e}^- & E = -0.54 \text{ V}
\end{align*}
\]

Thus there are oxidation states of manganese that are unstable in acid but stable in base. In the above discussion we have seen that the tendency for a species to accept or provide electrons, as quantified by emf values, may be strongly dependent on pH. Our examination has been restricted to aqueous solutions of MnO\(_4^-\) in which the pH is neither 0 nor 14. A fuller picture of the equilibrium chemistry of manganese, showing a broad range of pH and \( E \) values, is given by a Pourbaix diagram (sometimes called a predominance area diagram) (Fig. 14.2).\(^{25}\) Diagrams of this type are temperature and concentration specific; in this case concentrations are 1.0 M for all species but \( \text{H}^+ \) and \( \text{OH}^- \) and the temperature is 25 °C.\(^{26}\) Dotted lines representing the oxidation and reduction of water have been added. Any species above or below these dotted lines will, in principle, oxidize or reduce water, respectively. In practice the range of stability in water is larger than that depicted because of overvoltage.

It is instructive to examine Fig. 14.2 in some detail. In this diagram we see horizontal, slanted, and vertical lines. The solid lines arise from values of \( E \) and pH at which two different oxidation states can exist in equilibrium. The equation for each solid line is given by:

\[
E = E^0 - \frac{(0.0592)(n)(\text{pH})}{\eta}
\]

where \( n \) is the number of electrons required to reduce the higher oxidation state and \( \eta \) is the number of hydrogen ions consumed. For example, at all points on solid line A, an equilibrium exists between \( \text{Mn}(s) \) and \( \text{Mn}^{2+}(aq) \). The line is horizontal because there is no pH dependence for the reduction:

\[
\text{Mn}^{2+}(aq) + 2\text{e}^- \rightarrow \text{Mn}(s)
\]

At some higher pH, \( \text{MnO}(OH)(s) \) becomes the predominant species and is shown by solid line B, the voltage varies with pH, consistent with the half-reaction:

\[
\text{MnO}(OH)(s) + \text{H}^+ + \text{e}^- \rightarrow \text{MnO}(OH)(s) + \frac{1}{2}\text{O}_2
\]

The vertical dashed line C shows the pH at which \( \text{Mn}^{2+}(aq) \) and \( \text{MnO}(OH)(s) \) exist in equilibrium at unit activity:

\[
\frac{\text{MnO}(OH)(s)}{\text{Mn}^{2+}(aq)} = K
\]

This, of course, is an equilibrium between two species of the same oxidation state and therefore does not involve oxidation or reduction.


\(^{26}\) Geologues often construct their Pourbaix diagrams based on very dilute solutions to correspond more closely to that found in nature.
Species existing at high voltages (e.g., MnO₄⁻) are good oxidizing agents while those at low voltages (metallic manganese) are good reducing agents. It is clear from Fig. 14.2 that manganese in the +2 oxidation state is the predominant species over a wide area of pH and potential combinations. The half-filled shell for Mn⁺⁺ is thought to be largely responsible for this stability.

Manganese(III) oxide, MnO₂(s), exists in equilibrium with Mn(OH)₂(s) (line D) if conditions are sufficiently basic or with Mn²⁺(aq) (line E) at somewhat lower pH values:

\[
\text{MnO}_2(s) + 2\text{OH}^- + 2\text{e}^- \rightarrow 2\text{MnO}_2^- + \text{H}_2\text{O} \quad (14.35)
\]

Lines G and F show equilibria between MnO₂(s) and Mn²⁺(aq) (acidic conditions) and between MnO₂(s) and MnO₃(s) (more basic conditions), respectively:

\[
\begin{align*}
\text{MnO}_2(s) + 4\text{H}^+ + 2\text{e}^- & \rightarrow \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O} & (14.36) \\
2\text{MnO}_3(s) + 2\text{H}_2\text{O} + 2\text{e}^- & \rightarrow 2\text{MnO}_4^- + \text{OH}^- & (14.37)
\end{align*}
\]

Above line H the predominant species is MnO₃⁻(aq), while below line H MnO₂(s) is dominant. At the far right side of the diagram, line H intersects with lines I and J, creating a small triangle of stability for MnO₄⁻(aq) and making it the predominant species in that area.
Alkalide anions, M\(^{-}\), discussed in Chapter 12, may be stabilized by various macrocyclic ligands.\(^{24}\) The dissolution of sodium and heavier alkali metals in ethers gives not only solvated M\(^{+}\) and e\(^{-}\), but also solvated M\(^{-}\), which results from disproportionation of the metal atom.\(^{29}\)

\[2\text{M}(s) \rightarrow \text{M}^{+}(\text{solv}) + \text{M}^{-}(\text{solv})\]  \hspace{1cm} (14.42)

**Group IIA (2)**

The relative ease with which both e electrons are lost from atoms of these elements leads to compounds in which only the +2 oxidation state is found. In general, as discussed in Chapter 4, M\(^{2+}\) is unstable with respect to disproportionation. The metals of this group are less strongly reducing than the alkali metals, but still must be considered strongly reducing.

\[\text{Ca}^{2+}(aq) + 2e^- \rightarrow \text{Ca}(s) \hspace{1cm} E^0 = -2.87 \text{ V}\]  \hspace{1cm} (14.43)

The end values range from -1.97 V for Be to -2.91 V for Ba.

**Group IIIB (3)**

Scandium, yttrium, and lanthanum are all quite active, resembling the alkaline earth metals (IIA, 2) to a certain degree. For example, they reduce water, react with oxygen, and dissolve in strong acids to give soluble salts. The +3 oxidation state is the only important one for this group, and aqueous M\(^{3+}\) cations have been extensively studied. Scandium\(^{3+}\), with its high charge and small radius, resembles Al\(^{3+}\) in its chemistry. The lanthanides will be discussed later in this chapter.

\[\text{Sc}^{3+}(aq) + 3e^- \rightarrow \text{Sc}(s) \hspace{1cm} E^0 = -2.09 \text{ V}\]  \hspace{1cm} (14.44)

**Group IVB (4)**

Titanium has a more extensive redox chemistry than either zirconium or hafnium. In addition to the +4 oxidation state, the most stable for all three elements of this group, titanium\(^{4+}\) and titanium\(^{2+}\) compounds are known. Titanium\(^{2+}\) is a good reducing agent and exists in aqueous solution as \([\text{Ti}(\text{OH})_2]^{2+}\) under acidic conditions. Titanium\(^{4+}\) reduces water, but in some instances the reaction appears to be sufficiently slow to allow this oxidation state to be detected. Significant hydrolysis of the +4 cations occurs, more so for the small titanium\(^{4+}\) than for the other two members of the group. Hydrolysis of Ti\(^{4+}\) leads to a mixture of species, including Ti\(^{2+}\), [Ti(OH)\(_2\)]\(^{2+}\), and various oligomers.\(^{30}\)

\[\begin{aligned}
\text{Ti(OH)}_2^{2+} & \rightarrow \text{Ti}^{2+} + \text{H}_2\text{O}^+ + \text{H}^+ + \text{Ti}^0 \\
\text{Zr}^{4+} & \rightarrow \text{Zr}^0 \\
\text{Hf}^{4+} & \rightarrow \text{Hf}^0
\end{aligned}\]

Potentials in parentheses are estimated values.

**Group VB (5)**

A wide range of oxidation states is known for all of the elements of this group, but only vanadium has an extensive redox chemistry.

\[\begin{array}{c}
\text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr}^{3+} + \text{H}^+ \\
\text{H}_3\text{MoO}_4 \rightarrow \text{Mo}^{6+} + \text{H}^+ \\
\text{H}_3\text{WO}_4 \rightarrow \text{W}^{6+} + \text{H}^+
\end{array}\]
The heavier congeners, molybdenum and tungsten, have a less interesting redox chemistry. The emfs are small and the differences relatively unimportant. The chemistry of these elements in iso- and heteropoly acids, multiple bonds, etc. is generally of more interest (see Chapter 16).

Some Descriptive Chemistry of the Metals

Group VIIIB (7)

The first member of this family, manganese, exhibits one of the most interesting redox chemistries known; thus it has already been discussed in detail above. Technetium exhibits the expected oxidation states, and associated with these are modest emf values. All of the isotopes of technetium are radioactive but \(^{99}\)Tc has a relatively long half-life (2.14 \(\times 10^5\) years) and is found in nature in small amounts because of the radioactive decay of uranium. Oxidation states of technetium range from +7 to +3, with some species (e.g., \(\text{TcO}_4^-\) and \(\text{Tc}^{3+}\)) unstable with respect to disproportionation.

The elements copper, silver, and gold show such anomalies that there sometimes appears to be little congruence as a family, with the member that is least reactive as a metal (Au) being the only one that has an appreciable chemistry in the +3 oxidation state and also the only one to reach the +1 and +5 oxidation states (CsAu and AuF\(_5\)). Although both copper and silver may be oxidized to +4, the members of the family more or less routinely (silver less frequently) violate the very useful rule of thumb you have seen earlier: The maximum oxidation state of an element is equal to or less than its group number (IB, IVB, VIIIB, etc.). Thus we have CuO\(_4^2-\), AgF\(_3\), and [AuCl\(_5\)]\(^-\)

Each member of the family has a different preferential oxidation state (Cu, +2; Ag, +1; and Au, +3). The one property they do have in common is that none has a positive emf for \(M -> M^{n+}\); therefore, the free metals are not affected by simple acids, nor are they readily oxidized otherwise, leading to their use in materials intended to last.\(^{31}\)

Group VIIIB (8, 9, 10)

Historically the triads of Fe, Ru, Os; Co, Rh, Ir; and Ni, Pd, Pt have been called collectively Group VIIIB. This heterogeneous assortment of elements was combined into a single family more from a desire not to have any group number exceed eight, a "magic number" in chemistry even before Lewis formalized it in his octet theory, than from any compelling logic. This, of course, ignored the fact that the set of five orbitals has a capacity of ten electrons, and thus there should be ten families of transition elements. Although not fully agreed upon by all chemists, the Commission on Nomenclature of Inorganic Chemistry (1990) has recommended that numbers 1–18 be used instead of Roman numerals followed by A and B designations. Thus the three triads now appear in separate groups (8, 9, and 10) and this perhaps is as it should be since the chemistry of iron is not more similar to that of nickel than it is to that of chromium.

Group IIB (11)

The heavier congeners, molybdenum and tungsten, have a less interesting redox chemistry. The chemistry of these elements in iso- and heteropoly acids, multiple bonds, etc. is generally of more interest (see Chapter 16).

The heavier congeners, molybdenum and tungsten, have a less interesting redox chemistry. The chemistry of these elements in iso- and heteropoly acids, multiple bonds, etc. is generally of more interest (see Chapter 16).
This together with their market value, has led to the term "coinage metals" for the members of this family. The electron configuration of Group 11B (12) is as follows:

\[
\begin{align*}
\text{Cu}^{2+} & : \text{Cu}^+ & : \text{Cu}^2+ \\
\text{Ag}^{1+} & : \text{Ag}^{2+} & : \text{Ag}^+ \\
\text{Au}^{3+} & : \text{Au}^{2+} & : \text{Au}^+ \\
\end{align*}
\]

Although copper forms compounds in any of four different oxidation states, only the +2 state enjoys much stability. The +3 state is generally too strong an oxidizing agent, though Cu(III) has been found in biological systems. Complexation by peptides can lower the reduction emf to the range 0.45-1.05 V. The free +1 ion will spontaneously disproportionate (+0.52 V > +0.16 V). Copper(I) compounds are known, however, in the form of complexes such as \([\text{Cu(CN)}_2]^+\), \([\text{CuCl}_2]^+\), and \([\text{CuCl}_4]^-\) or as the sparingly soluble halides.

Silver forms stable compounds only in the +1 oxidation state; all higher states being strong oxidizing agents. Even silver(I) is not overly stable, as shown by the large reduction potential (0.80 V), and has become a common oxidizing agent in inorganic and organometallic syntheses. The photosensitized reduction of silver halides is, of course, the basis of photography.

None of the oxidation states occurring in gold compounds can really be said to be thermodynamically stable. Gold(II) and gold(I) are subject to disproportionation. The reduction potential of gold(III) to gold(I) is marginally above that necessary to oxidize 
\[
\text{Hg}^{2+} \rightarrow \text{Hg}^+ + \text{e}^-
\]

Water, but the presence of complexing agents can stabilize +1 and +3, with the latter usually being more stable.

The characteristic oxidation state of the lanthanide elements is +3. The universal -1 configuration, however, the stable +3 cations of both the lanthanides and actinides, however, there is strict regularity; all have 5d^10, 6s^1, or 7s^2, 5d^10 configurations.

In many ways the chemical properties of the lanthanides are repeated by the actinides. Much use of this similarity was made during the early work on the chemistry of the synthetic actinides. Given that these elements were often handled in very small quantities and are radioactive, prediction of their properties by analogy to the lanthanide series proved very helpful. On the other hand, it should not be thought that the actinide series is merely a replay of the lanthanides. There are several significant differences between the two series related principally to the differences between the 4f and 5f orbitals.

The characteristic oxidation state of the lanthanide elements is +3. The universal preference for this oxidation state together with the notable similarity in size led to great difficulties in the separation of these elements prior to the development of 

The ability of mercury to form an Hg-Hg bond (cadmium to a much less extent) plus a greater tendency to form coordination compounds compared to the other members of the group increases the complexity of its Latimer diagram somewhat, but not much. Its electrochemistry is straightforward, with both mercury(I) and mercury(II) being stable in aqueous solution.

**The Lanthanide and Actinide Elements**

This section includes the chemistry of the elements La to Lu, and Ac to Lr. In addition, some speculations are made concerning heavier elements that may be synthesized in the future.

The lanthanides are characterized by gradual filling of the 4f subshell and the actinides by filling of the 5f subshell. The relative energies of the 4d and 5d (n = 1) orbitals are very similar and sensitive to the occupancy of these orbitals (Fig. 14.3).

The electron configurations of the neutral atoms (see Table 2.1) thus show some irregularities. Notable is the stable 4f^1 configuration found in Eu, Gd, Am, and Cm. For the +3 cations of both the lanthanides and actinides, however, there is strict regularity; all have 5d^10, 6s^1, or 7s^2, 5d^10 configurations.

In many ways the chemical properties of the lanthanides are repeated by the actinides. Much use of this similarity was made during the early work on the chemistry of the synthetic actinides. Given that these elements were often handled in very small quantities and are radioactive, prediction of their properties by analogy to the lanthanide series proved very helpful. On the other hand, it should not be thought that the actinide series is merely a replay of the lanthanides. There are several significant differences between the two series related principally to the differences between the 4f and 5f orbitals.

**Stable Oxidation States**

The characteristic oxidation state of the lanthanide elements is +3. The universal preference for this oxidation state together with the notable similarity in size led to great difficulties in the separation of these elements prior to the development of 

\[
\text{Zn}^{2+} \rightarrow \text{Zn}^+ \rightarrow \text{Zn}^{2+} \\
\text{Cu}^{2+} \rightarrow \text{Cu}^+ \rightarrow \text{Cu}^{2+} \\
\text{Ag}^{1+} \rightarrow \text{Ag}^{2+} \rightarrow \text{Ag}^+ \\
\text{Au}^{3+} \rightarrow \text{Au}^{2+} \rightarrow \text{Au}^+ \\
\text{Hg}^{2+} \rightarrow \text{Hg}^+ \rightarrow \text{Hg}^{2+} \\
\]

- Most chemists would consider the elements La and Ac to be of Group 3 and not lanthanides or actinides. However, it has been argued, based on electronic configurations that Eu and Ac are more properly placed in the periodic table as the first members of the lanthanide and actinide series and that Lu and Lr are best placed in Group 3. See Chapter 2 and Jensen, W. B. J. Chem. Educ. 1982, 39, 654-656.

- Compare the discussion of a similar problem in Section 2 orbitals in transition metals, Chapter 3.
Despite their propensity to form stable +3 cations, the lanthanides do not closely resemble transition metals such as chromium or cobalt. The free lanthanide metals are more reactive and in this respect are more similar to the alkali or alkaline earth metals than to most of the transition metals. They all react with water with evolution of hydrogen. One difference lies in the sum of the first three ionization energies—from 3500 to 4200 kJ mol\(^{-1}\) (36 to 44 eV) for the lanthanides, compared with 5230 kJ mol\(^{-1}\) (54.2 eV) for Cr\(^{3+}\) and 5640 kJ mol\(^{-1}\) (58.4 eV) for Co\(^{3+}\). A second factor is the heat of atomization necessary to break up the metal lattice: Transition metals with \(d\) electrons available for bonding are much harder and have higher heats of atomization than the alkali, alkaline earth, and lanthanide metals.

Two lanthanides, europium and ytterbium, are particularly similar to the alkaline earth elements. They have the lowest enthalpies of vaporization and the largest atomic radii of the lanthanides (Fig. 14.4), making them more similar to barium in their properties than to typical lanthanides. Presumably these elements donate only two electrons to the bonding orbitals ("bands") in the metal and may be said to be in the "divalent" state in the metal unlike their congeners. These same two elements resemble the alkaline earth metals in another respect—they dissolve in liquid ammonia to yield conducting blue solutions (see Chapter 10).

Although +3 is the most characteristic oxidation state of the lanthanides (the only one found in nature), the +2 oxidation state is of some importance.\(^{39}\) As might be anticipated from the above discussion, Eu\(^{2+}\) and Yb\(^{2+}\) are the most stable divalent species. These ions are somewhat stabilized by \(4f^4\) and \(4f^14\) configurations (from exchange energy) enjoying the special stability of half-filled and filled subshells.\(^{40}\) Aqueous solutions of Eu\(^{2+}\), Yb\(^{2+}\), and Sm\(^{2+}\) can be prepared, but all reduce water over time (Yb\(^{2+}\) and Sm\(^{2+}\) rapidly) and all are readily oxidized by oxygen. Other lanthanides (Nd, Dy, Tb, Ho) form M(II) compounds which are stable as solids (Table 14.3). Not all "divalent" lanthanide compounds are truly such; i.e., some do not contain M(II) ions (see above). For example, La\(_2\), Ce\(_2\), etc. have been formulated as M\(^{3+}\)(I\(^\text{I}\))\(^2+\). Although this formulation appears strange because of the free electron, it is not more so than Na\(^+\)\(e^\text{-}\) encountered in Chapter 10 or \([\text{K(crown-6)\(e\)(solvent)}]\) in Chapter 12. However, in contrast to the electrolytic behavior of these electrides in ammonia or crown ether solution, the lanthanide diiodides have delocalized electrons and are actually considered to be metallic phases.\(^{41}\)

Oxidation states higher than +3 are exhibited by Ce, Pr, and Tb, but only Ce\(^{4+}\) is stable (kinetically) in water. It is a very strong oxidizing agent in aqueous solution (\(E^\circ = 1.74\) V) and is used as a volumetric standard in redox titrations. Some of its salts [e.g., cerium(IV) ammonium nitrate, cerium(IV) sulfate] find application in


\(^{40}\) Exchange energy associated with nearly half-filled and filled configurations of samarium(II) and thulium(II) is not thought to contribute much to the stability of halide salts. See Johnson, D. A. J. Chem. Educ. 1988, 57, 475–477 for thermodynamic considerations.

Table 14.3

<table>
<thead>
<tr>
<th>Symbol</th>
<th>2+</th>
<th>3+</th>
<th>4+</th>
<th>5+</th>
<th>6+</th>
<th>7+</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ce</td>
<td>+</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pr</td>
<td>+</td>
<td>(+)</td>
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<tr>
<td>Nd</td>
<td>(+)</td>
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<td>Pm</td>
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<td>Sm</td>
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<td>Eu</td>
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<td>Gd</td>
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<td>Tb</td>
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<td>Ho</td>
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<td>Tm</td>
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<td>Yb</td>
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<tr>
<td>Lu</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

| Abbreviations: + , exists in solution; (+) , found in solid state only; (?), claimed but not substantiated. Bold face represents the most stable oxidation state. For lanthanides, see Meyer, G. Chem. Rev. 1986, 86, 95-140. For actinides, see Katz, J. J.; Morss, L. R.; Seaborg, G. T. In The Chemistry of the Actinide Elements; Katz, J. J., Seaborg, G. T., Morss, L. R., Eds.; Chapman and Hall: London, 1986; Vol. 2, Chapter 14.

organic chemistry as oxidizing agents. Although all of the actinides exhibit a +3 oxidation state, it is not the most stable one for several of them. Thorium(III) and protactinium(III) exist in the solid state only, and although uranium(III), neptunium(III), and plutonium(III) have an aquaoms chemistry, greater stability is found in higher oxidation states. In contrast to the lanthanides, the actinides utilize their f electrons more readily and thus exhibit positive oxidation states equal to the sum of the 7s, 6d, and 5f electrons: Ac(III), Th(IV), Pa(V), U(VI), and Np(VII). As in the first transition series, this trend reaches a maximum at +7, and there is a tendency toward lower maximum oxidation states (see Table 14.3). A reduced tendency to use 5f electrons as one progresses along the actinide series is apparent: U(III) may be oxidized with water, Np(III) requires air, and Pu(III) requires a strong oxidizing agent such as chlorine. The +4 state is the highest known for curium, berkeliunm, and californium, and beyond these elements only +2 and +3 oxidation states have been substantiated. Neptunium is actually more stable in solution as Neptunium(IV) than Neptunium(III) (cf. Ytterbium(III)).

The aqueous chemistry of the +3 and +4 actinide ions is complicated by their tendency to hydrolyze and polymerize. Higher oxidation states are represented by stable actinyl ions (e.g., M(IV), MO(IV), and MO(VI)).

As a consequence of the poor shielding of the 4f and 5f electrons, there is a steady increase in effective nuclear charge and consequent reduction in size with increasing atomic number in each series. Although this trend is apparent from the atomic radii (Fig. 14.4), it is best shown by the radii of the +3 cations (Fig. 14.5). There are two noticeable differences between the two series of ions: (1) although the actinide contraction initially parallels that of the lanthanides, the elements from curium on are smaller than might be expected, probably resulting from poorer shielding by 5f electrons in these elements; (2) the lanthanide curve consists of two very shallow arcs with a discontinuity at the spherically symmetrical Gd(III) ion. A similar discontinuity is not clearly seen at Cm(III).

A consequence of the lanthanide contraction is that when holmium is reached, the increase in size from n = 5 to n = 6 has been lost and Ho(III) is the same size as the much lighter Y(III) (104 pm) with correspondingly similar properties. The contraction does not proceed sufficiently far to include Sc(III) (83 pm), but its properties may be extrapolated from the lanthanide series, and in some ways it provides a bridge between the strictly lanthanide metals and the transition metals.

43 See Chapter 18 for relativistic considerations.
44 For other consequences, see Chapter 18.
The f orbitals

The f orbitals have not been considered previously except to note that they are ungerade (Chapter 2) and that they are split by an octahedral field into three levels, $t_{2g}$, $e_g$, and $a_g$ (Chapter II). A complete set of seven f orbitals is shown in Fig. 14.6. As with the d orbitals, there is no unique way of representing them, nor is there even a way which is optimum for all problems. Thus Fig. 14.6 presents two sets, a "general set" and a "cubic set." The latter is advantageous in considering the properties of the orbitals in cubic (i.e., octahedral and tetrahedral) fields.

As with other orbitals of the same type (same l), the f and d orbitals do not differ in the angular part of the wave function but only in the radial part. The f orbitals have a radial node which the d orbitals lack, but this is not likely to be of chemical significance. The chief difference between the two seems to depend on the relative energies and spatial distributions of the orbitals. The f orbitals populated in the lanthanides are sufficiently low in energy that the electrons are seldom ionized or shared (hence the rarity of lanthanide +4 species). Furthermore, the f electrons seem to be buried so deeply the atom that they are unaffected by the environment to any great degree. This point will be discussed further below. In contrast, the f electrons, at least in the earlier elements of the series, Th to Bk, are available for bonding, allowing oxidation states up to +7. In this respect these electrons resemble d electrons of the transition metals. Because of the higher oxidation states in the early actinides, it was once popular to assign these elements to transition metal families: thorium to VB, protactinium to VB (5), and uranium to VIB (6). In 1944 Seaborg suggested that this arrangement was incorrect and that the elements following actinium form a new "inner transition" series analogous to the lanthanides. This suggestion, known as the "actinide hypothesis," was useful in elucidating the properties of the heavier actinides and was fully substantiated by their behavior in the earlier actinides. Nevertheless, we should not lose sight of the fact that in the earlier actinides the 5f electrons are available for use and that these elements do show certain resemblances to the transition metals.

Absorption Spectra of the Lanthanides and Actinides

The absorption spectra of the lanthanide +3 cations are shown in Fig. 14.7. These spectra result from f-f transitions analogous to the d-d transitions of the transition metals. In contrast to the latter, however, the broadening effect of ligand vibrations is minimized because the f orbitals in the lanthanides are buried deep within the atom. Absorption spectra of the lanthanide cations are thus typically sharp and line-like as opposed to the broad absorptions of the transition metals.

The absorption spectra of a number of trivalent actinide ions are shown in Fig. 14.8. They may be conveniently divided into two groups: (1) Am$^{3+}$ and heavier actinides which have spectra that resemble those of the lanthanides; and (2) Pu$^{3+}$ and lighter actinides which have spectra that are similar to those of the lanthanides in some ways but exhibit broadening resembling that seen in the spectra of the transition metal ions. Apparently the greater "exposure" of the 5f orbitals in the lighter actinide elements results in a greater ligand-metal orbital interaction and some broadening.

Seaborg was warned not to publish his new periodic table because it would ruin his scientific reputation. He is quoted as saying sometime later, "I didn't have any scientific reputation so I published it anyway." For a discussion of this and other interesting historical developments in actinide chemistry, see George Kaufman's review, "Beyond Uranium" in Chem. Eng. News 1990, 68(47), 18-29.
Some Descriptive Chemistry of the Metals

Fig. 14.7 Absorption spectra of Pr³⁺, Nd⁴⁺, Pm⁴⁺, Sm¹⁺, Eu²⁺, Tb¹⁺, Dy¹⁺, Ho¹⁺, Er¹⁺, Tm¹⁺, Yb¹⁺ in dilute acid solution. Compare the sharpness of these with that of Ti⁴⁺ (Fig. 11.8), a first-row transition element. [Modified from Carnall, W. T.; Crosswhite, H. M. In The Chemistry of the Actinide Elements; Katz, J. J.; Seaborg, G. T.; Morris, L. R., Eds.; Chapman and Hall: New York, 1986; Vol. 2. Reproduced with permission.]

Fig. 14.8 Absorption spectra of trivalent actinide ions in dilute acid solution. [From Carnall, W. T.; Crosswhite, H. M. In The Chemistry of the Actinide Elements; Katz, J. J.; Seaborg, G. T.; Morris, L. R., Eds.; Chapman and Hall: New York, 1986; Vol. 2. Reproduced with permission.]

The Lanthanide and Actinide Elements

Magnetic Properties of the Lanthanides and Actinides

We observed in Chapter 11 that the paramagnetic moment of the lanthanide ions (Table 11.25) could be calculated from the expression, $g(JL + 1)J$ (Eq. 11.41). This approach is successful because spin-orbit coupling is large and only the ground state is populated. Ligand field effects are small because the 5f orbitals do not effectively interact with the ligands of the complex. For Sm³⁺ and Eu²⁺, spin-orbit coupling is not large enough to prevent occupation of the first excited state at room temperature, but if one includes this occupation in the calculation, good results are obtained.

The magnetic properties of the actinides are quite complex. Whereas the spin-only formula (ligand field effects large compared to spin-orbit coupling) gives reasonable results for the first-row transition compounds, and Eq. 11.41 (spin-orbit coupling large compared to ligand field effects) gives good results for the lanthanides, neither formula is adequate for the actinides. The 5f electrons of the actinides interact much more with ligands than do the 4f electrons of the lanthanides. As a result the spin-orbit coupling and ligand field effects are of comparable magnitude. Experimental values of the paramagnetic moment vary with temperature and in general are lower than those of the corresponding lanthanides.
The lanthanides behave as typical hard acids, bonding preferentially to fluoride and oxygen donor ligands. In the presence of water, complexes with nitrogen, sulfur, and halogen (except F⁻) donors are not stable. The absence of extensive interaction with the 4f orbitals minimizes ligand field stabilization energies. The lack of LFSE reduces overall stability but on the other hand provides a greater flexibility in geometry and coordination number because LFSE is not lost, for example, when an octahedral complex is transformed into trigonal prismatic or square antiprismatic geometry. Furthermore, the complexes tend to be labile in solution. Table 14.4 presents a summary of typical transition metal complexes.

One noticeable difference is the tendency toward increased coordination numbers in the lanthanide and actinide complexes. This is shown most readily by the early (and hence largest) members of the series when coordinated to small ligands. The structures of the crystalline lanthanide halides, MX₃, exhibit this effect. For lanthanum, coordination number 9 is obtained for all of the halides except LaF₃, whereas for lutetium, only the fluoride exhibits a coordination number greater than 6. The coordination number of the lanthanide ions in hydrated salts in which the anion is a poor ligand tends to be 9 as shown by many X-ray studies. The nine water molecules in [M(H₂O)₉]³⁺ are typically found in a tripodal trigonal prismatic arrangement. The degree of hydration in solution, however, has long been debated and many early experiments led to the conclusion that the degree of hydration decreases in progression along the series. Evidence came from several kinds of data such as the partial molar volumes of the hydrated lanthanide +3 ions.⁴⁷ As the central ion decreases in size, the partial molar volume decreases as expected until crowding of the ligands becomes too intense. At this point (Sm), a water molecule is expelled from the coordination sphere and the molar volume increases temporarily before resuming (Tb) a steady decrease (Fig. 14.9). Lanthanide lifetime studies have been interpreted to give formulations for hydrated Eu³⁺ and Tb³⁺ ions in solution of [Eu(H₂O)₉]³⁺ and [Tb(H₂O)₆]³⁺.⁴⁸ In these studies the experimental reciprocal lifetimes of ions in their excited states (r⁻¹) can be correlated to the number of water molecules in the first coordination sphere (Fig. 14.10). It was suggested that the larger early lanthanides have coordination numbers of 10, while the smaller, later lanthanides have coordination numbers of 9. As shown in Fig. 14.10, the number of coordinated water molecules diminishes as they are replaced by oxygen chelating ligands such as nitrikoacetate (nita) and ethylenediaminetetraacetate (edta). Recent neutron diffraction work, however, is in agreement with coordination numbers of 9 and 8 for the early lanthanides and 8 for the later ones.⁴⁹

The early separation of the lanthanides was beset by difficulties as a result of the similarity in size and charge of the lanthanide ions. The separations were generally based on slight differences in solubility, which were exploited through schemes of fractional crystallization. The differences in behavior resulting from a decrease in ion

**Table 14.4**

<table>
<thead>
<tr>
<th>Metal orbitals</th>
<th>Lanthanide ions</th>
<th>First series transition metal ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>4f</td>
<td>90-95 pm (1.06-0.85 Å)</td>
<td>3d</td>
</tr>
<tr>
<td>Ionic radius</td>
<td>6, 7, 8, 9</td>
<td>4, 6</td>
</tr>
<tr>
<td>Coordination</td>
<td>Trigonal prism, square</td>
<td>Strong metal-ligand orbital interaction</td>
</tr>
<tr>
<td>Coordination</td>
<td>coordination</td>
<td>Bond direction</td>
</tr>
<tr>
<td>numbers</td>
<td>polyhedra</td>
<td>Bond strength</td>
</tr>
<tr>
<td>Bonding</td>
<td>Little metal-ligand orbital interaction</td>
<td>Bond strengths</td>
</tr>
<tr>
<td>Bond direction</td>
<td>Little preference in bond direction</td>
<td>Bond strengths correlate with electropositivity, decreasing in the order: F⁻, OH⁻, H₂O, NO₃⁻, Cl⁻</td>
</tr>
<tr>
<td>Bond strengths</td>
<td>Bond strengths determined by orbital interaction, normally decreasing in following order: CN⁻, NH₃, H₂O, OH⁻, F⁻</td>
<td></td>
</tr>
<tr>
<td>Solution</td>
<td>Ionic, rapid ligand exchange</td>
<td>Often covalent; covalent complexes may exchange slowly</td>
</tr>
</tbody>
</table>

radius along the series are commonly attributed to a decrease in basicity, reflected by a decrease in solubility of the hydroxides, oxides, carbonates, and oxalates. The fractional crystallization and fractional precipitation methods are extremely tedious and have been replaced by more efficient techniques.

The decrease in basicity (or more realistically, the increase in acidity) of the lanthanides provides an opportunity for employing coordinating ligands to effect separation. Other things being equal, the more acidic a cationic species the more readily it will form a complex. In practice, the lanthanides are placed on an ion-exchange resin and eluted with a complexing agent, such as citrate ion or a-hydroxyisobutyrate ion. Ideally, the complexes should come off the column with minimal overlapping of the various bands (Fig. 14.11). Such processes have increased the amounts of lanthanides available and opened up many possibilities for commercial use, e.g., rare-earth phosphors for color television. The initial separations of many of the actinide elements as they were synthesized were effected by similar methods.

**Lanthanide Chelates**

The stability of lanthanide complexes can be increased by means of the chelate effect, and much early work was directed toward the elucidation of the stability of the lanthanide chelates. The fractional crystallization and fractional precipitation methods have been replaced by more efficient techniques. Other things being equal, the more acidic a cationic species the more readily it will form a complex. In practice, the lanthanides are placed on an ion-exchange resin and eluted with a complexing agent, such as citrate ion or a-hydroxyisobutyrate ion. Ideally, the complexes should come off the column with minimum overlapping of the various bands (Fig. 14.11). Such processes have increased the amounts of lanthanides available and opened up many possibilities for commercial use, e.g., rare-earth phosphors for color television. The initial separations of many of the actinide elements as they were synthesized were effected by similar methods.

**Figure 14.10** A plot of reciprocal luminescence lifetime ($t^{-1}$) vs. mole fraction of H$_2$O for D$_2$O/H$_2$O Tb(III) solutions. Here we see a coordination number of 9 for Tb(III) in contrast to a coordination number of 8 shown in Fig. 14.9. Experiments like these suggest that perhaps the early lanthanides have coordination numbers of 10 while the later ones have coordination numbers of 9. In the presence of a quadridentate ligand, nitrilotriacetate (nta), four water molecules are lost and the number of coordinated water molecules drops to five. When ethylenediaminetetraacetate (edta), a hexadentate ligand, is added, the number of water molecules drops to three. [From Horrocks, W. DeW.; Sudnick, D. R. Acc. Chem. Res. 1981. 14, 344-392. Reproduced with permission.]

Lanthanide Chelates

The stability of lanthanide complexes can be increased by means of the chelate effect, and much early work was directed toward the elucidation of the stability of the lanthanide chelates. The fractional crystallization and fractional precipitation methods have been replaced by more efficient techniques. Other things being equal, the more acidic a cationic species the more readily it will form a complex. In practice, the lanthanides are placed on an ion-exchange resin and eluted with a complexing agent, such as citrate ion or a-hydroxyisobutyrate ion. Ideally, the complexes should come off the column with minimum overlapping of the various bands (Fig. 14.11). Such processes have increased the amounts of lanthanides available and opened up many possibilities for commercial use, e.g., rare-earth phosphors for color television. The initial separations of many of the actinide elements as they were synthesized were effected by similar methods.

**Figure 14.11** Elution of trivalent lanthanide and actinide ions on a Dowex 50 cation-exchange resin with an ammonium a-hydroxyisobutyrate eluant. The band for Lr$^{3+}$ is predicted. [From Katz, J. J.; Morss, L. R.; Seaborg, G. T. In The Chemistry of the Actinide Elements: Katz, J. J.; Morss, L. R.; Seaborg, G. T., Eds.; Chapman and Hall: New York, 1986; Vol. 2, pp 133-1133. Reproduced with permission.]

Unfortunately, about half of the ligands that have been studied in complexes with all of the lanthanides show discrepancies from the simple picture presented above and must be considered type 2 ligands. In general, these may be characterized as having stability/atomic number curves similar to type 1 for the lighter lanthanides, usually with a break at gadolinium. The behavior of the heavier lanthanides is variable, however, often showing essentially no change in stability, sometimes even showing decreased stability with increasing atomic number. Furthermore, the placement of models. Figure 14.12 portrays the relative stabilities of various lanthanide chelates. Two types of behavior may be noted: (1) "ideal" behavior exemplified by chelates of ethylenediaminetetraacetate (edta) and the closely related trans-1,2-cyclohexanediiminetetraacetate (chda) and (2) "nonideal" behavior as exemplified by diethylenetriaminepentaacetate (dtpa) complexes. The former conforms to our expectations based on simple electrostatic or acid-base concepts of size and charge to change in stability with increasing atomic number. The discontinuity in crystal radii at this ion or, more plausibly, both may reflect small LFSEs associated with splitting of the partially filled f orbitals. The position of yttrium on these stability curves is that expected on the basis of the size—i.e., it falls very close to dysprosium. Unfortunately, about half of the ligands that have been studied in complexes with all of the lanthanides show discrepancies from the simple picture presented above and must be considered type 2 ligands. In general, these may be characterized as having stability/atomic number curves similar to type 1 for the lighter lanthanides, usually with a break at gadolinium. The behavior of the heavier lanthanides is variable, however, often showing essentially no change in stability, sometimes even showing decreased stability with increasing atomic number. Furthermore, the placement of
Some Descriptive Chemistry of the Metals

yi trium on these curves is variable, often falling with the pre-gadolinium elements rather than immediately after gadolinium as expected on the basis of size and charge alone.

Several factors have been advanced to account for the unusual behavior of the type 2 complexes. First, ligand field effects might be expected to influence the position of yttrium, since it has a noble gas configuration with no d or f electrons to provide LFSE, in contrast to all of the lanthanide ions except Eu³⁺ and Lu³⁺. Obviously, however, this is insufficient to account for the variable results for the Th³⁺-Ln³⁺ complexes. A second factor is the possibility of coordination numbers greater than 6, which may also vary along the series. Thus it is entirely possible that an effect similar to that seen previously for the degree of hydration is taking place. At some point along the series the decrease in metal ion size might cause the expulsion of one of the donor groups from a multidentate ligand and decreased stability. This point could be reached at different places along the series depending upon the geometry and steric requirements of the multidentate ligand. It should be remembered that the thermodynamic stability of complexes in aqueous solution reflects the ability of the ligand to compete at different places along the series depending upon the geometry and steric requirements of the multidentate ligand. For this reason it is not surprising that the situation is rather complicated.

Lanthanide and actinide complexes, La₅(L₅)₃ and An₅(L₅)₃, of sterically hindered β-diketonates [e.g., \text{Me₆C⁶H₃(OC)(O)C(Me)₃}²⁻ (dpm) and \text{F₆C₆H₃C₂F₆(OC)(O)C(Me)₃})²⁻ (fod)] are of considerable interest because of their volatility. Despite their high molecular weights, they have measurable vapor pressures at temperatures below the boiling point of water. This volatility has been exploited in

separating the lanthanides by means of gas chromatography. In addition they have applications as antiknock additives; in trace analysis, solvent extraction, and vapor plating of metals; and as homogeneous catalysts.

Perhaps β-diketonates such as dpm and fod have attracted greatest attention as NMR shift reagents. In 1969 Hinckley discovered that the complicated proton NMR spectrum of cholesterol is greatly simplified in the presence of Eu(dpm)₃. Simplification occurs because chemical shifts are induced by the paramagnetic lanthanide ion. An example of the effect is shown in Fig. 14.13. The proton NMR spectrum of heptanol, without a shift reagent, is very complicated because of accidental overlap of signals (Fig. 14.13a). In contrast, a spectrum of Eu(dpm)₃ in heptanol shows the resonance of each set of equivalent nuclei as independent signals (Fig. 14.13b). Although the availability of high-field NMR instruments has reduced the need for NMR shift reagents in organic chemistry, applications to biological systems (lipid bilayers, proteins, ion mobility) continue to grow.

At one time it was considered extremely unlikely that there would be any significant chemistry for elements with atomic numbers greater than about 100. The nuclear stability of the transuranium elements decreases with atomic number, so that the half-lives for the heaviest elements (Table 14.5) become too short for fruitful chemical studies (i.e., t½ = seconds). However, advanced chemical techniques have helped
Half-lives of selected actinide nuclides:

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic number</th>
<th>Mass number</th>
<th>Half-life</th>
</tr>
</thead>
<tbody>
<tr>
<td>Actinium</td>
<td>89</td>
<td>227</td>
<td>21.8 yr</td>
</tr>
<tr>
<td>Thorium</td>
<td>90</td>
<td>232</td>
<td>1.41 x 10^7 yr</td>
</tr>
<tr>
<td>Protactinium</td>
<td>91</td>
<td>231</td>
<td>3.28 x 10^7 yr</td>
</tr>
<tr>
<td>Uranium</td>
<td>92</td>
<td>238</td>
<td>4.47 x 10^7 yr</td>
</tr>
<tr>
<td>Neptunium</td>
<td>93</td>
<td>237</td>
<td>2.14 x 10^7 yr</td>
</tr>
<tr>
<td>Plutonium</td>
<td>94</td>
<td>239</td>
<td>24.58 yr</td>
</tr>
<tr>
<td>Americium</td>
<td>95</td>
<td>241</td>
<td>437 yr</td>
</tr>
<tr>
<td>Curium</td>
<td>96</td>
<td>248</td>
<td>3.4 x 10^6 yr</td>
</tr>
<tr>
<td>Berkelium</td>
<td>97</td>
<td>249</td>
<td>320 days</td>
</tr>
<tr>
<td>Californium</td>
<td>98</td>
<td>249</td>
<td>330 yr</td>
</tr>
<tr>
<td>Einstenium</td>
<td>99</td>
<td>253</td>
<td>20.5 days</td>
</tr>
<tr>
<td>Flerovium</td>
<td>100</td>
<td>257</td>
<td>100 days</td>
</tr>
<tr>
<td>Mendeleevium</td>
<td>101</td>
<td>256</td>
<td>1.27 h</td>
</tr>
<tr>
<td>Nobelium</td>
<td>102</td>
<td>255</td>
<td>3.1 min</td>
</tr>
<tr>
<td>Lawrencium</td>
<td>103</td>
<td>256</td>
<td>31 s</td>
</tr>
<tr>
<td>Rutherfordium</td>
<td>104</td>
<td>257</td>
<td>4.3 s</td>
</tr>
<tr>
<td>Hahnium</td>
<td>105</td>
<td>260</td>
<td>1.5 s</td>
</tr>
<tr>
<td>Unnilhexium</td>
<td>106</td>
<td>263</td>
<td>0.9 s</td>
</tr>
<tr>
<td>Unnilseptium</td>
<td>107</td>
<td>262</td>
<td>4.7 ms</td>
</tr>
</tbody>
</table>

The predicted island of stability at atomic number 114 and 184 neutrons may run northeast from lead represents the decreasing stability of the actinide series. The stability is proportional to the elevation of the islands above "sea level." The periods of nuclei in the regions of the "magic numbers" have been synthesized. Claims for element 116 have not been confirmed. There has been much speculation over the possibility of stable species of even higher atomic number. Theoretical calculations on the stability of nuclei predict minimal stability for atomic numbers 80, 82, 114, and 164. The prediction is borne out for 94Sm, which has more stable isotopes than any other element, and for 212Pb and 238U, which are the heaviest elements with nonradioactive isotopes. The stability of nuclei in the regions of the "magic numbers" has been described allegorically by Seaborg as mountains in a sea of instability, as shown in Fig. 14.14. The expected stability is proportional to the elevation of the islands above "sea level." The periods of nuclei running "northwest" from lead represent the decreasing stability of the actinide elements. The predicted island of stability at atomic number 114 and 184 neutrons may be accessible with new methods that make it possible to "jump" the unstable region and form these nuclei directly. Thus one might expect to find a group of relatively stable nuclei in the region of elements 113-115. The possibility of jumping to the next island (not shown) at atomic number 164 provides even more exciting (and improbable) possibilities to extend our knowledge of the chemistry of heavy elements.

Lawrencium completes the actinide series and fills the 5f set of orbitals. Rutherfordium and seaborgium were expected to be congeners of hafnium and tungsten and to be receiving electrons into the 6d orbitals. This process should be complete at element 112 (eka-mercury), and then the 7p orbitals would fill from element 113 to element 118, which should be another noble gas element. Elements 119, 120, and 121 should belong to Groups IA (1), IIA (2), and IIB (3), respectively. The first two will undoubtedly have 6p° and 6s° configurations. If the following elements parallel their lighter congeners, we might expect 121 (eka-actinium), to accept one 7d electron and the following elements (eka-actinides) to exceed with the filling of 6f° orbitals. Unfortunately, we know very little about the relative energy levels for these hypothetical atoms except that they will be extremely close. Thus, although Fig. 2.10 would predict the order of filling: 8s, 5f°, 6f°, 7d°, etc., it is not known whether this would be followed or not. Calculations indicate that the levels are so close together that "mixed" configurations (analogous to the 5g°/5f° configurations found in the lanthanides) such as 8s°/5f° or 8s°/6f° may occur. For this reason it does not seem profitable to speculate on the separate existence of the 5g° and 6f° configurations. Seaborg has suggested that the two series be combined into a larger series of 32 elements called the supertransactinides. His revised form of the periodic chart is shown in Fig. 14.15. The 6f° and 5g° elements form an extra long "inner transition" series followed by (presumably) a series of ten transition elements (eka-actinides) to proceed with the filling of 6d° orbitals. Unluckily, we know very little about the relative energy levels for these hypothetical atoms except that they will be extremely close. Thus, although Fig. 2.10 would predict the order of filling: 8s, 5f°, 6f°, 7d°, etc., it is not known whether this would be followed or not. Calculations indicate that the levels are so close together that "mixed" configurations (analogous to the 5g°/5f° configurations found in the lanthanides) such as 8s°/5f° or 8s°/6f° may occur. For this reason it does not seem profitable to speculate on the separate existence of the 5g° and 6f° configurations. Seaborg has suggested that the two series be combined into a larger series of 32 elements called the supertransactinides. His revised form of the periodic chart is shown in Fig. 14.15. The 6f° and 5g° elements form an extra long "inner transition" series followed by (presumably) a series of ten transition elements (eka-actinides) to exceed with the filling of 6d° orbitals, etc. Magic number nucleus 164 would thus be a congeners of lead (6d°-lead).
While much of the preceding is speculative, it is no more speculative chemically than Mendeleev's predictions of gallium (eka-aluminum) and germanium (eka-silicon). The speculation centers on the possible or probable stability of nuclei with up to twice as many protons as the heaviest stable nucleus. The latter falls outside the realm of inorganic chemistry, but the synthesis and characterization of some of these elements would be most welcome.

Several workers have predicted the properties of certain translawrencium elements. For example, the "inert pair effect" should be accentuated making the most stable oxidation states of eka-thallium, eka-lead, and eka-bismuth +1, 4-2, and 4-3, respectively. Relativistic effects become so important for these elements that eka-lead, with its 7p^2 configuration, may be thought of as having a closed shell. Its boiling point has been predicted to be 147 °C, based on heat of sublimation extrapolations (Fig. 14.16) and application of Trouton's rule. The possibility of forming elements with atomic numbers in the region of 164 is of considerable interest. As discussed in Chapter 18, elements following the completion of each new type of subshell (e.g., 2p^6, 3d^10, 4f^14) show "anomalous" properties, and thus the chemical properties of di-lead should be equally interesting.

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Problems

14.1 Flintkote has a smaller atomic radius than cesium and radium is smaller than barium. Explain. (See Pytklko, P. Chem. Rev. 1988, 88, 563-594.)

14.2 Account for the fact that a 27% contraction of metal occurs for 3d M (I)3+ ions (Se + to Cu3+) but only a 17% contraction occurs in the 5d series (Cu3+ to Au3+). (See Mason, J. I. Chem. Educ. 1988, 65, 17-20.)


14.4 Pyridinium chlorochromate and pyridinium dichromate are widely used in organic synthesis as oxidizing agents. What are the formulas and structures for these reagents? What advantages might they have over more conventional oxidizing agents such as potassium dichromate or potassium permanganate?

14.5 Ruthenium and osmium, unlike iron, form compounds with the metal in the +8 oxidation state. Can you think of a mechanism that achieves a +8 oxidation state in some of its compounds?

14.6 Compounds of iron exist in which there are 0, 1, 2, 3, 4, and 5 unpaired electrons. Find an example for each spin state. Classify these complexes as low spin or high spin.

14.7 The tendency of a metal ion to form compounds of high coordination numbers decreases across the first row of the transition elements. Explain.

14.8 Chromium(VI) oxide is strongly acidic; vanadium(V) oxide is amphoteric; titanium(IV) oxide is inert, and scandium(III) oxide is basic with some amphoteric properties.
   a. Explain the relative acidities of these oxides.
   b. Write chemical equations which show the amphoteric nature of vanadium(V) and scandium(III) oxides.

14.9 The following possible oxidizing strength of [FeOCl]+ is shown by its ability to liberate oxygen from water and to produce diiron from ammonium. Write balanced equations for these two reactions.

14.10 The following high-spin complexes of 1,2-bis(diphenylphosphino)ethane (dppe) have been prepared: [Cr(dppc)2]2-, [MnCl(dppe)], [FeCl(dppe)], and [CoCl(dppe)]. Suggest a structure for each and predict its magnetic moment. (See Hermens, A. R.; Grolim, G. S. Inorg. Chem. 1988, 27, 1775-1781.)

14.11 a. A decrease in the color of an [Fe(phen)]3+ solution is replaced by pale blue when current(V) sulfite is added to it. Explain.
   b. Whereas [Fe(tetraphenylporphyrin)][Cl3] and [Fe(tetraphenylporphyrin)][I3] are paramagnetic, [Fe(phen)]2+ is diamagnetic. Explain.

14.12 The complex, Ni(Ph2PCH2CH2PPh2)$_2$, is diamagnetic. Suggest a structure. The reactions of diphenylphosphinophosphine with nickel bromide represents one of the more unusual examples for its preparation:

\[ \text{Br} \quad \text{Br} \quad \text{Ni} \quad \text{PPh$_2$} \quad \text{PPh$_2$} \]


14.13 The reaction of cobalt(III) chloride(III) in pentane with t-methyl-acrylonitrile affords tetralene (t-butyl-cyclobutene). What is the oxidizing agent in this reaction? Express this reaction with a chemical equation. Draw the structure of the complex. Rationalize the observed magnetic moment (0.0 BM).

14.14 The anions Ni(NiSe4)$_2$ and Zn(NiSe4)$_2$ have been characterized. The nickel complex has a square planar geometry, but the zinc complex is tetrahedral. Other explanations as to why the nickel complex is not tetrahedral and why the zinc complex is not square planar.

14.15 The reaction of Ni(Cls) with bis-(dithiothreitol) disulfide [(CH$_2$)$_2$S$_2$]$_2$ has been reported. Discuss structural properties of this complex. What is the oxidizing agent in this reaction?

14.16 Pyridinium chlorochromate and pyridinium dichromate are widely used in organic synthesis as oxidizing agents. What are the formulas and structures for these reagents? What advantages might they have over more conventional oxidizing agents such as potassium dichromate or potassium permanganate?

14.17 The crystal structure of pyridinium chlorochromate has been reported. Draw structures of the cation and anion. Hydrogen bonding exists between the two ions.

14.18 Titanium reacts with chlorine to form TiCl$_3$ and TiCl$_4$. How might you separate these two products? (See Groves, T. J.; K. Int. J. Inorg. Chem. 1986, 19, 29-50.)

14.19 How would you prepare the following compounds?
   a. [Rh(NCCH$_2$CH$_2$NCS)][Cl$^-$]
   b. V(CN)$_5$(PF$_6$)$^-$
   c. [Ni(N$_2$)][VCl$_5$]

14.20 The purple color (FeCl$_3$) of bis(tetraphenylporphyrin)iron(III), exhibits an unusual coloration to certain ethylenes. Suggest a structure for this complex. Is it paramagnetic or diamagnetic? (See Hermens, A. R.; Grolim, G. S. Inorg. Chem. 1986, 25, 3126-3139.)

14.21 For many years Fe(III) has been thought to be nonmagnetic. Suggest reasons for its instability.

14.22 NaClO$_4$ reacts with triphenylphosphine to form triphenylphosphine oxide FeCl$_3$ and NaClO$_4$.

14.23 The purple color of Fe(III) has been reported to exist in some ethylenes. Suggest a structure for this complex. Is it paramagnetic or diamagnetic?

14.24 Sodium trichloroacetate reacts with sodium pentahalides to form pentahaloacetates. Suggest a structure for this complex. Is it paramagnetic or diamagnetic?

14.25 Sodium trichloroacetate reacts with sodium pentahalides to form pentahaloacetates. Suggest a structure for this complex. Is it paramagnetic or diamagnetic?
14.24 Explain the emfs of the silver halides in terms of their solubilities. What about silver acetate, which is soluble? Explain.

14.25 How can one verify, just by looking at the Latimer diagram of silver, that sodium thiosulfate is a redox agent? Explain.

14.26 When citing the Sandmeyer reaction, organic chemistry textbooks frequently write the needed copper(II) halide as CuCl₂, CuBr₂, etc. Comment.

14.27 Consider the complex ions dibromoaurate(I) and tetrabromoaurate(III). Which is more stable in aqueous solution? Explain.

14.28 Explain in terms of redox chemistry how the formation of chloro complexes stabilizes the metal ion. Why is this process (fixing) actually a redox reaction? Explain.

14.29 Predict whether each of the following reactions will proceed to the left or the right:

a. 2Fe⁺ + Sn²⁺ → 2Fe²⁺ + Sn⁴⁺
b. 2Cu⁺ + 4I⁻ → 2Cu(I) + I₂

c. 2Cu²⁺ + 4I⁻ → 2CuI(s) + I₂

d. VO₂⁺ + 2H⁺ + Cu⁺ → VO⁺² + Cu²⁺ + H₂O

14.30 Studies of radioisotopes, both natural and from fallout, in Mono Lake, California, showed that ²³⁵U, ²³⁸U, and ²³⁹Pu occur at lower levels than might have been expected. Some actinides such as ²³⁷Np, ²³⁹Pu, and ²⁴⁰Pu occurred at higher levels than expected, but others such as ²³⁷Ac and ²³⁴Am did not. The most notable characteristic of Mono Lake is its high alkalinity (pH = 10) caused by large amounts of carbonate ion (~0.3 M). Suggest factors that may be responsible for these relative abundances.

14.31 If you did not answer Problem 10.8 when you read Chapter 10, do so now.

14.32 In this chapter we have referred to the synthesis of heavy actinides. Take a trip to the library and answer the following questions:

a. Americium-243 can be obtained in kilogram quantities. Write an equation for a nuclear reaction for its preparation.

b. Nuclear reactors allow ²³⁹Pu to be produced by the ton. Write a nuclear equation for its synthesis.

c. Elements 107, 108, and 109 have been produced by a method known as “cold fusion.” Describe this method.

14.33 Plutonium-239 is an extremely radioactive alpha emitter. Shielding from alpha radiation, however, is easily accomplished with thin paper. Why then is ²³⁹Pu considered to be a dangerous isotope?

14.34 Actinide ions often form acidic solutions as a result of hydrolysis:

\[\text{M}^{n⁺} \rightarrow \text{M}^{(n-1)⁺} + \text{OH}⁻\]

Arrange the following sets of cations in order of their tendency to undergo hydrolysis:

a. Pu⁺⁴, Pu⁺³, Pu⁺²

b. Ac⁺³, U⁺³, Pu⁺³

14.35 There is no physiological process for plutonium removal from the body. Various chelating agents have been used as therapeutic reagents for its removal. One of these, shown below, is a tetracaetic ligand.

Speculate on how this ligand binds to Pu⁺³.

14.36 Paramagnetic ions may alter NMR chemical shifts by what is known as a contact shift or by what is known as a pseudocontact shift. Consult an NMR book and explain the difference.

14.37 Anhydrous LnX₃ can be prepared from the reaction of Ln metal and HgX₂. Write the balanced equation for this reaction. Can you name an attractive feature of this reaction? When aqueous solutions of CeCl₃ and CeCl₄ are concentrated, CeCl₄(H₂O)₂ and CeCl₃(H₂O)₃, respectively, crystallize. Suggest structures for both salts. Do you think heating these salts might be a good route for preparing anhydrous CeCl₃ and CeCl₄?

14.38 Goggles made of didymium (a mixture of Pr and Nd) are preferred for glassworking to absorb the glare from sodium. Explain why these goggles are more suitable than a pair made with TiO₂, for example.

14.39 Biochemists sometimes think of Ln³⁺ ions as analogues of Ca²⁺. Discuss reasons why there might be a resemblance between Ln³⁺ and Ca²⁺. Any notable differences? In what ways might biochemists exploit a resemblance?

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14.40 There has been a tendency to view the lanthanide elements as having nearly identical chemistry. In recent times this view has been criticized. Standard enthalpy changes for three reactions are plotted in Figure 14.17. How do you account for the dramatic differences shown in plots (a) and (b)? Can you provide an explanation for the "bumps" at Eu and Yb in plot (c)?

Fig 14.17 Variations in standard enthalpy changes, $\Delta H^\circ$, at 298.15 K for reactions of lanthanides: (a) $M_3^{(aq)} + \text{edta}^{(aq)} \rightarrow M(\text{edta})^{(aq)}$; (b) $M(MCl)_{2(s)} + 5\text{Cl}_2(g) \rightarrow M\text{Cl}_3(s)$; (c) $M(s) + \text{ICl}_2(g) \rightarrow M\text{Cl}_3(s)$. Open and closed circles represent estimated and experimental values, respectively. [From Johnson, D. A. J. Chem. Educ. 1980, 57, 475-477. Reproduced with permission.]

An organometallic compound is generally defined as one that possesses a metal-carbon bond. The bonding interaction, as delineated by the journal Organometallics, must be "ionic or covalent, localized or delocalized between one or more carbon atoms of an organic group or molecule and a transition, lanthanide, actinide, or main group metal atom." Despite this rather rigorous definition, the borderline that distinguishes organometallic chemistry from other branches is sometimes unclear. For example, all chemists would undoubtedly characterize nickel tetracarbonyl, Ni(CO)$_4$, as an organometallic compound even though carbon monoxide is hardly a typical organic compound. Likewise organoboranes, organosilicon, organarsenic, and organotellurium compounds are included in organometallic chemistry even though boron, silicon, arsenic, and tellurium are borderline metals. Traditional inorganic chemicals such as sodium cyanide, although possessing a metal-carbon bond, are not normally categorized as organometallic compounds.

Organometallic chemistry can be viewed as a bridge between organic and inorganic chemistry. On the practical side, nearly 25 billion dollars was realized from industrial processes utilizing homogeneous catalysis based on organometallic chemistry in 1985, and it is predicted that the role of organometallics in the production of pharmaceuticals, agricultural chemicals, flavors, fragrances, semiconductors, and ceramic precursors will continue to expand during the next decade. Organometallic catalysts have been used in a number of valuable sources which can provide varied perspectives on a definition for organometallic chemistry as well as expanded coverage of virtually every topic included in this chapter. See: Elschenbroich, C.; Salzer, A. Organometallics. VCH: Weinheim, 1992.

1. There are a number of valuable sources which can provide varied perspectives on a definition for organometallic chemistry as well as expanded coverage of virtually every topic included in this chapter. See: Elschenbroich, C.; Salzer, A. Organometallics. VCH: Weinheim, 1992.

will become increasingly important in an age when temperature (and hence fuel) needs to be minimized in chemical processes. As petroleum reserves are depleted, it is likely that such catalysis will play a major role in converting synthesis gas, derived from coal, into useful organic intermediates.

The 18-Electron Rule

The first attempt to account for the bonding in transition metal complexes was made by Sidgwick, who extended the octet theory of G. N. Lewis to coordination compounds. Ligands were considered to be Lewis bases which donated electrons (usually one pair per ligand) to the metal ion which in turn acted as a Lewis acid. Stability was assumed to be attendant to a noble gas configuration for the metal. The sum of the electrons on the metal plus the electrons donated from the ligands was called the effective atomic number (EAN), and when it was equal to 36 (Kr), 54 (Xe), or 86 (Rn), the EAN rule was said to be obeyed. An alternate and more general statement is that when the metal achieves an outershell configuration of \( ns^{2} \) or \( nd^{10} \), there will be 18 electrons in the valence orbitals and a closed, stable configuration. This rule of thumb, which is referred to as the 18-electron rule, has the advantage of being the same for all rows of the periodic chart, eliminating the need to remember a different EAN for each noble gas. Furthermore, the number is an easy one to recall since it is merely the total capacity of nine orbitals, one set each of s, p, and d orbitals. Because the rule is obeyed with rather high frequency by organometallic compounds, especially those containing carbonyl and nitrosyl ligands, it has considerable usefulness as a tool for predicting formulas of stable compounds.

As with most rules of thumb, the 18-electron rule is not always strictly obeyed: Stable complexes with both more than and fewer than 18 outer shell electrons are fairly common. Insight into the connection between stability of organometallic compounds and the 18-electron rule—and a basis for rationalizing the exceptions—can be gained by reviewing the molecular orbital description of bonding in complexes (Chapter 11). For an octahedral complex (Fig. 11.20), the most stable arrangement will be that in which all of the bonding orbitals (\( e_g \)) are fully occupied and all of the antibonding orbitals are empty. Since there are nine bonding molecular orbitals, this will require 18 electrons, as predicted by the 18-electron rule. Complexes with fewer than 18 electrons therefore tend to adhere to the rule if they have large \( \Delta_e \) values, making occupation of the antibonding \( e_g \) orbital unfavorable. Included in this category are complexes of second- and third-row transition metals, which are never found to have more than 18 electrons beyond the core MOs. There may well be fewer than 18 electrons, however, if the ligands do not provide stabilization of the \( e_g \) level by \( \pi \) bonding. This is observed for complexes such as \( [\text{WCl}_{6}]^{3-} \) (14 electrons), \( [\text{TiF}_{6}]^{3-} \) (15 electrons), \( [\text{Cr} \cdot \text{O}]^{3+} \) (16 electrons), and \( [\text{Ph}_{3} \text{P}]^{3+} \) (17 electrons). Ligands such as CO and NO, which are high in \( \pi \) acceptor bonding, are very effective at stabilizing the \( e_g \) orbitals. This leads to a larger \( \Delta_e \) value and an increase in the total bonding energy (Figs. 11.27 and 11.28). As a result, octahedral carbonyl and nitrosyl complexes are found to seldom depart from the 18-electron rule.

If \( \Delta_e \) is small, as is the case for first-row transition metal complexes, occupation of the weakly antibonding \( e_g \) orbitals is easily possible. As a result, stable complexes with 19 electrons (\( [\text{Co}(\text{H}_{2} \text{O})_{6}]^{3+} \)), 20 electrons (\( [\text{Ni} \cdot \text{c} \cdot \text{c}]^{2+} \)), 21 electrons (\( [\text{Cu} \cdot \text{NH}_{2}]^{2+} \)), and 22 electrons (\( [\text{Zn} \cdot \text{NH}_{2}]^{2+} \)) are well known. Transition metals on the left side of the periodic table have few outer shell electrons to begin with and to reach a total of 18 may require more ligands than is sterically possible (the nonexistent \( [\text{PF}_{6}]^{3-} \) would obey the 18-electron rule). For these metals, stable complexes having fewer than 18 electrons are thus fairly common: \( [\text{TiF}_{6}]^{3-} \) (12 electrons), \( [\text{CrF}_{6}]^{3-} \) (13 electrons), \( [\text{Cr} \cdot \text{NCS}]^{3+} \) (15 electrons), etc.

The picture is somewhat more complicated for complexes of other geometries. In the case of tetrahedral imido- or nitrido- complexes, the four \( \sigma \) bonds from the carbonyl groups result in four strongly bonding molecular orbitals (\( s \) and \( t \)), accommodating 18 electrons (Fig. 11.21). The remaining ten electrons must occupy the \( e_g \) and \( f \) orbitals, which are formally nonbonding and antibonding, respectively. Since \( \Delta_e \) is relatively small, occupation of the antibonding level is not energetically costly and the complex is stable. With only four ligands (capable of contributing two electrons each), any tetrahedral complex in which the metal has fewer than ten electrons available obviously will have fewer than 18 electrons in total in the molecular orbitals. Thus tetrahedral exceptions to the 18-electron rule, such as the stable 12-electron species \( [\text{FeCl}_{4}]^{-} \), are quite common.

Square planar \( d^2 \) transition metal complexes are consistent exceptions to the 18-electron rule. The combination of eight metal \( d \) electrons and two electrons from each of the four ligands gives a total of 16. Yet these complexes possess such high stability that it is often said they obey a 18-electron rule. With 16 electrons, all of the bonding molecular orbitals in a square planar complex are occupied (Fig. 11.22); any additional electrons would have a destabilizing effect because they would occupy antibonding orbitals. The addition of one ligand (donating two electrons) could convert a square planar species into a five-coordinate, 18-electron complex, and in fact, five-coordinate complexes are quite common (see Chapter 12). Yet in many instances the added ligand leads to a less stable complex.

In general, the conditions favoring adherence to the 18-electron rule are an electron-rich central metal (e.g., one that is in a low oxidation state) and ligands that are good \( \pi \) acceptors.

The 18-electron rule has remarkable utility for predicting stabilities and structures of organometallic compounds. By counting the number of outer shell electrons surrounding each metal atom in a complex, it is possible not only to predict whether the complex should be stable, but in some cases, whether there will be metal-metal bonds, whether the ligands will be bridging or terminal, etc. There are two popular procedures for electron counting, the so-called neutral atom and oxidation state methods, each with its ardent supporters. Either method may be used quite successfully, but care must be taken not to mix the two. In other words, a strict loyalty to one procedure or the other is required when counting electrons in a particular molecule or ion. The neutral atom method is perhaps more foolproof because it does not require correct assignment of oxidation states, which can sometimes be difficult for organometallic compounds.

To use either electron-counting procedure, it is necessary to know how many electrons each ligand in a complex donates to the metal. Table 15.1 gives electron contributions for a variety of ligands for both the neutral atom and oxidation state

---

Table 15.1

<table>
<thead>
<tr>
<th>Ligand Type</th>
<th>Oxidation State</th>
<th>Neutral Atom Count</th>
<th>Counted for Metal Atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terminal C</td>
<td>6e&lt;sup&gt;-&lt;/sup&gt;</td>
<td>6</td>
<td>18</td>
</tr>
<tr>
<td>Terminal N</td>
<td>6e&lt;sup&gt;-&lt;/sup&gt;</td>
<td>6</td>
<td>18</td>
</tr>
<tr>
<td>Bridge C</td>
<td>6e&lt;sup&gt;-&lt;/sup&gt;</td>
<td>6</td>
<td>18</td>
</tr>
<tr>
<td>Bridge N</td>
<td>6e&lt;sup&gt;-&lt;/sup&gt;</td>
<td>6</td>
<td>18</td>
</tr>
<tr>
<td>Bridge S</td>
<td>6e&lt;sup&gt;-&lt;/sup&gt;</td>
<td>6</td>
<td>18</td>
</tr>
<tr>
<td>Bridge P</td>
<td>6e&lt;sup&gt;-&lt;/sup&gt;</td>
<td>6</td>
<td>18</td>
</tr>
<tr>
<td>Bridge As</td>
<td>6e&lt;sup&gt;-&lt;/sup&gt;</td>
<td>6</td>
<td>18</td>
</tr>
</tbody>
</table>

The electron count for neutral ligands is the same by either method; thus phosphines and CO are listed as two-electron donors in both columns of the table. The electron count for three complexes involving these ligands, Cr(CO)<sub>6</sub>, Ni(PF<sub>3</sub>)<sub>4</sub>, and Fe(CO)<sub>4</sub>PP<sub>3</sub>, would be

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Oxidation State</th>
<th>Counted for Metal Atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(CO)&lt;sub&gt;6&lt;/sub&gt;</td>
<td>6e&lt;sup&gt;-&lt;/sup&gt;</td>
<td>18</td>
</tr>
<tr>
<td>Ni(PF&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;4&lt;/sub&gt;</td>
<td>8e&lt;sup&gt;-&lt;/sup&gt;</td>
<td>18</td>
</tr>
<tr>
<td>Fe(CO)&lt;sub&gt;4&lt;/sub&gt;PP&lt;sub&gt;3&lt;/sub&gt;</td>
<td>8e&lt;sup&gt;-&lt;/sup&gt;</td>
<td>18</td>
</tr>
</tbody>
</table>

The electrons counted for the metal atom in each of these complexes are those in its valence s and d orbitals. Metals having odd numbers of electrons obviously cannot satisfy the 18-electron rule by simple addition of CO (or other two-electron ligands) because the resulting moiety will necessarily also have an odd number of electrons. For example, Mn(CO)<sub>5</sub> and Co(CO)<sub>4</sub> are both 17-electron species and, consistent with prediction, do not exist as stable molecules. However, their corresponding anions, [Mn(CO)<sub>5</sub>]<sup>-</sup> and [Co(CO)<sub>4</sub>]<sup>-</sup>, are stable species and conformed to the 18-electron rule:

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Oxidation State</th>
<th>Counted for Metal Atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(CO)&lt;sub&gt;5&lt;/sub&gt;</td>
<td>5e&lt;sup&gt;-&lt;/sup&gt;</td>
<td>10</td>
</tr>
<tr>
<td>Co(CO)&lt;sub&gt;4&lt;/sub&gt;</td>
<td>6e&lt;sup&gt;-&lt;/sup&gt;</td>
<td>12</td>
</tr>
</tbody>
</table>

The dimeric species, Mn<sub>2</sub>(CO)<sub>10</sub> and Co<sub>2</sub>(CO)<sub>8</sub>, also are stable and are diamagnetic. If it is assumed that each compound has a metal-metal single (two-electron) bond, the electron count yields a total of 18 for each metal:

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Oxidation State</th>
<th>Counted for Metal Atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn&lt;sub&gt;2&lt;/sub&gt;(CO)&lt;sub&gt;10&lt;/sub&gt;</td>
<td>10e&lt;sup&gt;-&lt;/sup&gt;</td>
<td>20</td>
</tr>
<tr>
<td>Co&lt;sub&gt;2&lt;/sub&gt;(CO)&lt;sub&gt;8&lt;/sub&gt;</td>
<td>8e&lt;sup&gt;-&lt;/sup&gt;</td>
<td>16</td>
</tr>
</tbody>
</table>

The molecular structure of the manganese dimer clearly reveals that there is an Mn—Mn bond (Fig. 15.1a, b). In the cobalt structure, two of the CO ligands are bridging, i.e., they are simultaneously bound to both Co atoms (Fig. 15.1c, d). This does not affect the electron count, however, because CO and other neutral ligands donate two electrons to a complex whether they are terminal or bridging (Table 15.1):
more extended π systems exhibit a greater number of bonding modes. For example, 
the cyclopentadienyl ligand may be pentahapto, tri-, or mono-

\[
\begin{align*}
\eta^1 \text{C}_5\text{H}_5^+ & \quad \eta^1 \text{C}_5\text{H}_5 \quad \eta^1 \text{C}_5\text{H}_5^- \\
\end{align*}
\]

The power of the 18-electron rule for predicting structures of complexes involving 
unsaturated ligands can be illustrated with W(CO)_2(C_2H_4). If both C_2H_4 ligands were 
pentahapto, the compound would have 30 electrons, two more than the optimum for 
stability. However, if one of the ligands is presumed to be pentahapto and the other 
trihapto, we have an 18-electron complex:

\[
\begin{align*}
\text{W(CO)}_2 & \quad \eta^1 \text{C}_2\text{H}_4 \\
\end{align*}
\]

This predicted structure is indeed the one observed.6

Finally, in applying any electron-counting procedure to organometallic com-
plexes, we must remember that it is merely a formalism—albeit a very useful one. We 
must resist any tendency to presume that either method presented here, or the 18-
electron rule for that matter, reveals anything about electron distribution in a 
metal-ligand bond or mechanistic details about how a complex forms. What an 
electron-counting exercise does provide is a good first approximation of the stability 
and structure of an organometallic complex, thus serving much the same function as a 
Lewis diagram does for main group compounds.

### Metal Carbonyl Complexes

Almost all of the transition metals form compounds in which carbon monoxide acts as 
a ligand. There are three points of interest with respect to these compounds: (1) Carbon 
monoxide is not ordinarily considered a very strong Lewis base and yet it forms 
strong bonds to the metals in these complexes; (2) the metals are always in a low 
oxidation state, most often formally in an oxidation state of zero, but sometimes also 
in a low positive or negative oxidation state; and (3) as already discussed, the 18-
electron rule is obeyed by these complexes with remarkable frequency, perhaps 99% of 
the time.

6 Huttner, G.; Bozinger, H. H.; Bell, L. G.; Friedrich, P.; Beneske, V.; Neugebauer, D. 

### Table 15.2

<table>
<thead>
<tr>
<th>Mononuclear</th>
<th>Dinitrile</th>
<th>Dinuclear</th>
<th>Trinuclear</th>
<th>Hexanuclear</th>
</tr>
</thead>
<tbody>
<tr>
<td>V(CO)_5</td>
<td>Mn(CO)_5</td>
<td>Co(CO)_5</td>
<td>Fe(CO)_5</td>
<td>Ni(CO)_5</td>
</tr>
</tbody>
</table>

* Evidence for the existence of V_2(CO)_9 at 10 K has been reported. Ford, T. A.; Huber, H.; 

Unfortunately, the strength of metal-metal bonds in transition metal compounds is hard to determine. 
For instance, the Mn—Mn bond strength in Mn_2(CO)_10 has been reported to be as low as 87 kJ/mol 
and as high as 127 kJ/mol.7 Pulsed laser-induced photodissociation calorimetry places the value 
as 179 ± 21 kJ/mol and is consistent with recent kinetic results. Goodwin, J. L.; Peters, K. S.; 
Yakovlev, V. Organometallics 1986, 5, 815-816.

\[\text{Na} + \text{V(CO)}_6 \rightarrow \text{Na}^+ + [\text{V(CO)}_6]^\cdot\] (15.2)

The molecular structures adopted by simple carbonyl complexes are generally 
compatible with predictions based on valence shell electron pair repulsion theory.

Three representative examples from the first transition series are shown in Fig. 15.2.

The second- and third-row transition metals form a number of compounds analo-
gous to those in Table 15.2, e.g., Mo(CO)_5, W(CO)_5, and Re(CO)_5. However, 
there are also some distinct contrasts between the first row and the heavier elements. 
For example, the binary carbonyl complexes of niobium and tantalum, unlike va-
nadium, are unknown and, whereas tetracarbonylchromium is stable, Ta(CO)_5 has only 
been observed at low temperatures. Likewise Os(CO)_5 and Ru(CO)_5 are less stable 
than Fe(CO)_5. The dinuclear monocarbonyl complexes of ruthenium and osmium, 
Ru(CO)_3 and Os(CO)_3, are also less stable than their iron congener, Fe(CO)_5.

Increasing metal-metal bond strength as one descends a column of the periodic table 
leads to much greater stability for Os(CO)_5 and Ru(CO)_5 relative to their mono-
carbonyl congeners. Fe(CO)_5 and Pd(CO)_4 have only 
been observed at low temperatures. Likewise Os(CO)_5 and Ru(CO)_5 are less stable 
than Fe(CO)_5.

Three representative examples from the first transition series are shown in Fig. 15.2.

![MnFe(CO)_12](image-url)
Inorganic Chains, Rings, Cages, and Clusters

atoms by methyl groups seems to stabilize these systems. A large series of peri-
archromatic chemistry of carbon, and to some extent it does. Substitution of hydrogen
considerable and growing body of knowledge of the chemistry of these systems, but
calculations. The aromatic stabilization of the anion is apparently responsible for the

Note that oxalic acid containing carbon in a comparable oxidation state but not aromatic has a

In a formal sense, silicon might be expected to parallel the extensive alicyclic and
aromatic chemistry of carbon, and to some extent it does. Substitution of hydrogen
atoms by methyl groups seems to stabilize these systems. A large series of perim-
tyl cyclic compounds can be synthesized by treatment of chlorosilanes with an active
metal over a prolonged period of time:

\[ \text{Me}_3	ext{SiCl}_2 + \text{Na/K} \xrightarrow{100-120^\circ C} (\text{Me}_3	ext{Si})_2 + (\text{Me}_3	ext{Si})_2 \]  
(16.72)

Such a structure requires bond angles of 60°, less than the smallest interorbital angle available using only s and p orbitals is 90° (pure p orbitals). The smaller bond angle in P₄ must be accomplished either through the introduction of d character or through the use of bent bonds. Ab initio calculations show the importance of d orbital participation. In spite of ring strain, the P₄ molecule is stable relative to P₅ or the nonexistent P₆. Nevertheless, the molecule is quite reactive. It can be stored under water, but it reacts readily with oxygen to form P₄O₁₀, often called phosphorus pentoxide, based on the empirical formula, P₂O₅:

\[ \text{P}_4 + \text{SO}_2 \rightarrow \text{P}_4\text{O}_{10} \]  
(16.73)

Other phosphorus oxides (P₂O₅, P₃O₄, P₅O₄, P₄O₁₀) are known but not easily prepared. For example, P₅O₄, a liquid at room temperature (mp 23 °C), can be obtained by controlled oxidation of P₄, followed by distillation:

\[ \text{P}_4 + 3\text{O}_2 \rightarrow \text{P}_4\text{O}_{10} \]  
(16.74)

This molecule (C₅₀ symmetry) has four lone pairs of electrons (one for each phosphorus) which can be donated to one, two, or three oxygen atoms to form other

Over previous years, various amounts of high polymer (it is very large) and discrete
cages are found a borough on the other. These classes are discussed elsewhere, and
this section will be restricted to certain nonmetal compounds having cage structures.

The simplest cage-type molecule is white phosphorus, P₄. Although P₄ molecules,
isostructural with C₆₀, are found in phosphorus vapor at higher temperatures, P₄ is
more stable at room temperature. This molecule is a tetrahedron of phosphorus
atoms:

\[ P_4 + 2O_2 \rightarrow P_4O_8 \]  

This structure requires bond angles of 60°, less than the smallest interorbital angle available using only s and p orbitals is 90° (pure p orbitals). The smaller bond angle in P₄ must be accomplished either through the introduction of d character or through the use of bent bonds. Ab initio calculations show the importance of d orbital participation. In spite of ring strain, the P₄ molecule is stable relative to P₅ or the nonexistent P₆. Nevertheless, the molecule is quite reactive. It can be stored under water, but it reacts readily with oxygen to form P₄O₁₀, often called phosphorus pentoxide, based on the empirical formula, P₂O₅:

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This molecular (C₅₀ symmetry) has four lone pairs of electrons (one for each phosphorus) which can be donated to one, two, or three oxygen atoms to form other
Preparation and Properties of Carbonyl Complexes

Some carbonyl complexes can be made by direct interaction of the finely divided metal with carbon monoxide:

\[ \text{Ni} + 4\text{CO} \rightarrow \text{Ni(CO)}_4 \text{(bp 43°C)} \]  
(15.3)

\[ \text{Fe} + 5\text{CO} \rightarrow \text{Fe(CO)}_5 \text{(bp 103°C)} \]  
(15.4)

Nickel tetracarbonyl is a highly toxic volatile colorless liquid that is shipped in cylinders pressurized with carbon monoxide. Its vapor is about six times as dense as air. Purification of nickel by the Mond process is based on the decomposition of \( \text{Ni(CO)}_4 \), the reverse of Eq. 15.3. The yellow-red iron pentacarbonyl slowly decomposes in air and is sensitive to light and heat. In fact, \( \text{Fe}_2(\text{CO})_9 \), an orange solid, is prepared by photolysis of \( \text{Fe(CO)}_5 \).

\[ \text{Fe(CO)}_5 \rightarrow \text{Fe}_2(\text{CO})_9 \text{(mp 100°C)} \]  
(15.5)

For most carbonyl complexes, however, the metal must be reduced in the presence of carbon monoxide:

\[ \text{CrCl}_3 + \text{Al} + 6\text{CO} \rightarrow \text{AlCl}_3 + \text{Cr(CO)}_6 \text{(mp 154°C)} \]  
(15.6)

\[ \text{Re}_2\text{O}_7 + 17\text{CO} \rightarrow 7\text{CO}_2 + \text{Re}_2(\text{CO})_10 \text{(mp 177°C)} \]  
(15.7)

In Eq. 15.7 the carbon monoxide itself is acting as a reducing agent.

Infrared spectroscopy is a particularly informative technique for characterizing carbonyl complexes because of the direct connection between the number of C—O absorptions and molecular structure. Another advantage to the method is that there are few absorptions in the 1800-2200 cm\(^{-1}\) window except for those arising from C—O stretching vibrations. We saw in Chapter II that the frequencies of these absorptions can provide information regarding the carbon-oxygen bond strength in coordinated CO. It is a straightforward matter to predict the number of C—O stretching bands expected for a carbonyl complex based on its symmetry. For a complex such as \( \text{Fe(CO)}_5 \) (D\(_{5h}\)), we would treat each C—O stretching vibration as a vector (Fig. 15.3) and then determine the symmetries of the set of vibrations by application of methods outlined in Chapter 3. The result is that the vibrational modes include two of \( A'_1 \) and one each of \( A'_2 \) and \( E' \) symmetries, of which only the \( A'_2 \) and \( E' \) are infrared active, according to the D\(_{5h}\) character table (Appendix D). Since one of these is nondegenerate and the other doubly degenerate, we expect the IR spectrum for \( \text{Fe(CO)}_5 \) to show two C—O stretching absorptions of unequal intensity (Fig. 15.4). Infrared C—O stretching frequencies for mononuclear carbonyl complexes of the first-row transition metals are given in Table 15.3.

The dinuclear cobalt complex, \( \text{Co}_2(\text{CO})_8 \) (Fig. 15.1), represents a large number of polynuclear carbonyl species containing bridging carbonyl ligands in addition to the terminal carbonyl ligands found in all binary metal carbonyl compounds. The —C=O representation implies that a CO ligand bound to a single metal is relatively unchanged from free carbon monoxide, i.e., that the carbon-oxygen bond remains a triple bond. That the C—O bond order is approximately three in a terminal CO ligand is reflected in carbon-oxygen stretching frequencies: 2143 cm\(^{-1}\) for free carbon monoxide and 2125-1850 cm\(^{-1}\) for terminal carbonyl groups. Bridging CO ligands, on the other hand, are electronically much closer to the carbonyl group of organic chemistry with a carbon-oxygen bond order of approximately two as found, for example, in ketones. Again, we may infer the bond order from carbon-oxygen stretching frequencies, which are typically between 1830 and 2000 cm\(^{-1}\).

Inorganic Chains, Rings, Cages, and Clusters

Te^{4+}, S^{2-}, Se^{2-}, S^{2-}, S^{2-}, and Te^{2+} Se^{2-}. The structures of S^{2-}, Se^{2-}, and Te^{2+} ions have been shown to be square planar.

\[ \text{S-S}^{+}, \text{Se-Se}^{+}, \text{Te-Te}^{+} \]

Note that these are isoelectronic with the previously mentioned S,N\textsubscript{2}. All three are thought to be stabilized to a certain extent by a Hückel sextet of \(\pi\) electrons.

Many cyclopolyphosphines are known. The simpler ones, (RP)\textsubscript{n} (n = 3-6) (Fig. 16.34), are prepared by pyrolysis or elimination reactions.

\[
\begin{align*}
\text{RPCl}_2 + \text{RH}_2 & \rightarrow (\text{RP})_2 + 2\text{HCl} \\
\text{RP}_n + n\text{HCl} & \rightarrow \text{RP}_n
\end{align*}
\]

In addition to the +3 oxidation state seen in the homocyclic rings discussed above, phosphorus rings exist in which the +5 oxidation state is exhibited:

\[
\begin{align*}
\text{H}_n\text{N} > \text{V} & \rightarrow \text{P} \rightarrow \text{OH} \\
\text{H}_n\text{O} & \rightarrow \text{P} \rightarrow \text{OH}
\end{align*}
\]

The union of this acid results from the oxidation of red phosphorus with hypohalites in alkaline solution:

\[
\text{P}_n^{2+} + 9\text{XO}^- + 6\text{OH}^- \rightarrow (\text{PO}_2)^{2-} + 9\text{X}^+ + 3\text{H}_2\text{O}
\]

There is a series of analogous cyclic thio phosphoric acids with the formula (HS\textsubscript{2}P)\textsubscript{n} that may be prepared by the oxidation of red or white phosphorus with polysulfides under a variety of conditions. For example, the reaction of white phosphorus with a mixture of sulfur and hydrogen sulfide dissolved in triethylamine (which acts as a base) and chloroform opens the phosphorus cage to form the tetrameric cyclic anion:

\[
P_4 + 4\text{Et}_3\text{N} + 2\text{H}_2\text{S} + 6\text{S} \rightarrow [\text{Et}_3\text{NH}]_4[P_4\text{S}_x]
\]

The square structure of the anion has been confirmed by X-ray crystallography.\textsuperscript{97}

A series of cyclopolyarsines is known. They may also be prepared by a generally useful reaction that is reminiscent of the Wurtz reaction of organometallic chemistry:

\[
\text{RAsCl}_2 \rightarrow \frac{n}{2} \text{RAs} + \text{As} \rightarrow \text{As} + 2\text{KCl}
\]

This compound is stable only at \(-30\) °C in the dark and in the absence of air. It spontaneously ignites on exposure to air.\textsuperscript{99}

Alkali metal pentaphosphacyclopentadienides (Li and Na) have been obtained in solution from reactions of red phosphorus and dihydrogenphosphide in dimethylformamide:

\[
P_5 + [\text{PH}_2]^+ \rightarrow \text{P} \rightarrow \text{P} + 2\text{KCl}
\]

Similarity to the C\textsubscript{5}H\textsubscript{5} anion is apparent if you allow each phosphorus a lone pair of electrons, which gives five \(\pi\) orbitals (with six electrons) available for \(\pi\) bonding. Transition metal complexes containing P\textsubscript{5} rings, however, were known prior to the synthesis of the free P\textsubscript{5} ligand (see Chapter 15).\textsuperscript{100} Examples are [(\text{R}^5\text{C}_5\text{Me}_2)\text{Fe}(\text{P})].

Infrared C—O stretching frequencies of mononuclear carbonyl complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Geometry</th>
<th>Point group</th>
<th>C—O stretching mode symmetries</th>
<th>IR active modes</th>
<th>Observed frequencies (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(CO)₄</td>
<td>Tetrahedral</td>
<td>T₄</td>
<td>A₁, T₂</td>
<td>A₁, T₂</td>
<td>2123 (CO₂), 2045</td>
</tr>
<tr>
<td>Fe(CO)₅</td>
<td>Trigonal bipyramidal</td>
<td>D₅h</td>
<td>2A₁, A₂, E, E</td>
<td>A₁, E</td>
<td>2002 (broad)</td>
</tr>
<tr>
<td>Ru(CO)₅</td>
<td>Trigonal bipyramidal</td>
<td>D₅h</td>
<td>2A₁, A₂, E, E</td>
<td>A₁, E</td>
<td>1999 (C₅H₁₅)</td>
</tr>
<tr>
<td>Os(CO)₅</td>
<td>Trigonal bipyramidal</td>
<td>D₅h</td>
<td>2A₁, A₂, E, E</td>
<td>A₁, E</td>
<td>2035</td>
</tr>
<tr>
<td>Cr(CO)₆</td>
<td>Octahedral</td>
<td>O₆</td>
<td>A₄, E, E, T₉, T₉</td>
<td>T₉</td>
<td>2006 (vapor)</td>
</tr>
<tr>
<td>Mo(CO)₆</td>
<td>Octahedral</td>
<td>O₆</td>
<td>A₄, E, E, T₉, T₉</td>
<td>T₉</td>
<td>2003 (vapor)</td>
</tr>
<tr>
<td>W(CO)₆</td>
<td>Octahedral</td>
<td>O₆</td>
<td>A₄, E, E, T₉, T₉</td>
<td>T₉</td>
<td>1998 (vapor)</td>
</tr>
</tbody>
</table>

1700 cm⁻¹ for bridging CO ligands, compared with 1715 ± 10 cm⁻¹ for saturated ketones. It would be false, however, to think of a bridging carbonyl group as a ketone. The M—C—M bond angle is 90° or less, compared to a C—C—C bond angle of about 120° for an organic ketone. Furthermore, a bridging CO ligand is almost always accompanied by a metal-metal bond, which tends to extensive delocalization in the M—C—M moiety involving overlap of metal orbitals with both carbon and oxygen orbitals of the CO ligand. The infrared spectrum of a metal carbonyl compound provides important information on the nature of the carbonyl groups present and may allow one to distinguish between a structure with only terminal carbonyls, such as Mn₅(CO)₁₀ and one containing one or more bridging carbonyl groups, such as Co₅(CO)₁₀. Note that alternative 18-electron structures may be drawn for these compounds—dimanganese decacarbonyl and dicobalt octacarbonyl with none, as alternative 18-electron structures may be drawn for these two compounds—dimanganese decacarbonyl and dicobalt octacarbonyl with none, as shown in Fig. 15.6. Although the bridged dimanganese compound is unknown, there is infrared evidence that in solution the dicobalt compound exists as an equilibrium mixture of three isomeric forms, one of which is the structure shown in Fig. 15.4.

Fig. 15.5 Overlap of π and σ orbitals of bridging carbonyl ligands with the d orbitals of metal atoms. The π orbital of CO can donate electron density to the metal orbitals and the empty σ orbital of CO can accept electron density from the d orbitals. (From Kostid, N. M.; Fenske, R. F.; Inorg. Chem. 1983, 22, 666-671. Reproduced with permission.)

Fig. 15.6 Alternative structures for dimanganese decacarbonyl and dicobalt octacarbonyl. Structure (a) is unknown, but there is infrared evidence for the existence of (b) in solution.

The bridged form is the only one observed in the solid state, however.

The dimanganese and cobalt carbonyl complexes, as well as a number of similar compounds, may be rationalized on the grounds that the 17-electron mononuclear units must form a metal-metal bond in order to provide each metal atom with 18 electrons. There is another group of polynuclear carbonyl complexes that may be regarded as “carbon monoxide deficient” in the sense that they can be constructed from the simple binary complexes by replacing one or more carbonyl groups with metal-metal bonds. For example, in addition to Fe(CO)₅, Table 15.2 shows two other complexes of iron: diron monocarbonyl, Fe₂(CO)₃, and triron dodecacarbonyl, Fe₃(CO)₁₂. These compounds, as well as the tetranuclear Ca₂(CO)₁₂, obey the 18-electron rule if metal-metal bonds are included in the formulations:

2Fe 18e⁻ 3Fe 24e⁻ 4Co 36e⁻
5CO 18e⁻ 12CO 24e⁻ 4Fe 24e⁻
M—M 2e⁻ 3M—M 6e⁻ 6M—M 12e⁻
Fe₂(CO)₃ 36e⁻ or 18e⁻/Fe or 18e⁻/Fe

Without metal-metal bonds, these complexes would have 17, 16, and 15 electrons per metal atom, respectively. The deficiencies are compensated by one, two, and three M—M bonds per metal. Structures for the two iron complexes are shown in Fig. 15.7.

In the tetranuclear complex, the four metal atoms are arranged in the form of a tetrahedron with the CO atoms occupying the corners and the six metal carbonyl bonds forming the edges. Larger clusters such as Ca₂(CO)₁₂ are also known, but the 18-electron rule breaks down for complexes with more than four metal atoms. In these species, electron delocalization is extensive, and other models (described in Chapter 16) are of greater value.¹⁰


When we consider that complexes with chelating ligands (see Chapters 11 and 12) are compounds with rings, we realize that rings with metal atoms are quite common. In addition to these, however, new classes of compounds are appearing regularly in which metal atoms have replaced nonmetal atoms of traditional nonmetallic heterocycles. Replacing a Ph₃ group of a trimeric cyclophosphazene with C₃W yields planar [Cl₃WN(PPh₂)₃] and replacing two Ph₃ groups of a tetrameric cyclophosphazene with VCl₄ gives planar [Cl₂VN(PPh₂)₂].

Isolobal relationships between metal and nonmetal fragments will undoubtedly continue to be exploited and intense activity can be expected in this area for some time to come.

Several elements form homocyclic rings. Rhombic sulfur, the thermodynamically stable form at room temperature, consists of S₅ rings in the crown conformation. Unstable modifications, Sₖ, are known which include n = 6 through n = 36. In fact, sulfur has more allotropes than any other element. Selenium also forms five-, six-, seven-, and eight-membered rings, but they are unstable with respect to the chain form.

Organoselenium chemistry has become an important player in the rings of sulfur. The existence of an isolobal relationship between S and Cp₂Ti leads to the prediction that it should be possible to substitute the latter for the former in sulfur rings. The formal replacement of one sulfur atom in S₅ by Cp₂Ti gives Cp₂TiS₄ (or replacing two sulfur atoms in Sₖ by two Cp₂Ti units gives 1,5-(Cp₂Ti)₂S₆). In practice one takes these reactions in the reverse direction. For example, S₅, which is unstable with respect to S₆, may be prepared from the readily available Cp₂TiS₅ complex.

Two reactions are shown in the reverse direction. For example, S₅, which is unstable with respect to S₆, may be prepared from the readily available Cp₂TiS₅ complex.

\[
2\text{NH}_₃ + \text{H}_₅ + \frac{1}{2} \text{S}_{₅} \rightarrow (\text{NH}_₄)₂ \text{S}_{₅} \xrightarrow{\text{Cp}_₂\text{Ti}} \text{Cp}_₂\text{TiS}_{₅} \tag{16.61}
\]

\[
\text{Cp}_₂\text{Ti} + \text{S}_{₇} + \text{SCl}_₅ \rightarrow \text{S}_{₇} \rightarrow \text{Cp}_₂\text{TiCl}_₅ \tag{16.63}
\]

The S₅⁻ anion that forms in the first step is one of several polysulfides (S₆⁻, S₇⁻, S₈⁻, S₉⁻), all of which have open chain structures. The versatility of Cp₂TiS₅ as a precursor to other rings and sulfur-carbon compounds is shown in Fig. 16.33.

Oxidation of several nonmetals in strongly acidic systems produces polyatomic cationic species of the general type Yₙ⁺. Among those characterized are S₅⁺, Se₅⁺.

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Oxidation of several nonmetals in strongly acidic systems produces polyatomic cationic species of the general type Yₙ⁺. Among those characterized are S₅⁺, Se₅⁺.

Fig. 16.33 Reactions of Cp₂TiS₅. [From Draganjac, M.; Rauschfuss, T. B. Angew. Chem. Int. Ed. Engl. 1985, 24, 742-757. Reproduced with permission.]

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Whereas the 18-electron rule is of great aid in predicting metal-metal bonds, it does not assist us in distinguishing between bridging and terminal CO ligands, inasmuch as the electron count is the same for either mode of bonding. Polynuclear carbonyls both with and without bridging CO units are common. Among those lacking CO bridges are $M_2(CO)_{10}$ ($M = Mn, Tc, Re$), $M_3(CO)_{12}$ ($M = Ru, Os$), and $Ir_4(CO)_{12}$.

New carbonyls of osmium [e.g., $Os_4(CO)_{14}$, $Os_4(CO)_{15}$, $Os_4(CO)_{16}$, $Os_5(CO)_{10}$, $Os_5(CO)_{11}$, $Os_6(CO)_{12}$, $Os_7(CO)_{13}$] are being discovered with regularity and all found thus far are essentially nonbridging.

A beautiful series of tetranuclear osmium complexes, $Os_4(CO)_{14}$, $Os_4(CO)_{15}$, and $Os_4(CO)_{16}$ has been prepared (Fig. 15.8). Consistent with the 18-electron criterion, these complexes have 4, 5, and 6 metal-metal bonds, respectively. In $Os_4(CO)_{14}$, four of the carbonyl ligands are weakly semibridging and ten are nonbridging. The term semibridging is used to describe CO ligands that are unequally shared between two metal centers, making them intermediate between terminal and bridging in their ligation.

Weakly semibridging carbonyls, such as those in $Os_4(CO)_{14}$, are nearly linear but show some distortion toward the second metal. Of course it is not always clear whether departures from linearity arise from interaction with the metal or because of packing forces in the crystalline solid. All CO ligands are fully nonbridging in the puckered $Os_4(CO)_{14}$, described as a metal carbonyl analogue of cyclobutane. The dark red crystals of $Os_4(CO)_{14}$ possess nearly planar Os$_4$ units with only terminal CO ligands.

The existence of both bridged and nonbridged forms of Co$_2(CO)_8$ in solution reveals how little difference in energy exists between the two isomers. The factors causing carbonyl ligands to bridge or not bridge are not at all well understood. Steric factors are probably important, for just as vanadium hexacarbonyl refuses to dimerize (it would become seven-coordinate), a bridged dimanganese decacarbonyl would have a coordination number of 7 or more (depending upon the number of bridges) rather than 6. Not even a trace of a bridged dimanganese isomer has been detected in equilibrium with the nonbridged species, in contrast to the observations for cobalt and iron. However, steric considerations do not account for the common observation that...
An even larger number of binary sulfur–nitrogen cations and anions are known. Reduction of $S_4N_4$ (with metallic potassium or sodium azide) yields the planar six-membered ring, $S_3N_2$. (Fig. 16.32a). At first glance one might think that this is another benzene analogue. An electron count dispels that notion as there are ten $\pi$ electrons instead of six. Still, the Hückel $4n + 2$ rule is obeyed and the system satisfies the requirement for aromaticity. However, four of the $\pi$ electrons occupy antibonding orbitals, which has the effect of weakening the $S$–$N$ bond (Fig. 16.32b).

Sulfur–nitrogen compounds often have unpredictable structures. One example is the sulfur diimide, $PhSN=S=NSPh$. for which the following three configurations could be envisioned:

Configuration (a) is preferred rather than the more open structures (b) and (c). This runs counter to our intuition that the most hindered structure would be least stable. The separation between the end sulfur atoms is only 329 pm, compared with the van der Waals sum of 360 pm, suggesting significant sulfur–sulfur interaction. In fact one can write resonance structures such as:

which might lead us to believe that a ring structure is a better description. However, ab initio self-consistent field calculations do not support the ring description but rather reveal that the unusual conformation is the result of electronic interactions between nitrogen and sulfur lone pairs.

Reduction of tetrasulfur tetranitride with tin(II) chloride produces tetrasulfur tetraimide, $S_4(NH)_4$. isoelectronic with sulfur, $S_4$. Like sulfur, the tetraimide also exists in a crown configuration. As $S$ and $NH$ are isoelectronic, it has been possible to produce a series of ring compounds, $S_4(NH)_x$, that includes all possible isomers except those with $N$–$N$ bonds.

Not only can $S_4N_4$ be reduced as illustrated in the preceding example, but it can also be oxidized. When it is subjected to chlorine, trihazyl trichloride is produced:

$$3S_4N_4 + 6Cl_2 \rightarrow 4N_3S_3Cl_3$$

This compound may be converted into the corresponding thionite or oxidized to sulfanuryl chloride:

$$2S_4N_4 + Cl_2 \rightarrow 2N_3S_3Cl_2$$
within a given family, the heavier congeners tend to have fewer bridges than the lighter ones. Thus Fe₂(CO)₁₂ (or Fe₂(μ-CO)₂(CO)₁₀) (Fig. 15.7a, b) and Co₂(CO)₁₄ (or Co₂(μ-CO)₂(CO)₁₀) (Fig. 15.9) are bridged and Os₂(CO)₁₄ and Ir₂(CO)₁₄ (Fig. 15.9) are unbridged. Although steric hindrance cannot be the explanation here, it may be that a size effect of a different sort is operating. As the M—M bond lengths (Co < Ir), the M—C bond must lengthen even more or the M—M—C single must open up, or both. Either of these structural changes could destabilize the structure, though it is not clear that this is the explanation. The remarkable carbon monoxide ligand can also bridge three metal atoms.¹⁶

Four of the eight triangular faces in octahedral Rh₆(CO)₁₆ [Rh₂(μ-CO)₂(CO)₁₄] (Fig. 15.10) contain carbonyl groups bridging three metal atoms. The corresponding cobalt compound is thought to have a similar structure.¹⁷

The elucidation of the structures of polynuclear carbonyls is a challenging area. Bridging carbonyl ligands can often be detected via their infrared absorptions, but in the case of complicated structures, spectral interpretation can be difficult because sometimes other absorptions, such as overtones or combination bands, appear in the carbonyl region. Infrared spectroscopy does have one advantage over methods such as X-ray crystallography in its ability to study structures in solution, which may differ from those found in the solid state. X-ray crystallography provides unambiguous information on structure but occasionally is beset with difficult problems arising from disorder (see Chapter 3). A classic example is trirhenium dodecacarbonyl, for which disorder in the solid prevented a complete solution to the crystal structure for many years.¹⁸ The available X-ray data were compatible with a triangular array of iron atoms and so a structure similar to that of the isoelectronic Os₂(CO)₁₄, which has only

Fig. 15.9 Structures of Co₄O₉(CO)₁₄, Os₄O₉(CO)₁₄, and Ir₄O₉(CO)₁₄.

Terminal CO ligands, was suggested. A weak band at 1875 cm⁻¹ in the solid state infrared spectrum of Fe₃(CO)₁₂ was dismissed as Fermi resonance or as arising from crystalline interactions rather than fundamental C—O vibrations. The simple model was finally overthrown by Mössbauer evidence which proved that the three atoms are not in identical environments.¹⁹ Subsequent refinement of the X-ray structure showed that the iron atoms do indeed form a nearly equilateral triangle, with one Fe—Fe pair being bridged by two CO ligands (Fig. 15.7a, b).²⁰ The solution structure, however, is still under discussion. A recent EXAFS study of frozen solutions suggests that whether Fe₃(CO)₁₂ exists as a fully unbridged species or as a mixture of bridged and unbridged forms depends on the solvent.²¹ An IR study also supports the existence of a mixture of bridged and unbridged structures in solution.²² That the molecule is trihedral in both solution and solid states seems clear from a number of spectroscopic investigations, including IR and variable-temperature NMR. Among the attempts that have been made to elucidate the nature of this trihedral process are studies of various derivatives of the dodecarbonyl compound.²³

Numerous anionic carbonyl complexes, also called carbonylate ions, are known. These ions generally conform to the 18-electron rule and are of interest because of the information they provide regarding bonding and structure as well as for their usefulness in the synthesis of other carbonyl derivatives. They are often electronically and structurally related to neutral carbonyl complexes (Table 15.4). For example,
Polymeric chain, band, and sheet silicate structures have been discussed previously (page 742), and it should not be surprising to learn that cyclic silicate anions, such as \([\text{Si}_4\text{O}_{10}^2\text{]}\) and \([\text{Si}_6\text{O}_{12}^6\text{]}\) (Fig. 16.28) are known. These anions are sometimes referred to as metasilicates in line with the older system of nomenclature, which assigned or- to the most fully hydrated species [as in "orthosilicic acid," \(\text{Si(OH)}_4\)] and meta to the acid (and anion) from which one mole of water has been removed [either in fact or formally; for example, "metasilicic acid," \(\text{OSi(OH)}_2\)].

Isoelectronic with cyclic silicates are cyclic metaphosphates. The simplest member of the series is the trimetaphosphate anion, \([\text{P}_3\text{O}_{9}^3\text{]}\). The tetrametaphosphate anion, \([\text{P}_4\text{O}_{12}^4\text{]}\), is also well known. By careful chromatographic separations of the glassy mixture of polymeric phosphates and metaphosphates known as Graham's salt it is possible to show the existence not only of tri- and tetrametaphosphates, but also pentameta- and hexametaphosphates. The separation is effected and some qualitative knowledge of structure is gained from the fact that two factors play a role in the mobility of phosphate anions: (1) Higher molecular weight anions move more slowly than do lower members of the series; and (2) the ring or metaphosphate anions move more rapidly in basic solution than do the straight-chain anions of comparable complexity (Fig. 16.29).

In progressing from silicon to phosphorus, the increase of one in atomic number results in a corresponding decrease of one per central atom in the anionic charge of the rings. Further progression from trimetaphosphate to sulfur trioxide results in a neutral molecule, trimeric sulfur trioxide. This form is known as \(\gamma\text{-SO}_3\) and is isoelectronic and isostructural with the analogous trimetasilicate and trimetaphosphate anions. It exists in a chair form and is thermodynamically unstable with respect to two other forms: \(\beta\text{-SO}_3\), which consists of infinite chains, and \(\alpha\text{-SO}_3\), which probably consists of infinite sheets caused by cross-linking. Traces of moisture convert the \(\gamma\text{-SO}_3\) form into the \(\alpha\text{-SO}_3\) and \(\beta\text{-SO}_3\) forms.

Compounds which contain sulfur-nitrogen rings were known in the last century, but many new ones have been prepared in the last decade. It is currently an area of considerable interest. The ammonolysis of sulfur monochloride, \(\text{S}_2\text{Cl}_2\), either in solution in an inert solvent or heated over solid ammonium chloride, yields tetrasulfur tetranitride:

\[
\text{S}_2\text{Cl}_2 + 2\text{NH}_4\text{Cl} \rightarrow 2\text{S}_3\text{N}_4 + 2\text{Cl}_2
\]

The name hexametaphosphate has caused confusion over the years. On the basis of erroneous reasoning concerning the nature of double salts, the term hexametaphosphate was assigned to Graham's salt of empirical composition \(\text{Na}_6\text{P}_2\text{O}_{17}\). It has also been applied to the related commercial product (Calgon) in which the Na/P ratio is 1:1. The true metaphosphate contains a twelve-membered phosphorus-oxygen ring and is but a very minor component of the mixture known as Graham's salt.
of being dispersed throughout the reaction medium. The cryptand is added to coordinate the potassium ion, creating a large cation which allows isolation of the large anion. There is evidence that uncoordinated alkali metal ions prevent formation, or stimulate decomposition, of \([\text{Ti(CO)}_6]^-\). The reaction is run under Ar instead of N\(_2\) since the former is less reactive. Only carefully purified carbon monoxide can be used because traces of impurities such as H\(_2\), N\(_2\), or CO compete in the reaction. Finally, the reduction must be carried out at low temperatures (~70 °C) to minimize side reactions. The product of this reaction is air sensitive in reactions with O\(_2\), as are most carbonylate anions. Such reactions require special equipment such as Schlenk glassware or a glove box, which are standard items in any modern organometallic laboratory. It should also be noted that highly reduced anions may be shock sensitive, as are Na\(_2\)MCOC\(_3\) (\(M = \text{Cr}, \text{Mo}, \text{W}\)), K\(_2\)[V(CO)\(_5\)], and Cs\(_2\)[Ta(CO)\(_5\)].

Not all reactions leading to carbonylate anions require strong reducing agents. Some involve reduction of the metal by carbon monoxide already present in the metal carbonyl or disproportionation of the complex. In fact, the first synthesis of a metal carbonylate involved the former procedure:

\[
\text{Fe(CO)}_5 + 4\text{OH}^- \rightarrow [\text{Fe(CO)}_5\text{H}^+]^+ + \text{CO}_3^{2-} + 2\text{H}_2\text{O} \quad (15.11)
\]

Often a Lewis base will effect disproportionation of a complex:

\[
3\text{Mn(CO)}_5\text{H}_2 + 12\text{py} \rightarrow 2[\text{Mn(CO)}_5\text{py}]^+ + 4[\text{Mn(CO)}_5]^+ + 10\text{CO} \quad (15.12)
\]

\[
\text{Mn(CO)}_5\text{H}_2 + 2\text{dppe} \rightarrow [\text{Mn(CO)}_5\text{dppe}]^+ + [\text{Mn(CO)}_5]^+ + 3\text{CO} \quad (15.13)
\]

\[\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\]

The reaction with the relatively hard base, pyridine, has long been recognized as disproportionation but reaction 15.13 with the softer phosphine base has only recently been fully elucidated. Numerous bimetallic carbonylate anions are also well known. Among them are \([\text{Cr(CO)}_5\text{H}]^2^+\) and \([\text{Fe(CO)}_5]^2^+\), which are isoelectronic and isostructural with \([\text{Mn(CO)}_5]^2^+\) and \([\text{Co(CO)}_5]^2^+\), respectively.

### Carbonyl Hydride Complexes

Addition of carbonylate ions often results in the formation of carbonyl hydride complexes, which may be regarded as the conjugate acids of the carbonylates:

\[
[\text{Cr(CO)}_5]^2^- + \text{H}_2\text{O} \rightarrow \text{HCr(CO)}_5\text{H}^+ + \text{HO}_2^- \quad (15.14)
\]

\[
[\text{Re(CO)}_5]^2^- + \text{H}_2\text{O} \rightarrow \text{HR(cCO)}_5 + \text{OH}^- \quad (15.15)
\]

\[
[\text{Fe(CO)}_5]^2^- + \text{H}^+ \rightarrow [\text{HFe(CO)}_5]^+ + \text{H}_2\text{Fe(CO)}_5^- \quad (15.16)
\]

The stronger bases can be protonated with acids that are even weaker than water.

\[
[\text{Cr(CO)}_5]^2^- + \text{MeOH} \rightarrow [\text{HCr(CO)}_5\text{H}]^+ + \text{MeOH}^- \quad (15.17)
\]

---


25 Citi, K.-M.; Frenzich, S. R.; Philson, S. B.; Ellis, J. E. J. Am. Chem. Soc. 1988, 110, 303-304. Also see Ellis, J. E.; Citi, K.-M. J. Am. Chem. Soc. 1999, 121, 6022-6025, for preparation of [1H(CO)] by a similar method.


moisture. However, it has been found that trimeric chlorophosphazene can be polymerized thermally:

\[
\begin{array}{c}
\text{Cl} \\
\text{N} \\
\text{Cl} \\
\text{Cl} \\
\end{array}
\rightarrow
\begin{array}{c}
\text{N=P=Cl} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\end{array}
\]

If this is done carefully, extensive cross-linking does not take place and the polymer (n = 15,000) remains soluble in organic solvents. The reactive chlorine atoms are still susceptible to nucleophilic attack and displacement:

\[
\begin{align*}
\{\text{PCl}_3\}_n + 2n\text{NaOR} & \rightarrow \{\text{P(OR)}_2\}_n + 2n\text{NaCl} \\
\{\text{PCl}_3\}_n + 2n\text{R}_2\text{NH} & \rightarrow \{\text{P(NR}_2\}_n + 2n\text{HCl}
\end{align*}
\]

By varying the nature of the side chain, R, various elastomers, plastics, films, and fibers have been obtained. These materials tend to be flexible at low temperatures, and water and fire resistant. Some fluoroalkoxy-substituted polymers (R = CH\_2\_CF\_2) are so water repellent that they do not interact with living tissues and promise to be useful in fabrication of artificial blood vessels and prosthetic devices.

Although the hydrolytic stability of some phosphazene polymers makes them attractive as structural materials, it is possible to create hydrolytically sensitive phosphazenes that may be useful medically as slow-release drugs. Steroids, antibiotics, and catecholamines (e.g., dopamine and epinephrine) have been linked to a polyphosphazene skeleton (Fig. 16.27) with the intention that slow hydrolysis would provide these drugs in a therapeutic steady state.\textsuperscript{49}

Materials containing an inorganic polymeric backbone often have useful electrical, optical, and thermal properties. In addition they are being explored for use as precursors to ceramics. One way to alter the properties of a polymer is to make changes in the backbone. Recently, Manner and Allcock\textsuperscript{50} have shown that a C—Cl group may be substituted for one of the PC\_2 groups in (PC\_2\_N\_3) to give a ring that forms a polymer with carbon in its backbone:

\[
\begin{array}{c}
\text{Cl} \\
\text{P} \\
\text{N} \\
\text{Cl} \\
\end{array}
\rightarrow
\begin{array}{c}
\text{C=N} - \text{P=N} - \text{P=N} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\end{array}
\]

This polymer is the first example of a poly(carbophosphazene).


The reaction in Eq. 15.18 leads to a product with bridging hydride ligands; the nature of the bonding in complexes of this type will be discussed later in this section.

In addition to the protonation route, hydrido complexes may be prepared by reaction of carbonyl complexes with hydride donors:

\[ \text{Fe(CO)}_3 + \text{H} \rightarrow \text{Fe(CO)}_3\text{H} \]  
(15.19)

In a mechanistically similar reaction hydroxide ion can serve as the source of hydrogen:

\[ \text{Fe(CO)}_3 + \text{OH}^- \rightarrow \text{Fe(CO)}_3\text{OH}^- \]  
(15.21)

Addition of excess base in these reactions generates the dianionic starting material in Eq. 15.16. The intermediate shown in Eq. 15.19, which has a coordinated formyl group \([\text{COH}]^-\), has been isolated and characterized. Its counterpart in the \(\text{OH}^-\) reaction is a hydroxycarbonyl complex (see Problem 15.45). Both \(\text{HCo(CO)}_4\) and \(\text{HCr(CO)}_6\) have acid strengths similar to that of \(\text{HCl}\) in water, i.e., they are essentially completely dissociated in aqueous solution. At the other extreme, \(\text{ReCO}_3\text{H}\) is such a weak acid that its conjugate base is readily hydrogenated by water (Eq. 15.13). The dianion, \(\text{H}_2\text{Fe(CO)}_4\), was the first carbonyl hydride complex to be synthesized, having been prepared by Willard Hieber in 1931. It is a yellow liquid, unstable above \(-10^\circ C\), and behaves as a dibasic acid in water (\(pK_a^1 = 4.41, pK_a^2 = 1.4\)). The large difference in the two ionization constants provided the first evidence that the hydrogen atoms in the complex were both bound to the same atom (and hence to the iron atom). The \(pK_a^1\) values of a variety of metal carbonyl hydride complexes are given in Table 15.5.

Although in many respects carbonyl hydride complexes may be regarded as acids, they also show some similarities to the basic hydrides of the main group metals e.g.,

<table>
<thead>
<tr>
<th>Compound</th>
<th>(pK_a(H_2O))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{HCO}_2\text{C(OH)})</td>
<td>strong</td>
</tr>
<tr>
<td>(\text{HCO}_2\text{C(OH)}\text{PPh}_3)</td>
<td>5.4</td>
</tr>
<tr>
<td>(\text{HCO}_2\text{C(OH)}\text{Cp}^*\text{CO}_2)</td>
<td>8.0</td>
</tr>
<tr>
<td>(\text{HCO}_2\text{C(OH)}\text{Cp}^*\text{CO}_2\text{Ph})</td>
<td>12.9</td>
</tr>
<tr>
<td>(\text{HCO}_2\text{C(OH)}\text{Cp}^*\text{CO}_2\text{Me})</td>
<td>13.6</td>
</tr>
<tr>
<td>(\text{HCO}_2\text{C(OH)}\text{Cp}^*\text{CO}_2\text{Ph})</td>
<td>6.2</td>
</tr>
<tr>
<td>(\text{HCO}_2\text{C(OH)}\text{Cp}^*\text{CO}_2\text{Me})</td>
<td>11.1</td>
</tr>
<tr>
<td>(\text{HCO}_2\text{C(OH)}\text{Cp}^*\text{CO}_2\text{Ph})</td>
<td>10.1</td>
</tr>
<tr>
<td>(\text{HCO}_2\text{C(OH)}\text{Cp}^*\text{CO}_2\text{Me})</td>
<td>very weak</td>
</tr>
</tbody>
</table>

Because water is a poor solvent for most transition metal hydrides, acidities were determined from equilibrium measurements in nitromethane and \(pK_a^1\) values in water were estimated from the equation: \(pK_a^1(H_2O) = pK_a^1(\text{MeNO}_2) - 7.5\).
Dewar and coworkers offered an alternative view.\textsuperscript{79} In their model the $d_{xy}$ and $d_{yz}$ orbitals are hybridized to give two orbitals which are directed toward the adjacent nitrogen atoms (Fig. 16.25). This allows for formation of three-center bonds about each nitrogen.\textsuperscript{79} This scheme, sometimes called the "island" model, results in delocalization over selected three-atom segments of the ring, but nodes are present at each phosphorus atom since the two hybrid orbitals of phosphorus are orthogonal to each other. Evidence has been offered in support of both models, but neither theory has been confirmed to the exclusion of the other. A third viewpoint holds that $d$ orbital participation is relatively unimportant in the bonding in these molecules.\textsuperscript{81}

The structures of tetrameric phosphazenes are more flexible than those of the trimers. The structure of (NPMe\textsubscript{2})\textsubscript{4} is planar, but others are found in a variety of conformations (tub, boat, chair, crown, saddle, and structures in between). The particular structure adopted is not very predictable and suggests that intermolecular forces play a major role. The tetrameric chlorophosphazene has been isolated in two forms (Fig. 16.26),\textsuperscript{82} the most stable of which assumes a chair arrangement (sometimes called the $T$ form). The other form (less stable $K$) has a tub conformation. An interesting feature of these compounds is that the nonplanar structures do not militate against extensive delocalization in the rings. The corresponding organic compound, cyclooctatetraene, $C\textsubscript{8}H\textsubscript{8}$, is nonaromatic for two reasons: (1) Its nonplanar, chair structure precludes efficient overlap; and (2) it does not obey the Hückel rule of bonding. Both the Craig/Paddock and Dewar models predict that the $\pi$ electron count is either equal to (Dewar) or more than (Craig/Paddock) that of the trimer. Tetramer is stabilized by delocalization (unlike cyclooctatetraene) and the stabilization is either equal to (Dewar) or more than (Craig/Paddock) that of the trimer.

Our discussion has dealt with trimeric and tetrameric phosphazenes, but many other ring sizes have been synthesized. For example, all of the compounds, (NPMe\textsubscript{2})\textsubscript{x}, ($x = 3$ to $12$), have been studied crystallographically.\textsuperscript{83} Furthermore, the first cyclophosphazene has been prepared:\textsuperscript{84}

\begin{equation}
\begin{align*}
{(\text{Pr} \textsubscript{2})N}_4 \rightarrow (\text{Pr} \textsubscript{2})_4N^4 \rightarrow (\text{Pr} \textsubscript{2})_4N^4 = (\text{Pr} \textsubscript{2})_4N^4
\end{align*}
\end{equation}

Diphosphazenes were long thought to be too unstable for isolation because of ring strain.

Phosphazenes can be polymerized and in many instances their polymers have advantages over the carbon-based polyolefins and polyesters.\textsuperscript{85} However, commercial application is not as well developed as for the silicones ($R$\textsubscript{3}SiO)\textsubscript{n}, (see page 739). Early studies were hampered by the sensitivity of the phosphorus-chlorine bond to

\textsuperscript{80} See page 791 for a discussion of three-center bonding.
NaH, LiAlH$_4$). For instance, they can act as reducing agents toward many organic compounds and are capable of hydrogenating alkenes and alkynes. Thus their H ligands are intermediate between the strictly hydridic hydrogens in the saline hydrides and the protonic hydrogens in compounds with nonmetals (e.g., HCl, NH$_3$).

Hydride ligands bound to transition metals generally give proton NMR signals that are considerably upheld from TMS (0 to -60 ppm), a feature that has been quite useful in characterizing hydride complexes. For example, 'H chemical shifts for H$_2$Fe(CO)$_4$ and [HFe(CO)$_4$]$^-$ are -11 and -9 ppm, respectively, while typical values for organic compounds are downfield from TMS (0 to +15 ppm). One should not conclude, however, that the upheld chemical shifts in hydride complexes arise because of high electron density about hydrogen. It is rather thought to be the result of paramagnetic contributions from the nearby transition metal.

The reaction of hydrogen gas with a transition metal complex can lead to a monohydride complex, as shown in Eq. 15.26, or to a complex with two coordinated H atoms. One of the more famous examples of the latter is the reversible reaction of Vaska's complex, Ir(CO)$_2$Cl$_2$(PPh$_3$)$_2$, with hydrogen:

$$\begin{align*}
\text{L} & \quad \text{Cl} \\
\quad & \quad \text{H} \\
\quad & \quad \text{Cl} \\
\quad & \quad \text{L}
\end{align*}
$$

This reaction has the characteristics of an oxidative addition (page 689): the formal oxidation state of Ir increases from +1 to +3 and the coordination number increases from 4 to 6. The process is believed to proceed via a concerted mechanism:

$$\begin{align*}
\text{M} + \text{H}_2 & \rightarrow \left[ \begin{array}{c}
\text{M} \\
\text{H} \\
\text{H}
\end{array} \right] \\
& \rightarrow \left[ \begin{array}{c}
\text{M} \\
\text{H} \\
\text{H}
\end{array} \right]
\end{align*}
$$

The proposed intermediate in this scheme represents an alternate mode of coordination for two H ligands—as a coordinated H$_2$ molecule. Although the intermediate in Eq. 15.28 has not been isolated, a number of other dihydrogen complexes have been.

The first was prepared in 1983:

$$\text{Mo(CO)}_3(\text{cht}) + 2\text{PPH}_3 \rightarrow \text{Mo(CO)}_3(\text{PPH}_3)_2 + \text{cht} \quad (15.30)$$

$$\text{Mo(CO)}_3(\text{PPH}_3)_2 + \text{H}_2 \rightarrow \text{Mo(CO)}_3(\text{PPH}_3)_2(\text{H}_2) \quad (15.31)$$

(ccht = cycloheptatriene)

The dihydrogen ($\tau^2$-H$_2$) ligand in this complex exists with its H—H bond intact (Fig. 15.11). Since the discovery of the first H$_2$ complex, many others have been characterized, including some which for years had been presumed to be cis dihydrogen complexes.

It was not a simple matter to prove that the complex in Eq. 15.31 should be viewed as M(H$_2$) rather than cis-M(H)$_2$ (see below). Even though it was possible to grow a crystal and subject it to X-ray analysis, some questions remained unresolved. The X-ray data gave H—H bond lengths of 74(16) pm and 84 pm, respectively, compared to 74 pm in uncoordinated H$_2$. These results strongly suggested that the H—H bond had not been broken, but the inherent uncertainty associated with locating hydrogen atoms left some room for skepticism. Synthesis of an $\pi^2$-HD complex eliminated this doubt. The proton NMR spectrum of the complex revealed an H—D coupling constant of 33.5 Hz, comparable to 43.2 Hz for uncoordinated H—D. The significance of these values is appreciated when they are compared to hydride-deuteride coupling (less than 2 Hz) in complexes in which bond distances are too great for an H—D bond to exist. In this instance, it was spectroscopy instead of crystallography that provided the final confirmation of structure.

Complexes which contain the $\tau^2$-H$_2$ ligand are now referred to as nonclassical, while those in which the H—H bond has been severed are called classical.

$$\begin{align*}
\text{M} & \quad \text{H} \\
& \quad \text{H}
\end{align*}
$$

Nondicalssical Classical

The difficulties encountered in firmly establishing the structure of the first dihydrogen complex still have not been entirely overcome. The H—D coupling constant experiment described above offers a method of distinguishing between the classical and nonclassical forms, but it is not applicable if the system is rapidly fluxional.
separate is the trimer, \( n = 3 \). Smaller amounts of the tetramer and other oligomers up to \( n = 8 \) have been characterized and higher polymers exist as well (see below). Analogous bromo compounds may be prepared in the same manner, except that bromine must be added to suppress the decomposition of the phosphorus pentabromide:

\[
PBr_5 + Br_2 \rightarrow NPBr_3\]  
\[
PBr_3 \rightarrow \frac{NaBr}{H_2O} [NPBr_3]_3 \]  

The fluoride must be prepared indirectly by fluorination of the chloride:

\[
[NPCl_3]_3 + 6NaF \rightarrow [NPF_3]_3 + 6NaCl \]  

The halide trimers consist of planar six-membered rings (Fig. 16.23).\(^{77}\) The bond angles are consistent with sp\(^2\) hybridization of the nitrogen and approximately sp\(^3\) hybridization of the phosphorus. Two of the sp\(^2\) orbitals of nitrogen, containing one electron each, are used for σ bonding and the third contains a lone pair of electrons. This leaves one electron left for the unhybridized p orbital.

![Fig. 16.23](image)

The four sp\(^3\) hybrid orbitals (housing four electrons) of phosphorus are used for σ bonding leaving a fifth electron to occupy a d orbital. As shown in Fig. 16.22, resonance structures can be drawn analogous to those for benzene indicating aromaticity in the ring. However, the situation is more complex than these simple resonance structures indicate. The planarity of the ring, the equal P—N bond distances, the shortness of the P—N bonds, and the stability of the compounds suggest delocalization. However, not all phosphazenes are planar, and the absence of planarity does not appear to make them any less stable. Furthermore, the phosphazenes yield UV spectra unlike those of aromatic organic compounds and they are much more difficult to reduce. Thus the extent of delocalization and the nature of the aromaticity have been debated for years. Unlike in benzene, π bonding in cyclophosphazenes involves d and p orbitals. There have been several descriptions offered for such dπ—pπ bonding. Craig and Paddock suggested the following model.\(^{78}\) The dπ orbital of the phosphorus atom overlaps with the pπ orbital of the nitrogen atoms adjacent to it (Fig. 16.24a). As a result of the gerade symmetry of the d orbitals, an inevitable mismatch in the signs of the wave functions occurs in the trimer (see Fig. 5.10) resulting in a node which reduces the stability of the delocalized molecular orbital. The dπ orbital, which is perpendicular to the dπ orbital, can also overlap with the pπ orbitals of nitrogen, but in this case no nodal surface results (Fig. 16.24b). There may also be in-plane π bonding between the sp\(^3\) nonbonding orbital of nitrogen and the dπ and/or dπ orbitals of phosphorus (Fig. 16.24c,d).

\[^{77}\text{Allcock, H. R.; Harris, P. J.} \text{Inorg. Chem.} \text{1981, 20, 2844-2848.}\]

\[^{78}\text{Small deviations from planarity found for the chloride, bromide, and fluorsolve may be the result of packing effects. The P—N bonds appear to be flexible and angle changes lead to little stability loss.}\]

\[^{78}\text{Paddock, N. L.} \text{Q. Rev. Chem. Soc.} \text{1964, 18, 146.}\]
Infrared analysis is difficult because M—H absorptions tend to be weak. Neutron diffraction requires large crystals, and X-ray diffraction is not precise enough for locating H atoms. An NMR method has been developed for differentiating classical and nonclassical structures that is based on the assumption that hydrogen nuclei involved in nonclassical coordination will have significantly faster relaxation rates than those involved in classical coordination. In this approach, the measured spin-lattice relaxation time, $T_1$, is correlated with the $\text{H—H}$ bond distance and hence with the angle of coordination. Application of the method to the hydrogen dimer of Yaska’s complex (Eq. 15.28) and to $\text{H}_2\text{FeCO}$, discussed earlier led to the conclusion that both are best regarded as classical complexes. Recent reports have urged caution in applying the $T_1$ criterion, based on the finding that the ranges of relaxation rates for classical and nonclassical formulations overlap.

The metal-H$_2$ bond may be profitably compared with a metal-carbonyl bond since both involve $\sigma$ donation to the metal by the ligand and both ligands can accept $\pi$ electron density into antibonding orbitals. The accepting orbitals for CO are empty $t^*$ orbitals, whereas for H$_2$ they are $\sigma^*$ orbitals (Fig. 11.23). Like the C—O bond, the H—H bond is weakened as a result of this metal-ligand $\pi$ interaction. A strong $d\sigma^{-}$ interaction can sever the H—H bond and lead to formation of a classical complex.

Some special note should be made of the structure and bonding in complexes containing a bridging hydride ligand. Probably the most famous bridged hydride is diborane, B$_2$H$_6$, discussed more extensively in Chapter 16, in which two of the H atoms bridge the pair of boron atoms. Useful parallels may be drawn between the hydride bridges in borohydrides and those in metal complexes. The complex $[\text{OCO}]\text{Cr—H—Cr(CO)}_3$ is similar to $[\text{BH}_2—\text{H—BH}_2]$ in the sense that both can be said to involve donation of a bonding pair of electrons (those in the B—H and Cr—H bonds of $[\text{BH}_2]$) and $[\text{Cr(CO)}_3]$ to a Lewis acid (BH$_2$ or Cr(CO)$_5$).

$$\text{H}_2\text{Cr—H—Cr(CO)}_3$$

In molecular orbital terms, the donation can be viewed as a HOMO—LUMO interaction (Chapter 9). Double hydrido bridges, as found in $\text{B}_2\text{H}_6$, also are exhibited by bimetallic species such as the chromium anion formed in Eq. 15.18. The similarity between these two bridged ligands is underscored by the fact that their Lewis acid and Lewis base fragments can be interchanged: $[\text{Cr(CO)}_5]$ reacts with BH$_2$ to form.

$$\text{H—H—Cr(CO)}_5$$

The bridging hydride interaction, whether it involves two boron atoms, two metal atoms, or one boron and one metal atom, is best described in terms of a three-center, two-electron bond (see Chapter 16).

Many of the reactions of metal carbonyl complexes parallel closely those of certain nonmetallic elements and compounds. For example, the MnCO$_5$ fragment has 17 valence electrons, one short of the total necessary to fill the 18-electron rule. It is analogous to the chlorine atom and the methyl free radical, each with seven valence electrons, one short of a noble gas configuration. The compounds and reactions of the pentacarbonyl fragment may thus be related to similar ones for chlorine or the methy1 group. All three are formally free radicals and much of their chemistry derives from pairing the odd electron. The manganese carbonyl normally exists as a dimer, Mn$_2$(CO)$_9$, (cf. Cl$_2$, C$_2$H$_6$), but it may be reduced to the monon complex, Mn(CO)$_4$, (cf. C$^+$, CH$_4$), which is the conjugate base of an acid, H$_2$MnCO$_5$, (cf. HCl, CH$_3$). Furthermore, it will combine with other species having a single unpaired electron, for example, R and R', to form neutral molecules, RMnCO$_5$, (cf. RCI, RC$_2$H) and MnCO$_5$, (cf. HCl, CH$_3$). The three fragments may be considered as electronically equivalent groups or as isolobal fragments.

The concept is an outgrowth of equating the Lewis octet rule of organic and main-group chemistry with the 18-electron rule of transition metal organometallic chemistry. Of course one should not push these ideas too far. For example, pentacarbonylchloromanganese is a much weaker acid than is HCl, and methane is normally not considered to be an acid at all. The isolobal formalism is more concerned with structural predictions based on electronic similarities than with topics like polarity.

Isolobal fragments have relationships that go beyond simple electron counting. The calculated electron density of the MnH$_2$ fragment (isolobal with MnCO$_5$, but simpler for calculation) may be compared with that of the methyl radical, CH$_3$ (Fig. 15.12). When one examines the overlap integrals of these two isolobal fragments with respect to an incoming probe such as a hydrogen atom, the results are remarkably similar (Fig. 15.13). The manganese fragment always has a somewhat greater overlap, but the dependence on distance is essentially identical.

Table 15.6 lists a number of examples of isolobal metal fragments that are isolobal with main-group fragments. Metal fragments with 16 electrons will behave as Group VIA (16) elements. Thus Fe(CO)$_5$ may form H$_2$Fe(CO)$_5$, (cf. HCl and Fe(CO)$_5$) (cf. S$^2$). Fifteen-electron fragments such as Ir(CO)$_5$ are isolobal with CH and with Group VA (15) elements, such as phosphorus. Each of these is three electrons short of a closed shell and each has three directed orbitals which form a triangular face. Hence the complex Ir(CO)$_5$ is isoelectronic with the P$_2$ molecule (Fig. 15.14) as well as with tetraedrate. (CH)$_4$.

40 The isolobal concept is based on the work of Derek H. Jones, who was writing his thesis in 1969 on the subject. The concept has been extended to include other fragments and other types of bonding, such as those involving oxygen and nitrogen.
Boron nitride exists in two derivatives: addition to borazine (Eqs. 16.39 and 16.41), but special techniques are necessary to prepare the parent compound. It was first synthesized by the reduction of the chloro polymeric precursor may be used to deposit a uniform surface coating.

The electronegativities of B and P are similar, unlike those of B and N. As a result, polarization should be less extensive in this compound than in borazine. The B-N ring is planar, with equal BP bond lengths and shortened BP bonds, suggesting significant aromaticity. Even more recently the boron of borazine derivatives has been replaced with aluminum to give "alumazines."  

The boron-phosphorus analogue of borazine has been synthesized rather recently.  

Phosphazenes  

Early workers noted the extreme reactivity of phosphorus pentachloride toward basic reagents such as water or ammonia. With the former the reaction is reasonably straightforward, at least for certain stoichiometries:

\[
P_4Cl_6 + 6H_2O \rightarrow 6OPCl_3 + 6HCl
\]

\[
P_4Cl_6 + 6HCl \rightarrow 6OPCl_3 + 6H_2O
\]

For reactions with ammonia analogous products such as \(HN=PCl_3\) and \(HN=PNH_2\) were proposed, but characterization was hampered by incomplete reactions, separation-resistant mixtures, and sensitivity to moisture. Furthermore, gradual polymerization occurred with loss of ammonia to yield "phospham," a poorly characterized solid of approximate formula \((PNH)_x\), as the ultimate product. If instead of free ammonia its less reactive conjugate acid is used, reaction with PCl_3 proceeds at a moderate rate and the results are more definitive:

\[
NH_4Cl + PCl_3 \rightarrow \text{aluminum phosphazene (Al-Phazene)} \quad \text{(16.47)}
\]

If the product were a monomer, its structure could be derived as \(CH=N-N\), which is analogous to organic nitriles, R—C=N. For this reason the original name used for these compounds was phosphonitriles, phosphonitrilic chloride, etc. However, the products are actually either cyclic or linear polymers of general formula \([NPCl_2]_n\). Thus, by analogy with benzene, borazine, etc., these compounds have become known as phosphazenes. The major product of the reaction in Eq. 16.47 and the easiest to

Lynch, A. T.; Sneddon, L. G., J. Am. Chem. Soc., 1989, 111, 6011-6029. Boron nitride exists in two forms, one analogous to graphite and the other to diamond. The graphite form has layers in which the boron atoms lie above nitrogen atoms in the layer below. Although this material shares with the properties of being a lubricant, unlike graphite, it is an electrical insulator. The cubic form, second only to diamond in hardness, is an excellent synthetic abrasive.


Fig. 15.12 Calculated contour diagrams for the isolobal $\alpha$ orbitals of [MnH$_5$]$^+$ (left) and (CH$_3$)$_2$ (right). The contours are plotted in a plane passing through manganese and three hydrogen atoms and through carbon and one hydrogen. [From Hoffmann, R. Angew. Chem. Int. Ed. Engl. 1982, 21, 711-724. Reproduced with permission.]

Fig. 15.13 Overlap integrals for the interaction between the $\alpha$, frontier orbital of [MnH$_5$]$^+$ or (CH$_3$)$_2$ and a $\sigma$ orbital on H at a distance R from the Mn or C. [From Hoffmann, R. Angew. Chem. Int. Ed. Engl. 1982, 21, 711-724. Reproduced with permission.]

Table 15.6

<table>
<thead>
<tr>
<th>Fragment</th>
<th>CH$_4$</th>
<th>CH$_3$</th>
<th>CH$_2$</th>
<th>CH$_+$</th>
<th>C$_+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(CO)$_4$</td>
<td>Mn(CO)$_5$</td>
<td>Fe(CO)$_3$</td>
<td>Co(CO)$_3$</td>
<td>Cr(CO)$_3$</td>
<td>Ni(CO)$_3$</td>
</tr>
<tr>
<td>Fe(CO)$_3$</td>
<td>Co(CO)$_3$</td>
<td>Fe(CO)$_2$</td>
<td>Co(CO)$_2$</td>
<td>Cr(CO)$_2$</td>
<td>Ni(CO)$_2$</td>
</tr>
<tr>
<td>Cr(CO)$_3$</td>
<td>Fe(CO)$_3$</td>
<td>Fe(CO)$_2$</td>
<td>Co(CO)$_2$</td>
<td>Cr(CO)$_2$</td>
<td>Ni(CO)$_2$</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>H</td>
<td>CH$_2$</td>
<td>CH$_+</td>
<td>CH$_+$</td>
<td>CH$_2$</td>
</tr>
</tbody>
</table>

Fig. 15.14 Comparison of (a) Ir$_4$(CO)$_5$ and (b) P$_4$. Both are tetramers, composed of the isolobal fragments Ir(CO)$_3$ and P, respectively, each of which is trivalent. [Structure (a) from Wilkes, G. R.; Dahl, L. F. Perspectives in Structural Chemistry 1968, 2, 71. Reproduced with permission.]

the two compounds goes beyond the fact that both possess a four-membered ring. The building blocks of the two structures, CH$_2$ and Os(CO)$_4$, are isolobal fragments. In fact the isostructural series has been extended to include Os$_2$(CO)$_8$(CH$_2$)$_2$, which has two Os(CO)$_4$ and two CH$_2$ fragments in the ring, and Os$_2$(CO)$_8$(CH$_2$)$_3$, with a ring consisting of one Os(CO)$_4$ and three CH$_2$ units. Our earlier comparison of the bridging hydrides of boron and transition metals also could have been couched in terms of isolobality. The Lewis acids, BH$_4$ and Cr(CO)$_5$, are isolobal fragments, as are BH$_3^-$ and [HCr(CO)$_5$]$^-$. Less obvious than the above examples are isolobal relationships that exist between fragments which appear to have different numbers of frontier orbitals. The addition or subtraction of H$_2^+$ to an organic fragment does not change the number of electrons in its frontier orbitals. As a consequence, CH$_2$, CH$_3$, and CH$_4$ are isolobal fragments. This result is less surprising if you consider that there are a variety of ways in which the carbon atom may be hybridized. It is worth noting that if two fragments are both isolobal with a third, they are isolobal with each other as well.

We shall encounter further examples of isolobal fragments later in this and subsequent chapters, but for now we can sum up their essential features as follows:

Two fragments are isolobal if the number, symmetry properties, approximate energies, and shapes of their frontier orbitals and the number of electrons in them are similar.

density is localized on the nitrogen atoms (Fig. 16.22). This partial localization weakens the π-bonding in the ring. Each nitrogen receives more π-electron density from neighboring boron than it gives away as a π-donor. The net effect is that the charge density on nitrogen increases. In addition, nitrogen retains its basicity and boron its acidity. Polar species such as HCl can therefore attack the double bond between nitrogen and boron. Thus, in contrast to benzene, borazine readily undergoes addition reactions:

\[
\text{H}_2\text{N-B-N-H} + 3\text{HCl} \rightarrow \text{H}_2\text{N-B-Cl}_3 \tag{16.39}
\]

\[
\text{H}_2\text{N-B-N-H} + \text{HCl} \rightarrow \text{No reaction} \tag{16.40}
\]

The contrasting tendencies of the two compounds toward addition vs. aromatic substitution is illustrated by their reactions with bromine:

\[
\text{H}_2\text{N-B-N-H} + 3\text{Br}_2 \rightarrow \text{H}_2\text{N-B-Br}_3 \tag{16.41}
\]

\[
\text{H}_2\text{N-B-N-H} + \text{Br}_2 \rightarrow \text{H}_2\text{N-B-Br}_2 \tag{16.42}
\]

The electronic difference between benzene and borazine is further supported by the properties of compounds of the type (R-B-N)Cr(CO)_3. Although these are formally analogous to (η-6-C_6H_6)Cr(CO)_3, the bonding is not nearly so strong in the borazine complex—its ring-metal dissociation energy appears to be about one-half that of the arene complex. In addition, there is considerable evidence that the borazine molecule is puckered in these complexes. The actual structure appears to be intermediate between a true π complex and the extreme σ-only model.

---

Fig. 16.21 Electronic structures of (a) benzene; (b) borazine.

Fig. 16.22 Contour maps of the charge density in the molecular plane of (a) benzene; (b) borazine. [From Boyd, R. J.; Choi, S. C.; Hale, C. C. Chem. Phys. Lett. 1984, 112, 136-141. Reproduced with permission.]

---


Few complexes containing only nitrosyl ligands are well characterized, but many mixed carbonyl-nitrosyl complexes are known. They may be formed readily by replacement of carbon monoxide with nitric oxide:

\[
\text{Fe(CO)}_3 + 2\text{NO} \rightarrow \text{Fe(CO)}_2(\text{NO})_2 + 3\text{CO} \quad (15.33)
\]

\[
\text{Co}_2(\text{CO})_8 + 2\text{NO} \rightarrow 2\text{Co(CO)}_3(\text{NO}) + 2\text{CO} \quad (15.34)
\]

Unlike carbon monoxide, which can be used in excess at high temperatures and pressures, nitric oxide in excess can cause unfavorable oxidation, and at high pressures and temperatures it decomposes. Many of the current syntheses avoid the use of nitric oxide by substituting nitrosyl chloride, nitrites, or nitrosonium salts:

\[
\text{[Co(NO)(CO)}_3] + \text{CO} \rightarrow \text{Co}(\text{CO})_3 + \text{NO} \quad (15.35)
\]

\[
\text{Fe}(\text{CO})_3 + 2\text{NO} \rightarrow \text{Fe}(\text{CO})_2(\text{NO}) + 3\text{CO} \quad (15.36)
\]

Although the nitrosyl group generally occurs as a terminal ligand, bridging nitrosyls are also known:

\[
\text{O} = \text{N} \quad \text{N} = \text{O}
\]

As in the case of the corresponding carbonyl complexes, infrared stretching frequencies are diagnostic of the mode of coordination. For the product in Eq. 15.36, \(\nu(\text{terminal NO}) = 1672 \text{ cm}^{-1}\) and \(\nu(\text{bridging NO}) = 1505 \text{ cm}^{-1}\).

Since the nitrosyl cation, \(\text{NO}^+\), is isoelectronic with CO, it is not surprising that there is a great similarity in the behavior of the two ligands. They each have three bonding pairs between the atoms and lone pairs on both atoms. Although either atom in NO is a potential donor, the nitrogen atom coordinates preferentially to a carbon monoxide, avoiding a large formal positive charge on the more electronegative oxygen atom. However, in one important respect the nitrosyl group behaves in a manner not observed for carbon monoxide. Although most nitrosyl ligands appear to be linear, consistent with \(\sigma\) hybridization of the nitrogen, a few cases of distinctly bent species are known. A bent nitrosyl ligand is an analogue of an organic nitroso group, where the nitrogen atom (bent group) or whether there is a low-lying metal-based molecular orbital available to it. If there are available nonbonding MOs on the metal (electron-poor system), the pair can reside there and allow the nitrogen to function as an \(\pi\) donor with concomitant \(\pi\) back bonding. On the other hand, if all the low-lying orbitals on the metal are already filled (an electron-rich system), the pair of electrons cannot count for the linear case includes the nonbonding electron pair on nitrogen as well as the unpaired antibonding electron in NO:

\[
\text{M} + \text{NO} = \text{NO}^+ \rightarrow \text{M} = \text{N} = \text{O} \quad (15.39)
\]

In the oxidation state method, the ligand is viewed as a coordinated nitrosyl ion, \(\text{NO}^+\), when linear and a coordinated \(\text{NO}^+\) when bent; it is a two-electron donor in both forms.

The first well-characterized example of a bent nitrosyl ligand was that found in a derivative of Vaska's complex:

\[
\text{[Ir(Ph}_3\text{P)}_2(\text{CO})_3\text{Cl}] + \text{NO} + \text{BF}_4^- \rightarrow \text{[Ir(Ph}_3\text{P)}_2(\text{CO})_3\text{NO}][\text{BF}_4^-] \quad (15.40)
\]

The product is square pyramidal with a bent nitrosyl ligand (\(\text{M} = \text{N} = \text{O} = 124^\circ\)) at the apical position (Fig. 15.15a).

Other complexes with a bent \(\text{M} = \text{N} = \text{O}\) have been found, including the remarkable example \([\text{Ru}(\text{Ph}_3\text{P})_2(\text{NO})_2][\text{PF}_6^-]\), which contains both linear and bent nitrosyl groups (Fig. 15.15b). The question of whether a nitrosyl ligand will be linear or bent resolves itself into whether the pair of electrons in question will be forced to reside in an orbital on the nitrogen atom (bent group) or whether there is a low-lying metal-based molecular orbital available to it. If there are available nonbonding MOs on the metal (electron-poor system), the pair can reside there and allow the nitrogen to function as an \(\pi\) donor with concomitant \(\pi\) back bonding. On the other hand, if all the low-lying orbitals on the metal are already filled (an electron-rich system), the pair of electrons...
Borazines

The most important ring system of organic chemistry is the benzene ring, either as a separate entity or in polynuclear hydrocarbons such as naphthalene, anthracene, and phenanthrene. Inorganic chemistry has two (at least) analogues of benzene: boronates, $B_2N_2R_6$, and trimeric cyclopentaphosphazene compounds, $P_3N_6X_3$.

Borazine has been known since the pioneering work of Alfred Stock early in the 20th century. Stock’s work was important in two regards: He was the first to study compounds such as the boranes, silanes, and other similar nonmetal compounds, and he perfected vacuum line techniques for the handling of air- and moisture-sensitive compounds, invaluable to the modern inorganic chemist. Stock synthesized borazine by heating the adduct of diborane and ammonia:

$$3\text{BH}_3 + 6\text{NH}_3 \rightarrow 3[\text{BH}_3(\text{NH}_3)_2]^+ \text{BH}_4^- + 2\text{B}_2\text{N}_2\text{H}_6 + 12\text{H}_2$$

More efficient synthesis are:

$$\text{NH}_3 + \text{BCl}_3 \rightarrow \text{Cl}_3\text{B}_2\text{N}_2\text{H}_2 \text{NaBH}_4 \rightarrow \text{B}_2\text{N}_2\text{H}_6$$
$$\text{NH}_3 + \text{NaBH}_4 \rightarrow \text{B}_2\text{N}_2\text{H}_6 + \text{H}_2 + \text{NaCl}$$

N- or B-substituted borazines may be made by appropriate substitution on the starting materials prior to the synthesis of the ring:

$$[\text{RNH}_3]^+ + \text{BCl}_3 \rightarrow \text{Cl}_3\text{B}_2\text{N}_2\text{R}_3 \text{NaBH}_4 \rightarrow \text{H}_3\text{B}_2\text{N}_2\text{R}_3$$

or substitution after the ring has formed:

$$\text{Cl}_3\text{B}_2\text{N}_2\text{R}_3 + 3\text{LiR} \rightarrow \text{R}_3\text{B}_2\text{N}_2\text{R}_3 + 3\text{LiCl}$$

Borazine is isoelectronic with benzene, as $\text{B}_2\text{N}_2\text{H}_6$ is with $\text{C}_6\text{H}_6$. In physical properties, borazine is indeed a close analogue of benzene. The similarity of the physical properties of the alkyl-substituted derivatives of benzene and borazine is even more remarkable. For example, the ratio of the absolute boiling points of the substituted borazines to those of similarly substituted benzene is constant. This similarity in physical properties led to a labeling of borazine as “inorganic benzene.” This is a misnomer because the chemical properties of borazine and benzene are quite different. Both compounds have aromatic $\pi$-chains of electron density with potential for delocalization overall of the ring atoms. Due to the difference in electronegativity between boron and nitrogen, the cloud in borazine is “lumpy” because more electron delocalization is possible.

Borazine syntheses are reviewed in Borazine Heptatriaphosphorin: Springer-Verlag: New York, 1978; Vol. 17.

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**Fig. 16.20** $^1\text{O}$ NMR spectra of (a) $[\text{W}_6\text{O}_{19}]^{2-}$ and (b) $[\text{CpTtW}_2\text{O}_{19}]^{2-}$. Labels on spectral lines indicate assignments: line a to site A, line b to site B, etc.; * = impurity. [From Day, V. W.; Klumpp, W. G. Science 1985, 228, 533-541. Reproduced with permission.]
must occupy an essentially nonbonding orbital on the nitrogen, requiring trigonal hybridization and a bent system. A comparison of the bonding possibilities for NO and CO is shown in Fig. 15.16.

The metal-nitrogen bond lengths in the ruthenium complex containing both types of nitrosyl ligands (Fig. 15.15b) are in accord with the view just presented. In the linear system there is a short metal-nitrogen bond (173.8 pm) indicating substantial \( \pi \) bonding (as in metal carbonyls). The bent system, in contrast, shows a relatively long, essentially \( \sigma \)-only metal-nitrogen bond (185.9 pm). It would be expected that the N—O bond of a bent nitrosyl would be longer than that of a linear nitrosyl. However, the insensitivity of the NO bond length to small changes in bond order coupled with systematic errors in the crystallographic analysis make evaluation of such data difficult. Within experimental error, the bent and linear N—O bonds of \([\text{Ru(PPh}_3)_2(\text{NO})_2\text{Cl}]^+\) are the same length (117.0 and 116.2 pm). The N—O bond lengths in NO, NO, and NO are 106, 115, and 120 pm, respectively. We can only conclude that the NO bond order, for both the apical and basal arrangements, lies between two and three.

We can actually see the process of electron pair shift with a resultant change in structure in the complex ion \([\text{Co}((\text{diars})_2]^2+\) (where diars is a bidentate diarsine ligand) (Fig. 15.17). The 18-electron rule predicts that the nitrosyl group will be linear from being a three-electron donor to an orbital on nitrogen. This is in fact what happens and "sterrochemical control of valence" results.47 As NO goes from being a three-electron to a one-electron donor, a coordination site capable of accepting a pair of electrons becomes available.

![Figure 15.16](image)

**Fig. 15.16** Geometry (linear vs. bent) of nitrosyl ligands correlated with the hybridization of the nitrogen atom and parallel correlations for analogous compounds containing carbonyl ligands.


---

**Fig. 15.17** Stereochemical control of valence. Note localization of the lone pair on the nitrogen atom and bending of the nitrosyl group upon addition of thiocyanate ion to the coordination sphere. Bond lengths are in picometers. (From Enemark, J. H.; Feltham, R. D. Proc. Natl. Acad. Sci. USA 1972, 69, 3534. Used with permission.)

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**Dinitrogen Complexes**

Molecular nitrogen, \( \text{N}_2 \), is isoelectronic with both carbon monoxide and the nitrosyl ion but, despite the numerous complexes of CO and NO, for many years it proved to be impossible to form complexes of dinitrogen. This difference in behavior was usually ascribed to the lack of polarity of \( \text{N}_2 \) and a resultant inability to behave as a \( \pi \) acceptor.

The first dinitrogen complex, characterized in 1965, resulted from the reduction of commercial ruthenium trichloride containing some Ru(IV) by hydrazine hydrate. The pentaaamminedinitrogenruthenium(II) cation that formed could be isolated in a variety of salts.50 Soon other methods were found to synthesize the complex, such as the direct reaction with nitrogen gas:

\[
\begin{align*}
\text{[Ru(NH}_3)_5\text{N}_2]^2+ \quad & \xrightarrow{\text{N}_2} \quad \text{[Ru(NH}_3)_5\text{H}_2\text{O}]^{2+} \\
\text{[Ru(NH}_3)_5\text{H}_2\text{O}]^{2+} + \text{N}_2 & \rightarrow \text{[Ru(NH}_3)_5\text{N}_2]^2+ \\
\end{align*}
\]


51 Note, however, that the dipole moment of carbon monoxide is extremely small: 0.175 \times 10^{-30} \text{C m}.

In which many polyanions have been shown to function as ligands. In some instances the cation simply binds to bridging or terminal oxygen atoms found on the surface of the polyoxometalate anion. For example, $\text{Mn}^{2+}$ binds weakly to a terminal oxygen atom of $[\text{H}_2\text{W}_6\text{O}_{18}]^{12-}$; thus the anion functions as a monodentate ligand. If, however, the polyoxometalate anion has vacancies created by missing metal units (Fig. 16.18), coordination may occur by incorporating the cation into the vacancy (Fig. 16.19). Polyoxometalate structures with vacancies are referred to as lacunary species. These species may function as pentadentate ligands (e.g., six-coordinate Co in $[\text{SiW}_{12}\text{O}_{40}]^{3-}$) or tetradentate ligands (e.g., four-coordinate Cu in $[\text{PW}_{12}\text{O}_{40}]^{3-}$).

All facets of study have been greatly aided by the ease with which crystal structures may be obtained and by the availability of sensitive Fourier transform NMR spectrometers which allow nuclei such as $\text{O}^{17}$, $\text{V}^{51}$, $\text{Nb}^{95}$, and $\text{Mo}^{97}$ to be used for structural studies. Oxygen-17 NMR spectroscopy has proved to be particularly useful because $\text{O}^{17}$ chemical shifts are very sensitive to environment. As a result it is possible to distinguish between terminal and various kinds of bridging oxygen sites. The $\text{O}^{17}$ spectrum of $[\text{Mo}_6\text{O}_{19}]^{3-}$ and its structure are shown in Fig. 16.20.a,b. We see

---

The unexpectedly strong nucleophilicity of dinitrogen shown by its displacement of water in Eq. 15.42 is also exhibited in the formation of a bridged complex:

\[
{[\text{Ru(NH}_3)_2\text{N}_2]}^+ + [{\text{Ru(NH}_3)_2\text{H}_2\text{O}}]^+ \rightarrow {\text{[Ru(NH}_3)_5\text{N}_2\text{Ru(NH}_3)_2]}^+ + \text{H}_2\text{O}
\]

(15.43)

There are two structural possibilities for terminal dinitrogen ligands and two for bridged cases:

- M—N—N
- M—N—N—M

End-on terminal End-on bridging

M

\[
\begin{align*}
\text{side-on terminal} & \quad \text{side-on bridging} \\
\text{M—N—N} & \quad \text{M—N—N—M}
\end{align*}
\]

An X-ray study of the original ruthenium-dinitrogen complex\(^{57}\) indicated that the nature of the Ru—N—N linkage was end on, but disorder in the crystal prevented accurate determination of bond lengths. Since then, many structures of other dinitrogen complexes have been determined, including the bis(dinitrogen) crown thioether derivatives.\(^{58}\) The mean N—N bond length (110.7 pm) is slightly greater than that found in molecular nitrogen (109.8 pm), suggesting a weakening of the nitrogen—nitrogen triple bond from the donation of electron density to the metal.\(^{58}\)

The Raman stretching frequency of free N\(_2\) is 2331 cm\(^{-1}\). Upon coordination, this vibration becomes infrared active and shifts to a lower frequency. For example, strong N—N stretching bands appear at 2105 cm\(^{-1}\) for [Ru(NH\(_3\))\(_2\)N\(_2\)]\(^2+\) and at 1955 and 1890 cm\(^{-1}\) for [Ru(NH\(_3\))\(_2\)NH\(_2\)]\(^2+\). The superior accepting ability of CO also accounts for the instability of carbonyl dinitrogen complexes. Both Cr(CO)\(_5\)N\(_2\) and Cr(CO)\(_3\)N\(_2\) are isolated at room temperature.\(^{60}\)

Cr(CO)\(_5\)N\(_2\) have been investigated at low temperatures, but decompose when warmed.\(^{61}\) Replacing some of the carbonyls with phosphines can provide sufficient electron density to significantly enhance stability; hence, Mo(CO)\(_3\)(PCy\(_2\))\(_2\)N\(_2\) can be isolated at room temperature.\(^{61}\)

\[
\text{Mo(CO)}_3(\text{PCy}_2)_2 + \text{N}_2 \rightarrow \text{Mo(CO)}_3(\text{PCy}_2)_2\text{N}_2
\]

(15.44)

When dinitrogen functions as a bridging ligand, it usually exhibits end-on coordination; this is the case in the diruthenium complex of Eq. 15.43. For example, bridging side-on complexes are also known, however, and a recently reported example is also the first dinitrogen complex of an elemento (Fig. 15.10).\(^{57}\) In this samarium complex, obtained from the reaction of Sm(CO)\(_3\)N\(_2\) and Sm\(_2\), the two samarium atoms and the two nitrogen atoms are in a planar arrangement. The Sm—N bond distances suggest the presence of Sm—NII, implying a reduced N—N bond, but strongly enough the N—N bond distance (108.8 pm) is even shorter than that found in free dinitrogen.

The ability to synthesize complexes containing dinitrogen, especially those with considerable alteration of the electronic state of nitrogen, opens up possibilities of direct fixation of nitrogen from the atmosphere, a long-standing challenge to the chemist.\(^{56}\) It also provides insight into the closely related process of biological fixation of nitrogen and the enzyme systems involved (see Chapter 19).

---

**Metal Alkyls, Carbenes, Carbonyls, and Carbides**

Single, double, and triple bonds between carbon and nonmetals such as carbon, nitrogen, and oxygen have long occupied a central position in organic chemistry. The chemistry of metal-carbon single bonds in main group compounds (e.g., Grignard reagents and organometallic compounds) dates back to the 19th century. Transition metal compounds containing metal-carbon single, double, and triple bonds have become to be understood much more recently:

\[
\text{M} \rightarrow \text{CR}_3, \quad \text{M} \rightarrow \text{CR}_2, \quad \text{M} \rightarrow \text{CR}
\]

Although there are some early examples of complexes in which M—C single bonds are present (e.g., [Me\(_2\)PH], synthesized in 1907), the prevailing view for many years was that metal-carbon single bonds were inherently unstable.
It has been noted that there is a cavity in the center of the metatungstate ion. This cavity is surrounded by a tetrahedron of four oxygen atoms (Fig. 16.13) that is sufficiently large to accommodate a relatively small atom, such as P(V), As(V), Si(IV), Ge(IV), Ti(IV), or Zr(IV).

The 12-tungstoheteropoly anions are of general formula \([X_{12}W_iO_{40}]^{-n}\). Analogous molybdoheteropoly anions are also known. For example, when a solution containing phosphate and molybdate is acidified, the ion \([\text{PMo}_{12}O_{40}]^{3-}\) is formed. Obviously phosphorus-oxygen bonds are not broken in the process so we can view the product anion as the incorporation of \(\text{P}_4\) into an \(\text{Mo}_{12}O_{40}\) cage. Molybdoheteropoly anions of this type are of some importance in the qualitative and quantitative analytical chemistry of phosphorus and arsenic.

Between 35 and 40 heteroatoms are known to form heteropoly anions and their corresponding acids. Large heteroatoms such as \(\text{Ce}(IV)\) and \(\text{Th}(IV)\) are foundicosahedrally coordinated in salts such as \((\text{NH}_4)_2\text{H}_2\text{CeMo}_{12}O_{40}\) (Fig. 16.14). It is unique inasmuch as pairs of \(\text{Mo}_6\) octahedral groups are corner connected to each other.

Of the many other heteropoly acids, the 6-molybdotellurate species are of some interest. These form with heteroatoms \(\text{Tc}(VI)\) and \(\text{I}(VII)\) and tripositive metal ions such as \(\text{Rh}(III)\). All of these heteroatoms prefer an octahedral coordination sphere, which can be provided by a ring of six \(\text{Mo}_6\) octahedra (Fig. 16.15). Note that formally the 6-

heteropoly formulation can be applied to the heptamolybdate species discussed earlier if the seventh molybdenum atom is considered to be a pseudo-heteroatom. At one time it was felt that the 6-heteropoly acids should be isomorphous with the heptamolybdate. This is not the case as may be seen by comparison of Figs. 16.10c and 16.15. The structures are more similar than might be supposed, however, the principle difference being whether the heteroatom is surrounded by a planar ring of molybdenum atoms (6-heteropoly species, Fig. 16.16a) or a puckered ring (heptamolybdate, Fig. 16.16b). There are also more complicated heteropoly acids, including diheteropoly acids such as \([\text{P}_2\text{W}_6\text{O}_{34}]^{14-}\), which has been found to have a structure (sometimes called the Dawson structure) related to the 12-heteropoly acids (Fig. 16.17).

As a class, the isopoly and heteropoly anions offer several interesting facets for study. They may be considered small chunks of metal oxide lattices. As such they provide insight into catalysis by heterogeneous oxides, an approach that is currently enjoying strong interest for selective oxidation of organic molecules. As anions they show very low surface charge densities and low basicities. For example, we generally think of the perchlorate ion, \(\text{ClO}_4^-\), as having a very low basicity. One study has shown that the hexamolybdate \(-2\) ion and 12-tungstophosphate \(-3\) ion have lower basicities than perchlorate, and the 12-molybdophosphate \(-3\) ion is only slightly more basic than perchlorate. Nevertheless, a rich coordination chemistry is evolving.

---

28 The resulting structure, which has \(T_d\) symmetry, has come to be known as the Keggin structure, named after its discoverer.

29 The prefix \(12\) may be used to replace the more cumbersome "dodeca" to indicate the number of metal atom octahedra coordinated to the heteroatom.

30 One or more protons may be added to the anion with corresponding reduction of anionic charge.

years was that transition metal alkyls, unlike the main group alkyls, are thermodynamically unstable. This conclusion was reached because synthetic attempts to obtain compounds such as diethyliron or diethylcobalt (e.g., by reactions between FeBr₂ and EtMgBr) were unsuccessful. In fact transition metal-carbon bonds are in general no less strong than main group metal-carbon bonds (Table 15.7). However, it should be noted that, although metal-carbon bonds decrease in strength as the atomic number increases for the main group metals, they increase in strength as the atomic number increases for transition metals. Thus the early focus on the first-row transition series was least favorable from a thermodynamic point of view. However, the principal difficulty in obtaining transition metal-carbon bonds was not thermodynamic but kinetic. There are a number of favorable pathways available to metal alkyls for decomposition. One of the most important is β elimination (page 699):

\[
\text{M} - \text{CH}_2\text{CH}_2\text{R} \rightarrow \text{M} = \text{CH}_3 + \text{CH}_3\text{R}
\]

A great deal of synthetic success has been achieved by using alkyl groups that do not have β hydrogen atoms. Among these are PhCH₂, Me, and CH₂CH₂, none of which can decompose by β elimination.

### Table 15.2

<table>
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<td>D, kj mol⁻¹</td>
</tr>
<tr>
<td>TBC₃Me</td>
<td>351</td>
</tr>
<tr>
<td>Ti(CH₃₂)₂Me</td>
<td>198</td>
</tr>
<tr>
<td>Zr(CH₃₂)₂Me</td>
<td>249</td>
</tr>
<tr>
<td>H(C₂H₅)₂Me</td>
<td>266</td>
</tr>
<tr>
<td>TaMe₃</td>
<td>261</td>
</tr>
<tr>
<td>WMe₅</td>
<td>160</td>
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<td>Co(dppe)₂(CH₂Ph)</td>
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competing for the same vacant $\varepsilon_2$ metal orbital. Instead they are found opposite a bridging or internal oxygen. The effect is that the metal ion is displaced in the direction of the terminal oxygen, away from the oxygen opposite b (trans effect), just as you would predict based on a metal ion-metal ion repulsion model. Metal ions such as Al(III) or Ga(III) are poor acceptors. Thus their terminal oxygen atoms are not stabilized and can repeatedly attack other units to give continuing polymerization. The terminal oxygen atoms of the transition metal polyoxoanions, however, are stabilized by bonding and have less affinity for adjacent metal units.47

Although elucidation of various molybdate species continues, four appear to be most important: (1) the simple molybdate, $\text{MoO}_4^{2-}$, stable at high pH, (2) the heptamolybdate (also known as pararhombic), $[\text{Mo}_{7}\text{O}_{24}]^{12-}$ (Fig. 16.10c), formed in equilibrium with molybdate down to pH 4-5; (3) octamolybdate, $[\text{Mo}_{8}\text{O}_{26}]^{5-}$; (Fig. 16.10d),48 formed in more acidic solutions; (4) $[\text{Mo}_{12}\text{O}_{40}]^{3-}$, the largest isopolyanion known, present in solutions at about pH 1.8.49 From strongly acidic solutions can be precipitated polymeric $\text{MoO}_2 \cdot 2\text{H}_2\text{O}$ consisting of sheets of corner-shared $\text{MoO}_6$ octahedra.

The formation of alkyloxotungstates is similar to that described for the molybdates although the chemistry is even more difficult. The simple tungstate, $\text{WO}_4^{2-}$ exists in strongly basic solution. Acidification results in the formation of polymers built up from $\text{WO}_4$ octahedra. The nature of the tungsten species present depends not only on the present conditions (e.g., pH) but also on the history of the sample since some of the conversions are slow. Upon acidification of $\text{WO}_4^{2-}$, the tungstate $\text{W}_6^{12-}$, forms rapidly. Its protonated form, $[\text{HW}_6\text{O}_{12}]^{7-}$, has also been detected.50 From these solutions are precipitated salts of the dodecaoxotungstate, $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$ (paratungstate B), whose framework is shown in Fig. 16.14. From more acidic solutions it is possible to crystallize a second dodecaoxotungstate ion, $[\text{HW}_{12}\text{O}_{40}]^{8-}$ ("paratungstate A"). The structure of this ion, although built of the same $\text{WO}_6$ octahedra, is more symmetrical, resulting in a cavity in the center of the ion (Fig. 16.11b).51 In recent times many advances in isopoly anion chemistry have been made by shifting reaction chemistry from aqueous to aprotic solution. This can often be done by employing a solubilizing cation such as tetraethylammonium. For example, when $[\text{(Bu}_3\text{NH})_2\text{Na}]^+$ and $[\text{(Bu}_3\text{NH})_2\text{Na}]^+$ in acetonitrile a new isopolyvanadate forms:52

$$[\text{H}_2\text{V}_6\text{O}_{18}]^{2+} + 2\text{OH}^- \rightarrow 2[\text{V}_3\text{O}_6]^{14-} + \text{H}_2\text{O} \quad (16.33)$$

Fig. 16.11. The structures of two apex-shared dodecatungstate isopoly anions; (a) the paratungstate B ion, $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$; (b) the metatungstate ion, $[\text{HW}_{12}\text{O}_{40}]^{8-}$. [From Lipscomb, W. N., 

This anion (Fig. 16.12a) is of special significance because it is the first example of a transition metal polyoxovanadate cage that is built from corner-shared tetrahedra. In a similar vein, refluxing $[\text{Bu}_3\text{NH}]_2[\text{H}_2\text{V}_6\text{O}_{18}]^{2+}$ in acetonitrile leads to $[\text{MeCNCV}_3\text{O}_3]^{2+}$ (Fig. 16.12b) in which, remarkably, $\text{MeCN}$ is found inserted into a $[\text{V}_6\text{O}_{18}]^{12-}$ basket.53

Undoubtedly we can expect many interesting and novel isopolyanions to be isolated and characterized in the years ahead. The number of practical applications for these materials and their derivatives is impressive and extends to medicine, catalysis, and solid state devices.54

50 Prior to any definite knowledge of the structure or even of the empirical formula of each of the various paratungstate ions, they were arbitrarily assigned names such as A, B, X, Y, and Z. Much early confusion in this field occurred because workers referred to "paratungstate" without specifying which of the many possible species was being discussed.
52 Although it might appear that there is a similar, but smaller, cavity in the paratungstate B ion, the van der Waals radii of the oxygen atoms on the inner apices of the octahedra forming the structure effectively fill the cavity.
Substantial improvement in the convenience and scope of carbene synthesis followed by replacing diazomethane with other alkylating agents such as R-OBF or MeOSO₂F. (See Eqs. 15.148–150 for synthesis from [Cr(CO)₅].) Hundreds of carbene complexes of the type shown in Eq. 15.49 are known. They are characterized by having a metal in a low oxidation state, π-accepting auxiliary ligands, and substituents on the carbene carbon capable of donating π electron density. When they participate in reactions, the carbene carbon behaves as an electrophile. Complexes having these properties are known as "Fischer" carbenes. The usefulness of these complexes in organic synthesis is presently under intense investigation (see page 705).

Free carbenes exist in both triplet and singlet states but those containing a heteroatom (e.g., O or N), as found in Fischer carbenes, tend to be of the latter variety. Thus the free ligand may be represented as follows:

The pair of electrons in the π² orbital may be donated to a metal to form a π bond, and an empty π orbital is present to accept π electron density. Filled d orbitals of the metal may donate electrons to the π orbital to give a metal-carbon double bond, and electrons from filled π orbitals of the oxygen atom may also be donated to form a carbon-oxygen double bond (Fig. 15.20). Resonance form 15.20b appears to be dominant and, although the M—C bond is shorter than expected for a single bond, it is too long for an M—C double bond, leading to the conclusion that the bond order is between one and two.

Just ten years after the discovery of Fischer's electrophilic carbene, Schrock discovered a class of carbenes which are nucleophilic.

These nucleophilic carbenes are composed of early transition metals in high oxidation states, non-π-accepting auxiliary ligands, and non-π-donating substituents on carbon.

They are called "Schrock" carbenes to distinguish them from the Fischer carbenes. One way to view these complexes is in terms of two orbitals on the carbene, each having an unpaired electron (triplet state) overlapping with two metal orbitals, each of which provides an electron.

The electrophilic nature of a Fischer carbene is illustrated in the following reaction:

\[ (OC)₅CrC(OC)₅C≡C—NH \] (15.51)

In this reaction the nucleophile, NH₃, attacks the carbene carbon to form an intermediate which eliminates methanol. The reaction is favorable because nitrogen is not as electronegative as oxygen and its π-donating ability exceeds that of oxygen (stabilizing resonance form (b) in Fig. 15.20).

The nucleophilic nature of a Schrock carbene is seen in its reaction with Me₃Al:

\[ (η^5-C₅H₅)MeTa=CH₂ + AlMe₃ \rightarrow (η^5-C₅H₅)MeTa=CH₂AlMe₃ \] (15.53)
Inorganic Chains, Rings, Cages, and Clusters

756

16-Inorganic Chains, Rings, Cages, and Clusters

This expectation is borne out in a general way. For example, the metal radii (Table 4.4) are $V^+$ (74 pm), $Nb^{4+}$ (78 pm), $W^+$ (73 pm), $Mo^{5+}$ (74 pm), $Nb^{3+}$ (78 pm) = $Mo^{6+}$ (78 pm) = $W^{5+}$ (73 pm), $Nb^{5+}$ (78 pm). The coordination number of the metals changes from 4 to 6, and the basic building unit in the polymerization process becomes an octahedron of six oxide ions surrounding each metal atom. Unlike a tetrahedron, which can only link by sharing an apex, the resulting octahedra may link by sharing either an apex or edge (rarely a face) due to the relaxation of electrostatic repulsions in the larger octahedra. As a result, the structures tend to be small clusters of octahedra in the discrete polyanions, culminating in infinite structures in the oxides. When the edge sharing takes place, the structure may be stabilized (relative to electrostatic repulsions) if some distortion occurs such that the metal ions move away from each other. As the polymerization increases, it becomes more and more difficult to have all metal ions capable of moving to assist in this reduction in electrostatic repulsion. Ultimately the sharing of edges ceases since the requisite distortion becomes impossible. It might be expected that the smaller the metal ion, the less the repulsion and the larger the number of edge-sharing octahedra per unit. This expectation is borne out in a general way. For example, the metal radii (Table 4.4) are $V^+$ (74 pm), $Mo^{4+}$ (73 pm), $W^{4+}$ (74 pm), $Nb^{3+}$ (78 pm) = $Nb^{4+}$ (78 pm) = $W^{5+}$ (73 pm), $Mo^{6+}$ (78 pm) = $W^{5+}$ (73 pm).

Other metals such as vanadium have more complicated chemistry. The vanadate ion, $V_2O_7^{4-}$, exists in extremely basic solution (Fig. 16.9). Under very dilute conditions as the pH is lowered, polymerization occurs to give manometers:

$VO_4^{3-} \rightarrow VO(OH)_{2+} \rightarrow VO(\text{OH})_3^{2-} \rightarrow VO(\text{OH})_4^{3-} \rightarrow VO_2^+$

(16.32)

When solutions are more concentrated, however, protonation and dehydration occur to form $[V_2O_7]^{3-}$ and higher vanadates. Further polymerization occurs until hydroxyl $V_2O_7$ precipitates at low pH. The precipitation of vanadate(V) oxide from aqueous solution as well as the similar behavior of other metal oxides, such as MoO$_3$ and WO$_3$, stands in sharp contrast to the extremely hygroscopic behavior of the analogous nonmetal compounds P$_2$O$_5$ and S$_2$O$_8$.

The polymerization of vanadate, molybdate, and tungstate ions forming isopoly anions has received a great deal of attention. Early in the condensation process the isopoly anion formation instead form chains, sheets, or three-dimensional frameworks. Why does polymerization stop for isopoly anions? An oxygen atom in a terminal position in an isopoly anion is strongly bonded to a transition metal such as Mo(VI) or W(VI). These terminal oxygen atoms are never found truns to one another because they avoid

$Ta^{5+}$ (78 pm) and the most common corresponding edge-shared polyanions are $[V_2O_7]^{3-}$, $[MoO_4]^{3-}$, $[MoO_5]^{4-}$, $[W_2O_7]^{2-}$, $[W_2O_8]^{3-}$, $[Nb_2O_7]^{3-}$, and $[Ta_2O_7]^{3-}$. To form larger polyanions such as $[W_4O_{12}]^{4-}$ or $[Nb_4O_{12}]^{5-}$, edge sharing must give way to apex sharing. The isopoly anions may be considered to be portions of a closest packed array of oxide ions with the metal ions occupying the octahedral holes. The edge-sharing unit found in $[V_2O_7]^{3-}$ consists of two octahedra stacked as shown in Fig. 16.10. This seems to be the largest stacked-octahedral isopoly anion cluster compatible with metal-metal repulsions, and the remaining edge-shared structures represent portions of this unit.

However, explanations for growth limitation based on repulsion of metal ions may be somewhat oversimplified. Elements other than vanadium, niobium, tantalum, molybdenum, and tungsten do not form isopoly anions. Other ions which have appropriate radii (e.g., Al$^{3+}$, 67 pm; Ga$^{3+}$, 76 pm; Ti$^{4+}$, 67 pm) for discrete isopoly anion formation instead form chains, sheets, or three-dimensional frameworks. Why does polymerization stop for isopoly anions? An oxygen atom in a terminal position in an isopoly anion is strongly bonded to a transition metal such as Mo(VI) or W(VI). These terminal oxygen atoms are never found truns to one another because they avoid.

Fig. 16.9 Dominant evolutions of vanadium present in aqueous solution as a function of concentration and pH. (From Pope, M. T. Heteropoly and Isopoly Oxometalates; Springer-Verlag: New York, 1983. Reproduced with permission.)

Fig. 16.10 The structures of edge shared isopoly anions showing their relation to the M$_2$O$_3$ structure: (a) M = V; (b) M = Mo; (c) M = Mo; (d) M = Nb; Ta. (From Kapert, D. L. Inorg. Chem. 1969, 8, 1556 and Day, V. W.; Klemperer, W. G.; Maltbie, D. J. J. Am. Chem. Soc. 1987, 109, 2994-3002. Reproduced with permission.)
In many of their reactions, these carbones behave like the familiar Witting reagents,
Ph3P=CH2. Schrock carbones are important intermediates in olefin metathesis.66
Classification of carbene complexes as Fischer or Schrock perhaps focuses too
much on their similarities and too little on their differences. Both contain a metal-
carbon bond of order greater than one. Whether the carbene carbon tends to seek or
provide electrons will depend on the extent of σ bonding involving the metal and the
carbon substituents. Some carbene complexes lie between the Fischer/Schrock ex-
tremes, behaving in some reactions as nucleophiles and in others as electrophiles.69
A decade after the announcement of the metal-carbon double bond, Fischer’s
group reported the first complex containing a metal–carbon triple bond.70
\[
\text{W(OMe)3} \rightarrow \text{MeC} \quad \text{W(OMe)3} \rightarrow \text{MeC} \quad \text{W(OMe)3} \rightarrow \text{MeC}
\]
(15.54)
The carbonyl ligand may be viewed as a three-electron donor, similar to the nitrosyl
ligand, with a pair of electrons in an sp orbital and a single electron in a σ orbital.
Donation of the σ electrons and pairing the π electron with one from the metal atom
gives a σ bond and a π bond, respectively. The second π bond results from donation of
an electron pair from the metal atom to the empty σ orbital of the ligand.

\[
\text{R} = \text{CH} + \text{M} \rightarrow \text{R} - \text{C}=\text{M}
\]
(15.55)
Shortly after the preparation of the first carbonyl, Schrock’s group provided a high
oxidation state complement.71
\[
\text{W(OMe)3Cl} \rightarrow \frac{\text{MeC}}{\text{MeC}} \quad \text{W(OMe)3Cl} \rightarrow \frac{\text{MeC}}{\text{MeC}} \quad \text{W(OMe)3Cl} \rightarrow \frac{\text{MeC}}{\text{MeC}}
\]
(15.56)
It also proved possible to put alkyl, carbene, and carbyne ligands into the same
molecule.72
\[
\text{MeC} \quad \text{CMe} \quad \text{CH}_2\text{CMe}_2 \quad \text{MeC} \quad \text{CMe} \quad \text{CH}_2\text{CMe}_2
\]
Systematically removing hydrogen atoms from a methane molecule would leave us
with a carbon atom in the final step.
\[
\text{CH}_4 \rightarrow \text{CH}_3 \rightarrow \text{CH}_2 \rightarrow \text{CH} \rightarrow \text{C}
\]
(15.57)
We have thus far seen complexes containing alkyl, carbene, and carbyne ligands, and
if you have speculated about the possibility of atomic carbon functioning as a ligand,
your thoughts have been well placed. Complexes in which carbon is bound only to
metal atoms are known as carbido complexes (Fig. 15.21). The first example was
reported in 1962, before carbene and carbyne complexes were discovered, but until
recently, carbido complexes remained chemical oddities synthesized by a variety of
serendipitous routes.73 A carbon atom surrounded by metal atoms is not very reac-
tive, but if it can be exposed by removal of one or more metal atoms, it becomes a
reactive species. Oxidation of $\text{Fe}_2\text{C}(_2\text{CO})_2\text{S}_2$ (Eq. 15.185) removes two iron atoms as
Fe2+ and uncovers a positively charged carbon atom which can react with nucleophiles
such as carbon monoxide (see Eq. 15.186). In effect, this sequence creates a
carbon–carbon bond, which is always of interest to the organic chemist, and further-
more, the added carbon can be easily functionalized. Thus carbido complexes show
potential in organic synthesis.

![Fig. 15.21 Structural examples of carbido complexes: (a) Fe2C(OMe)2, (b) Fe2C(OMe)2, and (c) Au2PPh4C].](image-url)

\[\text{Fe}_2\text{C}(_2\text{CO})_2\text{S}_2 \rightarrow \text{Fe}_2\text{C}(_2\text{CO})_2\text{S}_2 \rightarrow \text{Fe}_2\text{C}(_2\text{CO})_2\text{S}_2 \rightarrow \text{Fe}_2\text{C}(_2\text{CO})_2\text{S}_2\]

(15.58)

...
Polymerization of $S_N$ to form $S(N)$ chains with minimal movement of atoms.

Illustrates many features: a conjugated single-bond-double-bond resonance system with nine electrons on each sulfur atom rather than a Lewis octet; every $S-N$ unit will thus have one antibonding $\pi^*$ electron. The half-filled, overlapping $\pi^*$ orbitals will combine to form a half-filled conduction band in much the same way as we have seen half-filled $\sigma$ orbitals on a mole of lithium atoms form a conduction band (see Chapter 7). Note, however, that this conduction band will lie only along the direction of the $(SN)$ fibers; the polymer is thus a "one-dimensional metal."

Similar to $(SN)$ in their one-dimensional conductivity properties are the stacked columnar complexes typified by $[\text{Pt(CN)}_4]^2-$ . These square planar ions adopt a closely spaced parallel arrangement, allowing for considerable interaction among the $d_z^2$ orbitals of the platinum atoms. These orbitals are normally filled with electrons, so in order to get a conduction band some oxidation (removal of electrons) must take place. This may be readily accomplished by adding a little elemental chlorine or bromine to the pure tetracyanoplatinate salt to get stoichiometries such as $K_3[\text{Pt(CN)}_4]Br_0.5$ in which the platinum has an average oxidation state of +2.3. The oxidation may also be accomplished electrolytically, as in the preparation of $\text{Rb}_2[\text{Pt(CN)}_4](\text{FHF})_n$ (Fig. 16.8), which has a short Pt—Pt separation (279.8 pm). [From Schultz, A. J.; Coffey, C. C.; Lee, G. C.; Williams, J. M. Adv. Chem.; 1977, 8, 2129. Reproduced with permission.]

Isopoly Anions

Transition metals in their higher oxidation states are formally similar to nonmetals with corresponding group numbers: V (VII) and P (VA) in $\text{VO}_4^{3-}$ and $\text{PO}_4^{3-}$; Cr (VIB) and S (VIA) in $\text{CrO}_4^{2-}$ and $\text{SO}_4^{2-}$; Mn (VIIB) and Cl (VIIA) in $\text{MnO}_4^{-}$ and $\text{ClO}_4^{-}$. The analogy may be extended to polyanions, such as dichromate, $\text{Cr}_2\text{O}_7^{2-}$; however, the differences in behavior between the metal and nonmetal anions are often more important than their similarities. Whereas polyphosphoric acids and polysulfuric acids form only under rather stringent dehydrating conditions, polymerization of some metal anions occurs spontaneously upon acidification. For example, the chromate ion is stable only at high pHs. As the pH is lowered, protonation and dimerization occur:

$$\text{CrO}_4^{2-} + H^+ \rightarrow \text{HCrO}_4^-$$
$$\text{HCrO}_4^- + H^+ \rightarrow \text{CrO}_4^{2-} + H_2O$$
$$2\text{H}_3\text{CrO}_4 \rightarrow \text{Cr}_2\text{O}_7^{2-} + 2\text{H}_2\text{O} + 3\text{H}^+$$

Treatment with concentrated sulfuric acid completes the dehydration process and red chromium(VI) oxide ("chromic acid") precipitates:

$$\text{Cr}_2\text{O}_7^{2-} + 6\text{H}^+ \rightarrow 2\text{CrO}_4^{2-} + 3\text{H}_2\text{O}$$

The structure of $\text{Cr}_2\text{O}_7^{2-}$ consists of infinite linear chains of $\text{Cr}_2\text{O}_7^{2-}$ tetrahedra.

\]
Nonaromatic Alkene and Alkyne Complexes

Alkene Complexes

Complexes between metal salts and alkenes have been known since 1827 but were not understood until the latter half of this century. For example, Zeise isolated stable yellow crystals after refluxing an alcoholic solution of platinum tetrachloride. The anion of Zeise's salt is now made from $K_2PtCl_4$ and $C_2H_4^+$. Its structure has shown that the ethylene occupies the fourth coordination site of the square planar complex with the C—C axis perpendicular to the platinum-ligand plane (Fig. 15.22). Relative to free ethylene, the C—C bond is lengthened slightly (from 133.7 pm to 137.5 pm), and the hydrogens are slightly tilted back from a planar arrangement.

A bond between the ethylene molecule and the metal ion may be considered as a dative σ bond to an available orbital on the metal. The bonding scheme (sometimes called the Dewar-Chatt-Duncanson model) is analogous to that in carbon monoxide. In extreme cases, such as $Pt(Ph_2P)C=C(Ph_2P)$ in which the metal is very electron rich, the metal binds to the ligand with a back electron donation. For a translation of Zeise's original paper, see Classics in Coordination Chemistry: Part 2, Koffman, G., Ed., Dover, New York, 1976, pp 31-37.

When a ligand is bound to a metal, its chemistry typically changes. For alkenes, the change is particularly dramatic. Free alkenes are susceptible to electrophilic attack.

$\text{[PtCl}_2]^2- + \text{CH}_2=\text{CH}_2 \rightarrow \text{[Pt(C}_2\text{H}_4\text{Cl}]_2 + \text{Cl} + \text{H}_2\text{O}$

(15.58)

Silver ions form similar alkene complexes which are soluble in aqueous solution and may be used to effect the separation of unsaturated hydrocarbons from alkanes. Catalysts for the polymerization of alkenes also form metal-alkene complexes which lead to polymerized product.

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A similar and even more extreme case of bond lengthening is found in complexes of $C_4(CN)_4$, in which the π accepting ability of the alkyne is enhanced by its electron-withdrawing substituents. Electron-rich metals and strongly electron-withdrawing alkyne substituents favor structure (b) while opposite conditions favor structure (a). Structure (b) suggests that the metal has been formally oxidized with the loss of two electrons. For further insight into the mode by which the $C_4(CN)_4$ ligand binds to metals, it is interesting to compare the structure of tetracyanoethylene oxide with that of a tetracyanoethylene nickel complex.77

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Both the C—C bond lengths [(1) = 149.7 pm; (2) = 147.6 pm] and the bending of the substituents out of the plane [(1) = 32.2°; (2) = 38.4°] are nearly the same. Although we can draw an alternative resonance form for the nickel complex, the bonding model shown is the only one applicable to the oxide. In view of the strong structural similarities, we can feel justified in using the cyclic structure as an approximation for certain complexes as well. When a ligand is bound to a metal, its chemistry typically changes. For alkenes the change is particularly dramatic. Free alkenes are susceptible to electrophilic attack.


The mention of the K⁺ ion presupposes knowledge of the nature of the potassium species present. Because of the similarity in energies of the valence and conduction bands, graphite can be either an electron donor or acceptor. Intercalation of potassium atoms into graphite results in the formation of K⁺ ions and free electrons in the conduction band. Graphite will react with an electron acceptor such as bromine to form CBr in which electrons have transferred from the valence band of the graphite to the bromine. Apparently, simple bromide ions are not formed, but polybromide chains form instead (see Chapter 12 for similar polyhalide chains). The expected Br—Br distance in such a polyhalide (154 pm) compares well with the distance between centers of adjacent hexagons in graphite (156 pm). In contrast, the expected Cl—Cl (224 pm) and I—I (292 pm) distances do not fit well with the graphite structure, and in fact these two halogens do not intercalate into graphite! In contrast, iodine monochloride (expected average I—Cl distance = 255 pm) does.

Both of the potassium and polybromide intercalation compounds are good conductors of electricity. In the potassium intercalant, the electrons in the conduction band can carry the current directly, as in a metal. In the compounds of graphite with polybromide, holes in the valence band conduct by the mechanism discussed previously for semiconductors (Chapter 7).

Recently, it has proved possible to intercalate a variety of organic molecules into molecular materials. Unlike the above examples these do not usually involve electron transfer. When single molecular layers of MoS₂, suspended in water, are shaken with water-immiscible organic molecules such as ferrocene, the latter is adsorbed onto the former. A highly oriented, conducting ferrocene-MoS₂ film results when exposed to a glass substrate. The interlayer spacing of MoS₂ increases by 560 pm upon ferrocene inclusion. It has been suggested that the best choice for producing a useful high-temperature superconductor may lie with incorporating an organic superconductor into a layered inorganic compound.

There is an unusual heteron chain, (SN), discovered in 1910, which did not receive detailed attention until the 1970s. Interest centers on the fact that although it is composed of atoms of two nonmetals, polymeric sulfur nitride (also called polythiazyl) has some physical properties of a metal. The preparation is from tetrafluorotetramine (see page 776):

\[
\text{S}_4\text{N}_4 \xrightarrow{\text{heat}} \text{S}_{2}\text{N}_2 \rightarrow (\text{SN})_2
\]  

(16.27)

The S₂N₂ is pumped in a vacuum line over silver wool at 220 °C, where it polymerizes slowly to a lustrous golden material. The resulting product is analytically pure, as it is necessary for it to show metallic properties to a significant degree; it has a conductivity near that of mercury at room temperature, and it becomes a superconductor at very low temperatures (below 0.26 K). X-ray diffraction studies show that the S₂N₂ chains have the structure shown in Fig. 16.6. This chain can be generated from adjacent square planar S₄N₄ molecules. The S—N bonds in this starting material have a bond order of 1.5 and a bond length of 1.54 pm, intermediate between single (1.74 pm) and double (1.54 pm) sulfur-nitrogen bonds. A free radical mechanism has been suggested leading to the linear chains of the polymer (Fig. 16.7). Since polymerization can take place with almost no movement of the atoms, the starting material and product are pseudomorphs and the crystallinity of the former is maintained.

If one attempts to draw a unique Lewis structure for the (SN) chain, one is immediately frustrated by the small number of electrons available. Many resonance structures can be drawn and they contribute to the hybrid structure, but the single structure:

\[
\text{S} \equiv \text{N}: \text{S} = \text{N}: \text{S} \equiv \text{N}: \text{S} = \text{N}: \text{S} \equiv \text{N}: \text{S} = \text{N}:
\]
but not to nucleophilic attack. When coordinated to a metal, the carbon atoms become somewhat more positive and a reversal of reactivity occurs, i.e., the alkene becomes susceptible to nucleophilic attack and loses its susceptibility to electrophilic attack.\(^{36}\)

### Alkyne Complexes

The chemistry of alkyne complexes is somewhat more complicated than that of alkene complexes because of the greater possibilities for π bonding by alkynes and the tendency of some of the complexes to act as intermediates in the formation of other organometallic compounds.

The simplest alkyne complexes, the metal acetylenes, resemble those of ethylene. For example, there are analogues of Zeise's salt in which an acetylene molecule is bound to platinum(II) and occupies a position like that of ethylene in Zeise's salt. In addition, there are \(\text{L}_2\text{Pt}^\text{(II)}\text{(C} = \text{C}=\text{CH})\) complexes that have structures paralleling that of \(\text{L}_2\text{Pt}^\text{(II)}\text{(H}_2\text{C} = \text{C}=\text{CH})\) (Fig. 15.24). For both of these Pt(II) complexes, an approximate square planar arrangement around the metal is found. Alkynes are more electronegative than alkenes and are therefore better π acceptors. Thus it is appropriate to view them as metallacyclopropenes.\(^{79}\)

![Fig. 15.24 Molecular structure of bis-(triphenylphosphine)-diphenylacetyleneplatinum(II)](image)

Alkynes have two π and two π* orbitals that can potentially interact with metal orbitals, and in some instances, it is thought that all of these are involved at the same time in a mononuclear complex. An extended Hückel calculation on \(\text{Mo(meso-tetra-p-tolylporphyrin)}\text{(H} = \text{CH})\) supports this view (Fig. 15.25).\(^{80}\) Thus both bonding orbitals of the alkyne \((\text{b}, \text{π})\) can donate electron density to molybdenum to form the \(\text{bt}\) and \(\text{b}^\text{π}\), MOs, and both antibonding orbitals \((\text{b}^\text{π}, \text{π}^\text{*})\) can accept electron density to form the \(\text{bt}^\text{π}\) and \(\text{b}^\text{π}\), MOs. Notice that both π bonding orbitals \((\text{bt}, \text{b}^\text{π})\) of acetylene interact significantly with metal d orbitals of the same symmetry.\(^{81}\)

![Fig. 15.25 Diagram showing interaction of the frontier orbitals of Mo(meso-tetra-p-tolylporphyrin) with those of acetylene. Strong interactions are represented with solid lines and weak ones with dashed lines.](image)

Both pairs of π electrons in an alkyne ligand are more likely to be involved in the bonding if it is coordinated to two metal atoms. If acetylene is allowed to react with dicobaltoctacarbonyl, two moles of carbon monoxide are eliminated:

\[
\text{Co}_2\text{(CO)}_8 + \text{HC}=\text{CH} \rightarrow (\text{H}_2\text{C})\text{Co}_2\text{(CO)}_6 + 2\text{CO}
\]

The production of two moles of carbon monoxide and the 18-electron rule lead us to predict that the acetylene molecule is acting as a four-electron donor. In fact this is just one of many complexes in which alkynes bind in this fashion.\(^{82}\) For example, the structure of the diphenylacetylene complex in Fig. 15.26 shows that the positions of the two rhodium atoms are such as to allow overlap with both π and π* orbitals in the carbon-carbon triple bond.\(^{82}\) The extent of back donation into the antibonding orbitals determines the lengthening of the C—C bond and the extent to which the C—H bonds are bent away from the complex. Bond length values vary greatly from system to system.

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\(^{36}\) For a further discussion of this reversal and others referred to as "umpolung," see Crabtree, R. H. The Organometallic Chemistry of the Transition Metals; Wiley: New York, 1988, p 91.


\(^{81}\) Berry, D. H.; Eisenberg, R. Organometallics 1987, 6, 1796-1805.
The analogous silicon compounds are also unstable, but the "dimethylsilicone" that forms is a mixture of linear polymers (and cyclic products to be discussed in the next section):

\[ \text{Me}_2\text{SiCl}_3 \xrightarrow{\text{H}_2}\text{O} \text{Si} = \text{O} \text{Si} = \text{O} \text{Si} = \text{O} \text{Si} = \text{O} \]  \hspace{1cm} (16.23)

Hundreds of thousands of tons of pure Si are produced every year by the reduction of \( \text{SiO}_2 \) in an electric furnace:

\[ \text{SiO}_2 + \text{C} \xrightarrow{\text{heat}} \text{Si} + \text{CO}_2 \]  \hspace{1cm} (16.24)

Although some of this is used for the production of ultra-pure silicon for semiconductors and for alloys with iron, aluminum, and magnesium, 98% goes for the production of methyl silicon chlorides:

\[ 3\text{CH}_2\text{SiCl}_3 + \text{Si} \xrightarrow{\text{heat}} \text{CH}_3\text{SiCl}_3 + \text{Si} \]  \hspace{1cm} (16.25)

\[ 2\text{CH}_3\text{SiCl}_3 + \text{Si} \xrightarrow{\text{heat}} (\text{CH}_3)_2\text{SiCl}_2 \]  \hspace{1cm} (16.26)

These products are separated by distillation and used to make over 500 million kg per year of silicone rubbers, oils, and resins. All of these materials repel water and are electrical insulators. The rubbers are flexible and the oils are liquids over a wide range of temperatures.

Intercalation compounds consist of layers ("sandwiches") of different chemical species. The name comes from that describing the insertion of extra days (such as February 29th) into the calendar to make it match the solar year. Most work on intercalation compounds has been on synthetic systems in which atoms, ions, or molecules have been inserted between layers of the host material. However, some aluminosilicates that we have encountered above provide useful examples. Thus talc and micas form layered structures with ions between the silicate sheets (Fig. 16.3). Some minerals, including all clays, have water molecules intercalated between the framework sheets. In some, such as vermiculite, the water may rapidly and dramatically be evacuated by heating. The water molecules leave faster than they can diffuse along the layers—exfoliation occurs. The result is the familiar expanded vermiculite used as a packing material and as a potting soil conditioner.

Another example of this type of intercalation compound is sodium beta alumina where the sodium ions are free to move between the spinel layers. The sodium ions can be replaced by almost any +1 cation such as Li⁺, K⁺, Rb⁺, Cs⁺, NH₄⁺, H₂O⁺, Tl⁺, Ga⁺, NO₂⁻, etc. The conductivity of these materials varies with the size of the ions moving between the fixed-distance (Al—O—Al) layers.

Graphite is perhaps the simplest layered structure. The interlayer C—C distance (142 pm) is twice the covalent radius of aromatic carbon (cf. 139 pm in benzene) and the interlayer C—C distance is 335 pm, twice the van der Waals radius of carbon. The sheets are held together by weak van der Waals forces. Many substances can be

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**Intercalation Chemistry**

Interlayered between the layers of graphite, but one of the largest and best studied is potassium, which can be intercalated until a limiting formula of C\(_8\)K is reached. This is known as the first-stage compound. The earlier, lower stages have the general formula C\(_{2n}\)K. The stages form stepwise as new layers of potassium are added, giving well-characterized compounds with \( n = 4, 3, 2 \) (Fig. 16.4). The final step (yielding stage I) includes filling in all of the remaining available sites (Fig. 16.5) in addition to forming the maximum number of layers. Presumably, further intercalation cannot take place because of electrostatic repulsion.

Upon intercalation, the graphite layers move apart somewhat (205 pm), though less than expected as estimated from the diameter of the potassium ion (304 pm or greater). This indicates that the K⁺ ion "reets" within the hexagonal carbon net, and one can even speculate about weak complexing to the carbon π-electron cloud.

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The first reaction takes place at ambient temperature and the second occurs when the system is heated. Initial formation of the monohapto complex is believed to be typical, but often this intermediate is not observed.

A second synthetic approach is to use a Grignard reagent and a metal halide:

$$\text{NiCl}_2 + 2\text{CH}_2=\text{CHCH}_2\text{MgCl} \rightarrow \text{Ni(1,3-C}_3\text{H}_5)_2 + 2\text{MgCl}_2 \quad (15.62)$$

The bis(1,3-allyl)nickel complex is a yellow, pyrophoric compound that melts at 1 °C. Its structure, which has been determined by neutron diffraction, illustrates some of the important features of these complexes (Fig. 15.28). The two terminal carbon atoms are further from the metal atom (202.9 pm) than is the central carbon atom (198.0 pm). Even so, the terminal carbon atoms are tilted toward the metal to provide better \(\pi\) overlap. The \(\text{C} - \text{C} - \text{C}\) bond angle is 120.5° and the mean \(\text{C} - \text{C}\) bond length is 141.6 pm, all of which is in agreement with a conjugated \(\sigma\) system. The anti (trans to meso) hydrogen atoms are bent away from the metal and the syn (cis to meso) and meso hydrogen atoms are bent toward the metal.

In addition to the stereochemistry possible for allyl complexes as a result of different \(\text{syn}\) and \(\text{anti}\) substituents, geometrical isomers are known which arise because of the position of the central allyl carbon atom relative to other ligands. Both \(\text{exo}\) and \(\text{endo-Ru}^{18}\text{C}_3\text{H}_5\) have been isolated (Fig. 15.29).}

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Quite remarkably the reaction occurs without the formation of the more thermodynamically favored trimethylamine. Although some dimethylamine is produced in the reaction, the channel size in which the reaction takes place favors the formation of methyamine. The process, as of this writing, is about to be commercialized by Du Pont.

We have seen previously shape-selective catalysis by ZSM-5 in the conversion of methanol to gasoline. Other commercial processes include the formation of ethylbenzene from benzene and ethylene and the synthesis of p-xylene. The other commercial processes include the formation of toluene to form xylene:

\[ \text{H}_3\text{C} - \text{CH}_2\text{CH}_3 + \text{H}_2\text{C} = \text{CH}_2 \rightarrow \text{H}_3\text{C} - \text{CH}(\text{CH}_3)\text{C}_6\text{H}_4 - \text{CH}_2\text{CH}_3 \]

The “linear” p-xylene can escape from the catalyst much more easily than the bent m- or o-xylene (see Figs. 1.4 and 1.5).

Transition metal ions in zeolites behave much as expected for ions in a weak oxide field, but often the metal ions are found in trigonal sites, so their spectra and magnetic properties are somewhat different from those of the more common octahedral and tetrahedral fields.

Another class of framework aluminosilicates is the ultramarines. They are characterized by an open framework and intense colors. They differ from the previous examples by having “free” anions and no water in the cavities. Ultramarine blue, which is the synthetic equivalent of the mineral lazuli, contains radical anions, \( \text{S}_4^2- \) and \( \text{S}_3^2- \). The dominant \( \text{S}_4^2- \) gives rise to its blue color. Ultramarine green also contains these two anions but in comparable amounts. Although these two anions are also found in ultramarine violet and pink, the characteristic color is due to a third species, perhaps \( \text{S}_5^2- \) or \( \text{S}_6^2- \). Structurally related, but colorless, minerals such as sodalite (containing chloride anions) and neselite (containing sulfite anions) are sometimes included in the broad category of ultramarines.

Zeotypes can be shaped to act as catalysts. For example, the methylation of toluene to form xylene:

\[ \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CH}(\text{OCH}_3)\text{CH}_3 \]

Zeolites also provide convenient framework sites for activating transition metal ions for redox catalysis. Iwamoto\(^7\) has described a Cu\( \text{II}/\text{Cu}\) exchanged zeolite that holds promise for the high-temperature conversion of NO\(_x\) (in diesel and auto exhaust) to \( \text{N}_2 \) and \( \text{O}_2 \):

\[ \text{NO} + \text{Cu}^{\text{II}}/\text{Cu}^{\text{I}} \rightarrow \text{N}_2 + \text{O}_2 \] (16.71)

Reducing capacity is enhanced by hydrocarbons (unburnt fuel) which provide a source of hydrogen.

Transition metal ions in zeolites behave much as expected for ions in a weak oxide field, but often the metal ions are found in trigonal sites, so their spectra and magnetic properties are somewhat different from those of the more common octahedral and tetrahedral fields.

In other instances product size and shape exclude this possibility. For example, in the methylation of toluene to form xylene:

\[ \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CH}(\text{OCH}_3)\text{CH}_3 \]

No cases are known in which edges or faces are shared:

\[ \text{Si}_4\text{O}_9 \rightarrow \text{Si}_4\text{O}_9+\text{H}_2\text{O} \] (16.22)

Pauling\(^7\) has listed a set of rules for predicting stability in complex crystals based on an ionic model. Although no one now accepts a purely ionic model for silicates and similar compounds, Pauling’s rules are still reasonably accurate as long as the partial charges on the atoms are sufficiently large to make electrostatic repulsions significant. Such repulsions militate against the sharing of edges or faces by tetrahedra since this places positive centers too near each other.

No section on heterocatenation would be complete without a discussion of silicic acid, \( \text{H}_3\text{SiO}_3 \). The term silicic acid was coined by analogy to ketone under the mistaken belief that monomeric \( \text{R}_2\text{SiO}_3 \) compounds could be isolated. Silicon compounds that are formally analogous to carbon compounds are found to have quite different structures. Thus carbon dioxide is a gaseous monomer, but silicon dioxide is an infinitely branched polymer. In a similar manner, gem-diols are unstable relative to ketones:

\[ \text{Me}_2\text{O}(\text{OH}) \rightarrow \text{Me}_2\text{O} + \text{H}_2\text{O} \] (16.22)
Organometallic chemistry leaped forward in the early 1950s when the structure of ferrocene, \( \text{Fe}(\text{C}_5\text{H}_5)_2 \), was elucidated. Prior to that, ideas regarding metal-ligand interactions included only the coordinate covalent bond (e.g., \( M—CO \)) and the covalent bond (e.g., \( M—CH_3 \)). It was revolutionary in bonding theory to propose a metal-ligand bond between a metal and the \( \pi \) orbitals of \( \text{C}_5\text{H}_5 \). Ferrocene was the first of many complexes which came to be known as metallocenes, a name which arose because they participated in reactions similar to those of aromatic molecules. For obvious reasons complexes in which a metal atom was found between two parallel carboxylic rings became known as “sandwich” compounds. Some of these are shown in Fig. 15.31. All of the complexes in Fig. 15.31, except the last two, obey the 18-electron rule. Depending on the electron counting method adopted, the cyclopentadienyl ligand may be viewed as either a five-electron donor (neutral atom) or a six-electron donor (oxidation state) (Table 15.1).

The 18-electron rule is not obeyed as consistently by these types of organometallic compounds as by the carbonyl and nitrosyl complexes and their derivatives. For example, in addition to ferrocene, \( \text{M}(\text{C}_5\text{H}_5)_2 \) compounds are known for most of the other elements of the first transition series (\( M = V, \text{Cr}, \text{Mn}, \text{Co}, \text{Ni} \)) and these cannot obey the 18-electron rule. However, only ferrocene shows exceptional thermal stability (stable to 500 °C) and is not oxidized by air. Furthermore, cobaltocene, \( \text{Co}(\text{C}_5\text{H}_5)_2 \), is readily oxidized to the 18-electron cobaltocenium ion, \( \text{Co}^+ (\text{C}_5\text{H}_5)_2^+ \), which reflects much of the thermal stability of ferrocene. Mixed cyclopentadienyl carbonyl complexes are common: \( \text{Fe}(\text{C}_5\text{H}_5)_2\text{Cr(CO)}_3 \), \( \text{Fe}(\text{C}_5\text{H}_5)_2\text{Ni(CO)}_3 \), \( \text{V}(\text{C}_5\text{H}_5)_2\text{Ni(CO)}_3 \), and \( \text{V}(\text{C}_5\text{H}_5)_2\text{Fe(CO)}_3 \). Of interest is the fact that among these compounds, the odd-electron-number elements (\( V, \text{Mn}, \text{and Co} \)) form monomers and the even-electron-number elements (\( \text{Cr}, \text{Fe}, \text{and Ni} \)) form dimers, which is in direct contrast to the behavior shown by the simple carbonyl complexes. Cyclopentadienyl derivatives are now known for every main group and transition metal of the periodic table and for most of the \( f \)-block metals.46

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**Metallocenes**

Organometallic chemistry leaps forward in the early 1950s when the structure of ferrocene, \( \text{Fe}(\text{C}_5\text{H}_5)_2 \), was elucidated. Prior to that, ideas regarding metal-ligand interactions included only the coordinate covalent bond (e.g., \( M—CO \)) and the covalent bond (e.g., \( M—CH_3 \)). It was revolutionary in bonding theory to propose a metal-ligand bond between a metal and the \( \pi \) orbitals of \( \text{C}_5\text{H}_5 \). Ferrocene was the first of many complexes which came to be known as metallocenes, a name which arose because they participated in reactions similar to those of aromatic molecules. For obvious reasons complexes in which a metal atom was found between two parallel carboxylic rings became known as “sandwich” compounds. Some of these are shown in Fig. 15.31. All of the complexes in Fig. 15.31, except the last two, obey the 18-electron rule. Depending on the electron counting method adopted, the cyclopentadienyl ligand may be viewed as either a five-electron donor (neutral atom) or a six-electron donor (oxidation state) (Table 15.1).

The 18-electron rule is not obeyed as consistently by these types of organometallic compounds as by the carbonyl and nitrosyl complexes and their derivatives. For example, in addition to ferrocene, \( \text{M}(\text{C}_5\text{H}_5)_2 \) compounds are known for most of the other elements of the first transition series (\( M = V, \text{Cr}, \text{Mn}, \text{Co}, \text{Ni} \)) and these cannot obey the 18-electron rule. However, only ferrocene shows exceptional thermal stability (stable to 500 °C) and is not oxidized by air. Furthermore, cobaltocene, \( \text{Co}(\text{C}_5\text{H}_5)_2 \), is readily oxidized to the 18-electron cobaltocenium ion, \( \text{Co}^+ (\text{C}_5\text{H}_5)_2^+ \), which reflects much of the thermal stability of ferrocene. Mixed cyclopentadienyl carbonyl complexes are common: \( \text{Fe}(\text{C}_5\text{H}_5)_2\text{Cr(CO)}_3 \), \( \text{Fe}(\text{C}_5\text{H}_5)_2\text{Ni(CO)}_3 \), \( \text{V}(\text{C}_5\text{H}_5)_2\text{Ni(CO)}_3 \), and \( \text{V}(\text{C}_5\text{H}_5)_2\text{Fe(CO)}_3 \). Of interest is the fact that among these compounds, the odd-electron-number elements (\( V, \text{Mn}, \text{and Co} \)) form monomers and the even-electron-number elements (\( \text{Cr}, \text{Fe}, \text{and Ni} \)) form dimers, which is in direct contrast to the behavior shown by the simple carbonyl complexes. Cyclopentadienyl derivatives are now known for every main group and transition metal of the periodic table and for most of the \( f \)-block metals.46

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Inorganic Chains, Rings, Cages, and Clusters

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**Table 16.1** Some natural and synthetic zeolites

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula (idealised composition)</th>
<th>Ring sizes</th>
</tr>
</thead>
<tbody>
<tr>
<td>faujasite*</td>
<td>Na\textsubscript{10}Al\textsubscript{8}Si\textsubscript{20}O\textsubscript{48}</td>
<td>4, 6, 12</td>
</tr>
<tr>
<td>natrolite*</td>
<td>Na\textsubscript{2}Al\textsubscript{2}Si\textsubscript{3}O\textsubscript{8}</td>
<td>4, 8</td>
</tr>
<tr>
<td>stilbite*</td>
<td>Na\textsubscript{4}Ca\textsubscript{6}Al\textsubscript{18}Si\textsubscript{36}O\textsubscript{72}</td>
<td>4, 6, 8, 10</td>
</tr>
<tr>
<td>Linde A*</td>
<td>Na\textsubscript{2}Al\textsubscript{2}Si\textsubscript{3}O\textsubscript{8}</td>
<td>4, 6, 10, 12</td>
</tr>
<tr>
<td>ZSM-5*</td>
<td>Na\textsubscript{3}Al\textsubscript{2}Si\textsubscript{3}O\textsubscript{8}</td>
<td>4, 5, 6, 7, 8, 10</td>
</tr>
<tr>
<td>boehmite*</td>
<td>Na\textsubscript{2}Al\textsubscript{2}Si\textsubscript{3}O\textsubscript{8}</td>
<td>4, 5, 6, 7, 8, 10</td>
</tr>
<tr>
<td>sodalite*</td>
<td>Na\textsubscript{6}Al\textsubscript{6}Si\textsubscript{6}O\textsubscript{24}</td>
<td>4, 6</td>
</tr>
<tr>
<td>mordenite*</td>
<td>Na\textsubscript{8}Al\textsubscript{12}Si\textsubscript{36}O\textsubscript{96}</td>
<td>4, 6, 8, 12</td>
</tr>
<tr>
<td>rho*</td>
<td>Na\textsubscript{12}Al\textsubscript{18}Si\textsubscript{36}O\textsubscript{96}</td>
<td>4, 6, 8</td>
</tr>
</tbody>
</table>

* Natural; substitution of ions often occurs in natural zeolites.

---

**Fig. 16.2** Stereoviews of: (a) sodalite, Na\textsubscript{2}Al\textsubscript{2}Si\textsubscript{3}O\textsubscript{8}·2H\textsubscript{2}O (ring sizes are 4 and 6 (220 pm)); (b) ZSM-5, Na\textsubscript{3}Al\textsubscript{2}Si\textsubscript{3}O\textsubscript{8}·2H\textsubscript{2}O (ring sizes are 4, 5, 6, 7, 8, 10 (528 pm)); (c) mordenite, Na\textsubscript{8}Al\textsubscript{12}Si\textsubscript{36}O\textsubscript{96}·2H\textsubscript{2}O (ring sizes are 4, 5, 6, 8, 12 (760 pm)). See also Fig. 1.3. Lines represent oxygen bridges; intersections of lines show positions of the aluminum and silicon atoms. Note increasing size of pore aperture (largest diameter given in parentheses). [From Meier, W. M.; Olson, D. H. Atlas of Zeolite Structure Types. 2nd ed.; Butterworths: London, 1987. Reproduced with permission.]

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Zeolites may also behave as acidic catalysts. The acidity may be of the Brønsted type if hydrogen ions are exchanged for mobile cations (such as Na\textsuperscript{+}) by washing with acid. If the zeolite is heated, water may then be eliminated from the Brønsted sites leaving aluminum atoms coordinated to only three oxygen atoms. Molecules small enough to enter, yet large enough to fit with reasonably large dipolar and London forces will be selectively adsorbed.

---

Heterogeneous catalysis by acidic zeolites is one of the most intensely investigated topics of chemistry. The reaction of ammonia with methanol to give methylamine can be catalyzed by acidic zeolite rho (Table 16.1).

\[
\text{MeOH} + \text{NH}_3 \xrightarrow{\text{acidic rho}} \text{MeNH}_2 + \text{H}_2\text{O}
\]

These will act as Lewis acids. The catalytic sites occur at high density and are uniform in their activity (as opposed to amorphous solids) because of the microcrystalline nature of the zeolites.

---

The importance of metallocenes and the complexity of their bonding make it worthwhile to describe them with molecular orbital theory. The properties of the molecular orbitals of the π system of cyclic polyenes may be briefly summarized as follows.

There is a single orbital at lowest energy that consists of an unbroken, i.e., nodeless “doughnut” of electron density above and below the plane of the ring. At slightly higher energy there is a doubly degenerate set of orbitals each of which has one nodal plane containing the principal axis. This is followed by another doubly degenerate set with two nodal planes and yet higher energy. This pattern continues with doubly degenerate orbitals of increasing energy and increasing number of nodal planes until the number of molecular orbitals is equal to the number of atomic p orbitals, i.e., the number of carbons in the ring. If this number is odd, the highest antibonding orbital is doubly degenerate; if the number is even, the highest antibonding orbital is nondegenerate.

The increasing number of nodes will result in molecular orbitals with symmetries (as viewed down the ring-metal-ring axis in the metallocene) of \( \sigma \) (complete cylindrical symmetry), \( \sigma_1 \) (one nodal plane), \( \sigma_2 \) (two nodal planes), etc. These orbitals on the two ligands can be added and subtracted to form ligand group orbitals (LGOs), which in turn can be combined with atomic orbitals of matching symmetry on the metal to form MOs. For example, consider the lowest energy ligand bonding orbital. If the wave functions for this orbital on the two rings in the metallocene are added, a gerade ligand group orbital of the same symmetry as an atomic \( \sigma \) orbital is produced. On the other hand, if the two wave functions are subtracted, an ungerade orbital LGO of the same symmetry as an atomic \( p \) orbital is obtained. In the same manner, other LGOs can be constructed by either adding or subtracting the higher molecular orbitals of the two rings. The resulting combinations are shown in Fig. 15.32.

Although symmetry considerations allow us to decide what molecular orbitals are possible, knowledge of relative energies and overlap integrals is necessary in order to estimate the nature of the resulting energy levels. The ordering of the energy levels has been the subject of much discussion. Photoelectron spectroscopy studies in conjunction with ligand field theory support the energy level diagram for ferrocene, shown in Fig. 15.33.

The \( \sigma_1 \) orbitals of cyclopentadiene are so stable relative to the metal orbitals that they interact but little, i.e., the ligand is a poor \( \sigma \) donor. On the other hand, the \( \sigma_2 \) orbitals are so high in energy compared to the metal orbitals of the same symmetry that they also interact very little. This is another way of saying that these empty orbitals are not good \( \pi \) acceptors. The \( \sigma_3 \) and \( \sigma_4 \) orbitals on the iron atom are at a high energy, and so these orbitals likewise do not contribute much to the bonding. The only orbitals that are well matched are \( \sigma_{5g} \) ring and metal (3d)

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Footnotes:
90 This is not the place to delve into the nature of organic ring systems. For a discussion of these, see Lawry, T. H.; Richardson, K. S. Mechanisms and Theory in Organic Chemistry; Harper and Row: New York, 1987.
91 This refers to nodal planes perpendicular to the plane of the ring. The ring itself must be a nodal plane since the π system is constructed from atomic \( p \) orbitals.
32 
example, crocidolite, Na₂Fe₃(OH)₆Si₂O₅(OH)₂ (also known as blue asbestos), and amosite (Mg, Fe)₂(OH)₆Si₂O₅(OH)₂, a gray-brown asbestos.²¹

Further linkage by the complete sharing of three oxygen atoms per silicon analogous to the edge bonding between many amorphous bands results in sheet structures (Fig. 16.1e). This yields an empirical formula of [SiO₂]₁²⁺.²² By itself, it is a rather unimportant structure. However, if we interweave layers of gibbsite, γ-Al(OH)₃, or brucite, Mg(OH)₂, we obtain important mineral structures: (1) A structure of repeated silicon layers bonded to aluminum layers with bridging —O—and —OH—is present in the kaolin (china clay) minerals, Al₂O₃Si₂O₅(OH)₄. (2) A structure of repeated pairs of silicon layers with aluminum layers between (and bridged with) —O—and —OH—is present in pyrophyllite, Al₂O₃Si₂O₅(OH)₄. (3) If Mg in the kaolin structure is replaced by Mg, the serpentine structure, Mg₃Si₂O₅(OH)₄, is formed. The dimensions of brucite, Mg(OH)₂, are slightly larger than those of the Si₂O₅(OH)₄ sheet, so the composite layers tend to curl. Fibers from the curled layers form chrysotile or white asbestos. (4) Similarly, talc, Mg₃Si₂O₅(OH)₄, is the magnesium analogue of pyrophyllite. These minerals tend to be relatively soft and slippery.

Further substitution can occur with one out of four silicon atoms in each Si₂O₅(OH)₄ unit replaced by aluminum. Because of the difference in charge between Al³⁺ and Si⁴⁺, a +1 cation must also be added. This muscovite (white mica), KAI₂Si₂O₅(OH)₄, is related to pyrophyllite. Phlogopite (Mg-mica), K(Mg, Fe)₂Al₂Si₂O₅(OH)₄, and biotite (black mica), K(Mg, Fe)₂Si₃Al₃O₉(OH)₃, are related similarly to talc. The micas are hard since the layers are composed of strong Al—O—Si bonds. However, they are relatively easily cleaved between the layers which are held together by the electrostatic interactions with the potassium cations.

There are more complicated structures intermediate between pyrophyllite and talc with variable substitution of Al³⁺ and Mg²⁺. Electro neutrality is maintained by hydrated cations between layers. Thus the montmorillonites are natural clays forming thiolacto aqueous suspensions that are used as well-drilling muds and in nondrip paints. They are derived from the formation Al₂O₃Si₂O₅(OH)₄ + variable amounts of water, Mg³⁺ (in place of some Al³⁺), and compensating cations, M⁺⁺ (M = Ca in fuller's earth, which is converted to bentonite, M = Na). Vermiculite likewise has variable amounts of water and cations. It dehydrates to a talc-like structure with much expansion when heated (one page 730).

The ultimate in cross-linking and sharing of oxygen atoms by silicon is the complete sharing of all four oxygen atoms per SiO₄ tetrahedron in a framework structure. Silicon dioxide can exist in several forms such as quartz (thermodynamically stable at room temperatures), tridymite, and cristobalite, as well as more dense varieties such as crocidolite and thomsonite that form under high pressure. With the exception of the latter, all of these contain silicate tetrahedra with complete sharing but with different linking arrangements of the tetrahedra.²² Finally, silicon dioxide also occurs as a glass with the tetrahedral disordered so that no long-range order exists.

We have seen that Al³⁺ may replace Si⁴⁺ so long as electro neutrality is maintained by compensating cations. Three classes of aluminosilicate framework minerals are of importance: the feldspars, zeolites, and ultrakations.

The feldspars. of general formula M₂Al₂Si₃O₈ (K, Na, Ca) are the most important rock-forming minerals, comprising two-thirds of igneous rocks such as granite, which is a mixture of quartz, feldspars, and micas. Feldspar weather to form clays: 4K₂OAl₂O₃ + 4CO₂ + 6H₂O —— 4K₂CO₃ + 2Al₂O₃Si₂O₅ + 8SiO₂.

The zeolites are aluminosilicate framework minerals of general formula Moz[(Al₂O₃)nSiO₂m] · xH₂O.²³ They are characterized by open structures that permit exchange of cations and water molecules (Fig. 16.2b). In the synthetic zeolites the aperture and channel sizes may sometimes be controlled by a sort of template synthesis—the zeolite is synthesized around a particular organosilicon cation. This yields channels of the desired size. The zeolite framework thus behaves in some ways like a clathrate cage about a guest molecule (Chapter 8). The synthesis of zeolites also involves several other factors such as the Al/Si ratio, the pH, the temperature and pressure, and the presence or absence of seed crystals:²⁴

\[
\text{Na}_x\text{SiO}_3 + x\text{Al(OH)}_3 \rightarrow \text{Na}_x\text{SiO}_3 \cdot x\text{Al(OH)}_3 \quad (16.15)
\]

\[
\text{Na}_x\text{SiO}_3 + x\text{Al(OH)}_2 \rightarrow \text{Na}_x\text{SiO}_3 \cdot x\text{Al(OH)}_2 \quad (16.16)
\]

\[
\text{Na}_x\text{SiO}_3 + x\text{Al(OH)}_3 \rightarrow \text{Na}_x\text{SiO}_3 \cdot x\text{Al(OH)}_3 \quad (16.17)
\]

In some instances attempts are made to synthesize naturally occurring zeolites. Boggins, shown on the cover of this book and discussed in Chapter 1, is such an example. Its low abundance in nature restricts studies which could demonstrate its usefulness.

Both natural and synthetic zeolites (Table 16.1) find wide application as cation exchangers since the ions can migrate rather freely through the open structure. Some cations will fit more snugly in the cavities than others. In addition, certain zeolites may behave as molecular sieves if the ions adsorbed in the cavities is completely removed. Various uncharged molecules such as CO₂, NH₃, and organic compounds can be selectively adsorbed in the cavities depending upon their size. Again, the zeolite framework behaves similarly to a clathrate cage except that the adsorbed molecules must be capable of squeezing through the preformed apertures rather than having the

²¹ Asbestos is a commercial term applied to a variety of minerals which can be woven into materials which are heat and fire resistant. The most common asbestos 95% of which is in chrysotile. It does not readily in long tissue and is much less dangerous than crocidolite, which is known to cause asbestosis and malignant mesothelioma (Mossman, B. T.; Bignon, J.; Corn; M., Seaton, A.: Nature 1988; 128, 145-187; Thomas, J. M.: Callow, C. A. R. Proc. Econ. Chem. 1987, 21, 4-15. The word zeolite, meaning boiling stone, was first used by the Swedish scientist, A. F. Cronstedt, in 1756 after he observed that water was evolved from a silicate when it was heated in a flame.

Fig. 15.33 Qualitative molecular orbital diagram for a metallocene. Occupation of the orbitals enclosed in the box depends on the identity of the metal; for ferrocene it is $e_1^*$ and $a_{1g}^*$.

Table 15.8

<table>
<thead>
<tr>
<th>Compound</th>
<th>Electron configuration</th>
<th>Unpaired electrons</th>
<th>Color</th>
<th>Melting point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp$_2$V</td>
<td>$e_1^<em>a_{1g}^</em>$</td>
<td>3</td>
<td>Purple</td>
<td>167-168</td>
</tr>
<tr>
<td>Cp$_2$Cr</td>
<td>$e_1^<em>a_{1g}^</em>$</td>
<td>2</td>
<td>Scarlet</td>
<td>172-173</td>
</tr>
<tr>
<td>Cp$_2$Mn</td>
<td>$e_1^<em>a_{1g}^</em>$</td>
<td>5</td>
<td>Amber</td>
<td>172-173</td>
</tr>
<tr>
<td>Cp$_2$Fe</td>
<td>$e_1^<em>a_{1g}^</em>$</td>
<td>0</td>
<td>Orange</td>
<td>173</td>
</tr>
<tr>
<td>Cp$_2$Co</td>
<td>$e_1^<em>a_{1g}^</em>$</td>
<td>1</td>
<td>Purple</td>
<td>173-174</td>
</tr>
<tr>
<td>Cp$_2$Ni</td>
<td>$e_1^<em>a_{1g}^</em>$</td>
<td>2</td>
<td>Green</td>
<td>173-174</td>
</tr>
</tbody>
</table>

Structures of Cyclopentadienyl Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Configuration</th>
<th>Unpaired electrons</th>
<th>Color</th>
</tr>
</thead>
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<tr>
<td>Cp$_2$V</td>
<td>$e_1^<em>a_{1g}^</em>$</td>
<td>3</td>
<td>Purple</td>
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<tr>
<td>Cp$_2$Cr</td>
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<td>Scarlet</td>
</tr>
<tr>
<td>Cp$_2$Mn</td>
<td>$e_1^<em>a_{1g}^</em>$</td>
<td>5</td>
<td>Amber</td>
</tr>
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<td>Cp$_2$Fe</td>
<td>$e_1^<em>a_{1g}^</em>$</td>
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<td>Orange</td>
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<td>Cp$_2$Co</td>
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<td>1</td>
<td>Purple</td>
</tr>
<tr>
<td>Cp$_2$Ni</td>
<td>$e_1^<em>a_{1g}^</em>$</td>
<td>2</td>
<td>Green</td>
</tr>
</tbody>
</table>
Silicate Minerals

Silicate minerals are a large group of mineral structures that form when silicon and oxygen form a very large number of compounds containing heterocatenated anions. (16.11)

\[
\text{H}_2\text{SO}_4 + \text{Si} = \text{H}_2\text{O} + \text{SiO}_2 + \text{OH}^{-} \quad (16.11)
\]

Condensed polyphosphates such as sodium triphosphate are of great industrial importance since they are used in large tonnages as "builders" in the manufacture of detergents. As such they function to adjust the pH and to complex water-hardeners such as Ca\(^{2+}\) and Mg\(^{2+}\). Industrially, sodium triphosphate is not made from the reaction of Eq. 16.12 but from dehydration of sodium hydrogen phosphate and sodium dihydrogen phosphate mixtures:

\[
5\text{Na}_2\text{HPO}_4 + \text{NaH}_2\text{PO}_4 \xrightarrow{\text{molecular}} 3\text{Na}_2\text{P}_2\text{O}_7 + 2\text{H}_2\text{O} \quad (16.12)
\]

Silicon forms a very large number of compounds containing heterocatenated anions. These are of great importance in the makeup of various minerals since about three-fourths of the earth's crust is silicon and oxygen. Simple silicate anions, \(\text{SiO}_4^{4-}\), are almost unknown. Amphiboles contain the \(\text{SiO}_4^{4-}\) repeating unit as well as metal and hydroxide ions, for example, in the band structure found in amphiboles (Fig. 16.1d). Transition metal ions in these structures behave as they do in complexes: Olivine gets its name from the greenish color caused by partial substitution of Fe\(^{2+}\) for Mg\(^{2+}\) ions in the octahedral holes. The hexa- or dioctahedral micas have also been shown to be orthosilicates, although the term "discrete" is universally applied to the orthosilicate ion and sometimes to the disilicate ion, they cannot be considered analogous of phosphate, \(\text{PO}_4^{3-}\) and the metal–oxygen bond in all silicates contains considerable covalent character. The orthosilicates contain no \(\text{Si-O-Si}\) linkages such as are present in the disilicate, chain silicates, and the cyclic compounds. Although one can formulate them as \(\text{Na}_2\text{Si}_{12}\text{O}_{22}^{15-}\), \(\text{Zr}_2\text{Si}_{12}\text{O}_{22}^{15-}\), or \(\text{M}_2\text{Si}_{12}\text{O}_{22}^{15-}\), as the more electropositive metal \(\text{M}^{2+} = \text{Na}^+, \text{Mg}^{2+}, \text{Fe}^{2+}, \text{Zr}^{4+}, \text{Al}^{3+}\) becomes more like silicon in character, it becomes more difficult to discern discrete silicate anions. When \(\text{M} = \text{Si}\), it becomes impossible and the result is \(\text{SiO}_2\) (page 744). Thus the aluminosilicates usually are treated as large covalent structures, and the hemimorphite mentioned above is better viewed as a 3-D structure related to the aluminosilicates than as \(\text{SiO}_2\), \(\text{ZrO}_2\), \(\text{FeO}_2\), \(\text{H}_2\text{O}\).

Alternatively, one can treat silicates as closest packed arrays of oxide ions with \(\text{Si}^{4+}\) ions filling into tetrahedral holes and other metal ions filling into either tetrahedral holes or into octahedral holes. For example, in the pyroxenes, the transition metal ions in these structures behave as they do in complexes: Olivine gets its name from the greenish color caused by partial substitution of Fe\(^{2+}\) for Mg\(^{2+}\) ions in the octahedral holes. The hexaoctahedral (H) ion has a similar green color. The site of garnets also comes from transition metal ions.

The next higher order of complexity consists of the so-called melilitean anions, which are cyclic structures \(^{37,38}\) of general formula \(\text{Si}_{12}\text{O}_{24}^{8-}\) occurring in melilitic, \(\text{Ba}_2\text{Si}_3\text{O}_5\), catapleite, \(\text{Na}_2\text{ZrSi}_5\text{O}_{10}\), dioctahedral, \(\text{Ca}_2\text{Si}_{12}\text{O}_{20}\), and beryl, \(\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}\). This is the most important mineral source of beryllium, and also may form gem-quality stones (see Problem 16.9).

Infinite chains of formula \(\text{Si}_n\text{O}_{2n}^{2-}\) are found in minerals called pyroxenes. In these chains the silicon atoms share two of the four tetrahedrally coordinated oxygen atoms with adjacent atoms (Fig. 16.1a). Examples of pyroxenes include enstatite, \(\text{MgSiO}_3\), diopside, \(\text{CaMgSi}_2\text{O}_6\), and the lithium orthosilicates, \(\text{Li}_2\text{SiO}_3\). If further sharing of oxygen atoms occurs by half of the silicon atoms, a double chain or bond structure is formed. This is the structure found in amphiboles (Fig. 16.1d). Amphiboles contain the \(\text{SiO}_4^{4-}\) repeating unit as well as metal and hydroxide ions, for example, in the amphibole structure.
pounds in which the rings are tilted with respect to one another. Examples are 

\[ \text{Cp}_2 \text{TaH} \] and \[ \text{Cp}_2 \text{TaCl}_2 \] (Fig. 15.35), in which the steric requirements of additional ligands prevent parallel rings. Lone pair requirements in \( \text{Sn(II)} \) and \( \text{Pb(II)} \) result in similar tilting of the rings in \( \text{Cp}_2 \text{Sn} \) and \( \text{Cp}_2 \text{Pb} \).  

Less clear are explanations for bent structures in \( \text{Cp}_2 \text{Sr} \) and \( \text{Cp}_2 \text{Ba} \) (Fig. 15.36), although packing forces may be responsible.  

Finally, there are compounds with more than two cyclopentadienyl rings. Examples in which several rings are attached to the same metal atom are (tetraakis(cyclopentadienyl))titanium (two rings are \( \eta^1 \) and two are \( \eta^2 \)) and tetrakis(cyclopentadienyl)uranium (all rings are \( \eta^2 \) and are arranged tetrahedrally, Fig. 15.35). A different type of structure is the layered arrangement of nickel atoms and cyclopentadienyl rings in \( [\text{Ni}_2 \text{Cp}_2]_n \), as shown in Fig. 15.37a. Complexes having this arrangement are often called "triplex deckers" and have been described with molecular orbital theory. A variety of center slices have been used in place of \( \text{Cp} \), as shown in Fig. 15.37. Progress also continues in the synthesis and bonding theory of tetradecaper sandwich complexes. 

There are a few compounds known having only one cyclopentadienyl ring per metal atom. Sodium cyclopentadienide, cyclopentadienylthallium(I) (vapor), and cyclopentadienylindium(I) (vapor) have structures that may be described as "opened sandwiches." In the solid, cyclopentadienylindium(I) polymerizes to form an infinite sandwich structure of alternating cyclopentadienyl rings and indium atoms. In addition to the monocyclopentadienyl compounds just described, there are some compounds which contain a single ring per metal atom with a variety of additional ligands, such as carbon monoxide, to complete the coordination sphere. Some examples are shown in Fig. 15.38.
Many different organic R groups have been incorporated into these polymers and a may be as large as 750,000. Low molecular weight polymers in which one of the R groups in H have also been produced. Their wide range of solubilities and electronic properties (selection delocalization occurs along the Si chain) have stimulated much commercial interest in recent times with possible applications in the areas of thermal precursors to silicon carbide, photoinitiators, photocatalysts, and microolithography. Fluorinated and chlorinated long-chain compounds are known to and including SiH, and SiHCl. It is worth mentioning that bulky substituents may enhance the stability of silanes relative to sulfanes. For example, SiBrCl can be distilled without decomposition at 725 °C, but C2BrCl decomposes to C2Br3 and Br2 at 200 °C.

The chemistry of germanes is similar to that of silanes. Heavier congeners of carbon, however, show severely restricted catenation properties. Distannane, Sn2H6, is known, although it is unstable. Plumbane, PbH6, is of marginal stability itself, and hence a large number of heavier analogues is not expected, although the interesting compound Pb4SnH6 has been synthesized.

Some other nonmetals such as nitrogen, phosphorus, and sulfur form chains, but their chemistry is less important than that of the polymers of Group IV (14). Although chain lengths for nitrogen up to eight atoms are known (most of which are extremely explosive), only hydroxide, H2N—N=H3, and hydrazine, H2N—N=H2, are stable at room temperature, and chains longer than 2-tetrazene, H2N—N=H3, and hydrazoic acid, HN3, are stable at room temperature, and chains longer than 2-tetrazene, H2N—N=H3, and hydrazoic acid, HN3, are stable at room temperature. The series of sulfanes, HS—H3, is fairly extensive, and chains up to n = 8 have been obtained in pure form. Diphosphine, P2H6, (very air-sensitive), is well known, and triphosphine, P3PH3, has been fully characterized. Tetraphosphine, P4PH3, and higher analogues have been identified spectroscopically in mixtures. The open-chain structures become increasingly unstable relative to cyclic structures (of which there are many) as the number of phosphorus atoms in the chain increases:

\[ \text{P}_2\text{H}_4 \rightarrow \text{P}_2\text{H}_6 + \text{P}_2\text{H}_4 + \text{PH}_3 \] (16.3)

Oxygen forms no chains longer than three atoms, and besides the familiar ozone, O3, and its union, O2+: few compounds are known, all of them are bisperhydridosilanes such as Si2COOC2F6.

The band gap in polysilanes approaches 4 eV compared to nearly 8 eV in saturated carbon polymers. For many heterocatenated compounds there are other, sometimes simpler, synthetic routes than the thermal elimination of water.

\[ \text{R}_2\text{AsAsR}_2 + x_2 \rightarrow 2\text{R}_2\text{AsX} \] (16.4)

\[ \text{Cl}_2\text{BBrCl}_{2} + \text{CH}_3 = \text{CH}_2 \rightarrow \text{Cl}_2\text{BCH}_2\text{CH}_2\text{BCl}_2 \] (16.5)

\[ \text{Cl}_4 + \text{OH}^{-} \rightarrow \text{HClO} + \text{Cl}^{-} \] (16.6)

\[ \text{HOOH} \rightarrow \text{H}_2\text{O} \] (16.7)

\[ \text{H}_2\text{PFC}_2 \rightarrow \text{PH}_2 + (\text{PH}_3) \] (16.8)

\[ \text{H}_3\text{NNH}_3 + \text{O}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O} \] (16.9)

The extensive chemistry of metul-metal bonds is sufficiently interesting to warrant separate treatment (page 807).

Although there is a paucity of inorganic compounds exhibiting true catenation, the phenomenon of heterocatenation, or chains built up of alternating atoms of different elements, is quite widespread. While homocatenated polysilanes are nearing commercialization (page 739), there are two classes of inorganic heterocatenated polymers that already enjoy wide application. These are the silicones, (SiO),, and the polyphosphazenes, [PN(OR),], discussed on page 749 and 773, respectively.

The simplest heterocatenated compounds are those formed by the dehydration of acids or their salts:

\[ 2\left[ \begin{array}{c} \text{O}^+ \\ \text{O}^- \end{array} \right] \rightarrow \left[ \begin{array}{c} \text{O}^+ \\ \text{O}^- \end{array} \right] + \text{H}_2\text{O} \] (16.10)

Such dehydration reactions were first effected by the action of heat on the simple acid phosphate salts and hence the resulting product was termed pyrophosphate (Gr. pyrophos, first). With an increased number of phosphoryl groups [OF2]n+ known, however, the preferred nomenclature has become diphosphate (n = 3), tripolyphosphate (n = 3), etc.

For many heterocatenated compounds there are other, sometimes simpler, synthetic routes than the thermal elimination of water.


3 The band gap in polysilanes approaches 4 eV compared to nearly 8 eV in saturated carbon skeletons. The polymers are insulators in pure form but often can be doped to give semiconductivity.

4 As with R., high molecular weight polymers—(R2Ge)n—have been recently characterized. See footnote II.


Fig. 15.37 Some known "triple deckers" containing cyclopentadienyl ligands.

There has been much discussion over the years regarding the C—C bond distances in the Cp ring. Five equidistant bonds is consistent with the electron delocalization found in the D\textsubscript{5h} cyclopentadienyl anion. If, however, there are two intermediate, one short, and two long C—C bonds, a structure closer to cyclopentadiene (C\textsubscript{5}) is present and suggests localized bonding. It would seem that an X-ray analysis would answer questions of this sort unequivocally but positional uncertainties caused by thermal ring motion often present a problem. Low temperature measurements minimize these effects and in some instances it is clear that not only are there different C—C bond lengths in the Cp ring but there are also small deviations from planarity. In Rh(Cp*[CO])\textsubscript{2}, C—C bond lengths of 138.8(3), 141.5(3), 144.7(7), 141.2(8), and 141.0(7) pm have been measured and a small distortion from planarity has been noted.\textsuperscript{103} It follows that not all carbon atoms of the Cp* are equidistant from Rh.

Distortions of Cp have mechanistic implications as well. When ReCpMe\textsubscript{3}(NO)(PMe\textsubscript{3}) reacts with two moles of PMe\textsubscript{3}, \eta\textsuperscript{5}-Cp rearranges to \eta\textsuperscript{3}-Cp:\textsuperscript{102}

\[ \text{Me} \quad \begin{array}{c} \text{Me} \\ \text{Mc} \\ \text{Mc} \\ \text{Mc} \\ \text{Mc} \\ \text{Mc} \\ \text{Mc} \\ \text{Mc} \\ \text{Mc} \\ \text{Mc} \end{array} \quad \text{Me} \quad \begin{array}{c} \text{Me} \\ \text{Mc} \\ \text{Mc} \\ \text{Mc} \\ \text{Mc} \\ \text{Mc} \\ \text{Mc} \\ \text{Mc} \\ \text{Mc} \\ \text{Mc} \end{array} \quad \text{H}_2 \]

As the five-electron donor converts to a one-electron donor, Re accepts an additional four electrons from the two trimethylphosphine ligands. One additional mole of PMe\textsubscript{3} causes loss of Cp* from the metal. It is highly likely that the \eta\textsuperscript{3}-Cp complex is an intermediate in the reaction although it was not detected. When Cp ligands are found coordinated in arrangements other than the symmetric \eta\textsuperscript{5}, we sometimes refer to them as "slipped" ring systems. The rhenium reaction is an extreme example in which the ring has been induced to slip completely off the metal atom (\eta\textsuperscript{5}—\eta\textsuperscript{3}—\eta\textsuperscript{1}). Thus one, two, and three vacant coordination sites become successively available on the metal in this reaction. Indenyl complexes have attracted much attention because they undergo substitution reactions much faster than Cp complexes.\textsuperscript{105} It is believed that an \eta\textsuperscript{3} intermediate is stabilized by formation of the aromatic benzo ring.\textsuperscript{106}

\textsuperscript{105} O'Connor, J. M.; Casey, C. P. Chem. Rev. 1947, 47, 207.
\textsuperscript{106} A ring slippage mechanism was first proposed in 1966. For a discussion of this work, see Basolo, F. Polyhedron 1994, 13, 1563-1575.
\textsuperscript{107} Habib, A.; Vanke, R. B.; Holt, K. M.; Cundiff, R. H. Organometallics, 1999, 8, 1225-1231.
Inorganic Chains, Rings, Cages, and Clusters

From topics discussed previously in Chapters 7 and 15 it should be obvious that there is no sharp distinction between inorganic and organic chemistry. Nowhere is the borderline less distinct than in the compounds of the nonmetals. Some, such as the halides and oxides, are typical inorganic compounds, but others, such as compounds of nonmetals with organic substituents, are usually called organic compounds. The situation is further complicated by the tendency of some nonmetals to resemble carbon in certain properties. This chapter discusses the chemistry of nonmetals in terms of one such property: their propensity to form chains, rings, and cages. Most metals show less tendency to form compounds of this type, and the length of the chains and size of the rings thus formed are restricted. However, the ease with which both metals and nonmetals and combinations of the two form clusters has only been recognized in the last decade and an explosive growth in this branch of chemistry is underway.2

1 In this area the nomenclature of the chemists is imprecise, to say the least. Thus it is common to distinguish between "organophosphorus compounds," such as P2H3 and Me2P(Si)2Me2, and "magnificent phosphorus compounds," such as PCH3 and Na2[P(SiMe3)]. While the latter undoubtedly belong to the province of inorganic chemistry, a chemist interested in the former is as apt to be an organic as an inorganic chemist.

2 There is no agreement on what compounds should be called clusters. Some believe that the term should be restricted to compounds which have metal-metal bonds (Cotton, F. A.; Wilkinson, G., Advanced Inorganic Chemistry, 5th ed.; Wiley: New York, 1988; p 1053). Others take a broader view that includes, for example, boranes (no metallic atoms present) or polyoxometal systems (only long-range metal-metal bonding possible).

3 This is a poor definition of organic chemistry, of course. Even the simplest organic compounds involve carbon and hydrogen, and inorganic chemists cannot resist pointing out that the most interesting parts of organic chemistry usually involve "organic" functional groups containing oxygen, nitrogen, sulfur, etc.

Although the congeners of carbon (especially silicon) and related nonmetals exhibit it to a reduced extent. Despite the fact that there appears to be no thermodynamic barrier to the formation of long-chain silanes, SiH2n+1, their synthesis and characterization are formidable tasks. Although silicon-silicon bonds are weaker than carbon-carbon bonds, the energy differences do not account for the observed stability differences. The explanation lies with the low-energy decomposition pathway available to silanes which is not available to alkanes. In addition to their inherent kinetic instability, silanes are difficult to handle because they are very reactive. Their reactions with oxygen, as shown in Eq. 16.2, appear similar to the alkane reactions of Eq. 16.1:

\[
\text{C}_n\text{H}_{2n+1} + \frac{3n+1}{2} \text{O}_2 \rightarrow n\text{CO}_2 + (n + 1)\text{H}_2\text{O} \\
\text{Si}_n\text{H}_{2n+1} + \frac{3n+1}{2} \text{O}_2 \rightarrow n\text{SiO}_2 + (n + 1)\text{H}_2\text{O}
\]

In fact both reactions are thermodynamically favored to proceed to the right. The important difference, not apparent in the stoichiometric equations, is the energy of activation which causes the paraffins to be kinetically inert in contrast to the reactive silanes. Further complications with silanes arise from lack of convenient syntheses and difficulties in separation. Nevertheless, compounds from \( n = 1 \) to \( n = 11 \) have been isolated, including both straight-chain and branched-chain compounds. We should not judge silicon's tendency to catenate by looking at these hydrides, however; a much different result is obtained when substituents other than hydrogen are present. Factors other than inherent Si—Si bond strength must be involved because it is possible to isolate a large number of polysilane polymers:

\[
\begin{align*}
R_1 & = \\
\underset{\text{Si}}{\text{Si—Si}}_{\text{n}} & = \underset{\text{Si}}{\text{Si—Si}}_{\text{n}}
\end{align*}
\]

4 At 400 °C, C2H6 decomposes 103 times faster than C6H6. It appears that because of the low-lying unoccupied 4f or 5d orbitals of Si, migration of a hydrogen atom with simultaneous cleavage of an Si—Si bond is possible. (Rice, M. A., In Homonuclear Rings, Chains and Macrocycles of Main-Group Elements, G. A. Whitegold, A. L. Ed.; Charles; New York, 1977.)

5 The difference in activation energy can be qualitatively described as follows: The reaction of Eq. 16.1 can be initiated by striking a match while the reaction of Eq. 16.2 merely requires allowing oxygen to contact the silicon. It has been stated that one of the prerequisites for the synthesis of silanes is a large amount of courage.


7 To quote Robert W. Wray: "Although the myth that silicon is not capable of extensive catenation still persists, very large cyclic polysilanes with molecular weights in the hundreds of thousands." Pure Appl. Chem. 1982, 54, 1011-1018.

We have already seen that metalloocene complexes often violate the 18-electron rule and that stability of these violators can be attributed to the nature of the molecular orbitals to which electrons are added or from which they are removed. In view of this electronic flexibility, it is perhaps not surprising that Cp ligands are capable of stabilizing a wide range of oxidation states. Normally we think of organometallic chemistry as being the domain of low oxidation state complexes, but increasing interest in high oxidation state complexes is apparent and often the cyclopentadienyl group is present as a stabilizing ligand. Oxidation of cyclopentadienyi complexes may lead to isolable oxo complexes as shown by the following hydrogen peroxide reaction:

\[
\text{CpRe(CO)}_3 \rightarrow \text{CpRe(O)}_3
\]

Some other oxo complexes are shown in Fig. 15.39. Although the oxide ligand is generally thought of as \( \text{O}^- \) rather than neutral \( \text{O} \), its similarity to the carbene ligand, \( \text{CR}_2 \) (which could also be viewed as \( \text{CR}^- \)), tends to be obscured as a result. Interest in oxo complexes is tied to their relationship to metal oxide catalysts which are widely used in organic synthesis.

Metallocenes such as Cp2Cr, Cp2Fe, and Cp2Co are considered to have strong covalent bonding between the metal and the rings. Although all of these metallocones are capable with respect to oxidation, etc., all have strong bonding with respect to dissociation of the rings from the metal atom (Table 15.9). The bonds between the metal and rings certainly have some polarity, but these compounds do not react like polar organometallic compounds (as exemplified by the well-known Grignard reagent):

\[
\text{RMgX + H}_2\text{O} \rightarrow \text{RH + MgXOH}
\]

Cp2Fe + H2O \rightarrow No reaction

Fig. 15.39 Cyclopentadienyl complexes in which the metal is in a high oxidation state.

In contrast, several compounds are known which contain a very reactive \( \text{C}_2\text{H}_2 \) group:

\[
\begin{align*}
\text{NaCp} + \text{H}_2\text{O} & \rightarrow \text{C}_2\text{H}_2 + \text{NaOH} \\
\text{MgCp}_2 + 2\text{H}_2\text{O} & \rightarrow 2\text{C}_2\text{H}_2 + \text{Mg(OH)}_2 \\
\text{SmCp}_2 + 3\text{H}_2\text{O} & \rightarrow 3\text{C}_2\text{H}_2 + \text{Sm(OH)}_3
\end{align*}
\]

These compounds are considered to have a salt-like nature and are usually referred to as metal cyclopentadienides rather than as cyclopentadienyl complexes, although the distinction is sometimes rather arbitrary. As is the case with all polar bonds, there is no sharp distinction between covalent and ionic bonding. Thus, although the lanthanide compounds are usually referred to as ionic, there may be a substantial amount of covalent character present.

The beryllium and magnesium compounds are of special interest with regard to the problem of covalent versus ionic bonding. Although magnesium cyclopentadienide (maquilloco) is structurally almost identical to ferrocene, it is thought to be essentially ionic. The sandwich structure should be the most stable one not only for covalent complexes utilizing \( \text{J} \) orbitals, but also from an electrostatic viewpoint for a cation and two negatively charged rings. The structure of the beryllium compound is unusual and still somewhat uncertain. Its large dipole moment rules out a ferrocene-like structure, and a single \( ^1\text{H} \) NMR signal, even at low temperatures, indicates a fluxional molecule. Both X-ray and electron diffraction data have been interpreted in terms of a "slipped sandwich" complex (Fig. 15.40) in which one Cp ring is pentagonal and the other is hexagonal. In solution the Cp rings appear to rock as the beryllium atom oscillates. [From Pratten, S. J.; Cooper, M. K.; Aroney, M. J.: Filipczuk, S. W. J. Chem. Soc. Dalton Trans. 1985, 1761-1765. Used with permission.]

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107 E.g., CO, which normally has little affinity for metals in high oxidation states, has been found in WCl(CO)(PMePh2)2ClCOO). Su, F.; Cooper, C.; Grob, S. J.; Kuechting, A. L.; Mayer, J. M. J. Am. Chem. Soc. 1986, 108, 3545-3547. Adk's groups may also stabilize high oxidation states, e.g., WMe4.

15.60 The first bis(hydroxymethyl) transition metal complex has been prepared. The synthesis
15.59 The solid state magic angle spinning 13C NMR spectrum of Fe(CO)5 shows a single
15.58 When (r)′-Me2C≡C(H)Nb(H)(CO) reacts with AIMe, a single nonionic product (I) is
15.57 Suggest a reaction mechanism for the following base-induced migration:
15.56 Why do alkenes and aromatics compose such a large fraction of the products from the
15.55 On page 643 the following statement was made, somewhat casually, in reference to
15.54 In this chapter we have examined examples of polynuclear metal carbonyl complexes as
15.53 Using data given in this book, calculate the standard enthalpies of reaction at 25 °C for:
15.52 In the hydrogenation of an alkene using Wilkinson’s catalyst, Rh(PPh3)3(R)(H)2 +
15.51 Consider the carbonylation of di-CH3Mn(CO)(CO2) with unlabeled CO. Assuming that
15.50 Metals in low oxidation states are usually strong reducing agents. Give an example of a
15.49 Upon encountering Ni(CO)4(CO2) for the first time, you might suppose that a typographical
15.48 The large difference in the two ionization constants provided the first
evidence that the hydrogen atoms in the complex were both bound to the same atom (and
to 1900 cm−1 for the starting material. The 1H NMR hydride chemical shift changes from
15.47 When 1'H-Me2C≡C(H)NH2H2C=NH(CO) reacts with AIBN, a single monomeric product (II) is
15.46 Why do alkenes and aromatics compose such a large fraction of the products from the
15.45 The solid state magic angle spinning 13C NMR spectrum of Fe(CO)5 shows a single
15.44 Amino alkenes such as H2NC(Me3)CH2CH=CH2 are catalytically converted to five-
15.43 The first bis(hydroxymethyl) transition metal complex has been prepared. The synthesis was
achieved by an interesting sequence of reactions. Diazomethane converted (1.5-
cyclooctadiene)diiodoplatinum(II) into (1.5-cyclooctadiene)dihydromethylplatinum(II).
Treatment of this complex with silver trifluoroacetate led to replacement of both iodine
atoms with trifluoroacetate. Methanalysis gave (1.5-cyclooctadiene)dihydroxy-
metal(III). Reaction of this complex with dihydroxycarbonyl resulted in
loss of water and intramolecular cyclization to form an oxametallacyclooctane complex of
platinum from which the diene was replaced by two triphenylphosphine ligands. Draw
structures of each of the complexes and reagents in the sequence. (See Hoover, J. P.;
15.61 The first example of a four electron donor, side on bridging thiocarbonyl, [HBPz3]-
(CO)5(W(H)3-CS)Mo(CO)5(lindenyl), has been reported. Draw the structure of this complex.
Why is the bridging CS group in this complex called side on instead of bridging? (See
Doyle, R. A.; Daniels, L. M.; Angelici, R. J.; Stone, F. G.; A. J. Am. Chem. Soc. 1989,
111, 4993–4997.)
15.62 Amino alkenes such as H2NC(Me3)CH2CH=CH2 are catalytically converted to five-
membered heterocycles by [(MeC5H4)2LaH2]. Give the steps of the reaction sequence
and incorporate them into a Tolman catalytic cycle. Present arguments against formation
of an La-alkene bond. (See Gugger, M. R.; Marks, T. J. J. Am. Chem. Soc. 1989, 111,
4108–4109.)
15.59 The solid state magic angle spinning 13C NMR spectrum of Fe(CO)5 shows a single
absorption at +26 °C but two signals (relative intensity = 2:3) at -148 °C. Provide an
explanation for these spectral observations. (See Harrison, B. E.; Whitmire, K. H.; J. Am.
15.60 The first bis(hydroxymethyl)transition metal complex has been prepared. The synthesis
was achieved by an interesting sequence of reactions. Diacetoacetamide (1.5-
15.58 When (r)′-Me2C≡C(H)Nb(H)(CO) reacts with AIMe, a single neutral product (II) is
obtained which shows a carbonyl stretching frequency of 1721 cm−1 compared to
1875 cm−1 for the starting material. The 1H NMR hydride chemical shift changes from
-5.59 ppm to -4.72 ppm in going from reactant to product. However, when (Cp′)2(Cp)2-
Bi=CH=CH2 reacts with AIBN, to give a single neutral product (IB), the CO stretching
frequency changes from 1863 cm−1 to 1900 cm−1 and the 1H NMR hydride chemical shift
changes from -5.48 ppm to -10.2 ppm. Suggest structures for products I and II and
rationalize their infrared and NMR data. (See Hoover, J. F.; Wissel, M. R.; J. Am.
15.57 Why do alkenes and aromatics compose such a large fraction of the products from the
reaction of methanol with ZSM-5 (Eq. 15.181)?
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15.55 On page 643 the following statement was made, somewhat casually, in reference to
15.54 In this chapter we have examined examples of polynuclear metal carbonyl complexes as
well as simple metal carbonyl hydrides. Consider now the polynuclear hydride complex,
H2O(CO)3. Rationalize the formulation of this species. From your application of the 18
electron rule, what can you say about the structure of this molecule? How is it
similar to or different from the complex CO2(CO)9 shown in Figure 15.9? (See Churchill
and
discussion of the 18-electron rule, what can you say about the structure of this molecule?
15.53 Using data given in this book, calculate the standard enthalpies of reaction at 25 °C for:
a. CH3OH(g) + CO(g) = CO2(g) + H2O(g)
b. CH3OH(g) + CO2(g) = CO2(g) + H2O(g)
15.52 In the hydrogenation of an alkene using Wilkinson’s catalyst, Rh(PPh3)3(R)(H)2 +
15.51 Consider the carbonylation of di-CH3Mn(CO)(CO2) with unlabeled CO. Assuming that
15.50 Metals in low oxidation states are usually strong reducing agents. Give an example of a
15.49 Upon encountering Ni(CO)4(CO2) for the first time, you might suppose that a typographical
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reaction of methanol with ZSM-5 (Eq. 15.181)?
15.55 On page 643 the following statement was made, somewhat casually, in reference to
One form of manganocene, Cp₂Mn, consists of infinite chains of CpMn fragments bridged by cyclopentadienyl rings in the solid. Upon being warmed to 159 °C the color changes from brown to orange and the product is homomorphous with ferrocene. It has been formulated as ionic, high spin \( d^5 \), \( Mn^{2+} \), \( 2Cp^- \). Evidence for ionic bonding is of three types: (1) Manganocene reacts instantaneously with iron(II) chloride in tetrahydrofuran to form ferrocene and is hydrolyzed immediately by water; (2) the dissociation energy (Table 15.9) is closer to that of magnesium cyclopentadienide than to that of the other transition metal metallocones; and (3) the magnetic moment of manganocene is 5.86 BM, corresponding to five unpaired electrons. All these data are consistent with a \( d^5 \) \( Mn^{2+} \) ion. The evidence is not unequivocal, however. Other metallocones such as chromocene react with iron(II) chloride to yield ferrocene as well, although admittedly not so rapidly. Assignment of "ionic bonding" to manganocene is reminiscent of similar assignments to other high spin complexes. The presence of high spin manganese and a lower dissociation energy for manganocene indicate the absence of strong covalent bonding (i.e., a small ligand field stabilization energy from the \( d^5 \) \( eg^0 \) configuration) but do not prevent the possibility of some covalent bonding. In any event, the stability of the half-filled subshell, \( d^5 \) configuration is responsible for the anomaly of manganocene.

This anomalous behavior disappears when methyl groups replace the hydrogen atoms of the ring (page 673). The \( \text{Cp}_2 \text{Mn} \) complex is low spin (one unpaired electron) and has chemistry similar to that of other metallocones.

The first metallocone was discovered by accident independently by two groups. In one group, an attempt was made to synthesize fulvalene by oxidation of the cyclopentadienyl ligand. Grignard reagent:

\[
\text{Fe} + 2\text{Cp}_2\text{H}_2 \rightarrow \text{Fe(Cp}_2\text{H}_2)_2 + \text{H}_2
\]

Sodium and thallium cyclopentadienide provide more versatile syntheses of ferrocene and other metallocones. The synthesis of fulvalene was unsuccessful, but a stable orange compound was isolated which was subsequently characterized and named ferrocene. The iron(II) is first reduced by the Grignard reagent to iron(0) which then reacts to form ferrocene:

\[
P_2 + 2\text{Cp}_2\text{H}_2 \rightarrow \text{Fe(Cp}_2\text{H}_2)_2
\]

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\[
P_2 + 2\text{Cp}_2\text{H}_2 \rightarrow \text{Fe(Cp}_2\text{H}_2)_2
\]
15.31 Isocyanides, RNC, and nitriles, RCN, are both well-known ligands. Complexes such as \( \text{CrCN(Me)} \) exist, but not complexes such as \( \text{Cr(NCMe)} \). Compare the bonding characteristics of these two ligands and account for the relative stabilities of these two complexes.

15.32 Predict the product of the following reaction:

\[ \text{H}_2\text{C}==\text{CH} + \text{CH}_2==\text{CH}_2 \rightarrow \text{H}_2\text{C}==\text{CHCH}_2\text{CH}==\text{CH}_2 \]

15.33 Nitriles are almost invariably bound to metals through nitrogen and exist in a linear arrangement. An exception to this is \( \text{H}_3\text{C}==\text{C}==\text{N}==\text{C}==\text{H}_2\text{N}==\text{C}==\text{H}_2\text{C}==\text{C}==\text{H} \). Draw the structure for this complex. Does it obey the 18-electron rule? (See Chock, P. A.; Knoke, C. B.; Hawthorne, M. F. *Organometallics* 1988, 7, 650-660.)

15.34 Thermodynamically, cis-\( \text{Mo}==\text{C}==\text{O}(\text{PPh}_3\text{CH}_2\text{CH}_2\text{PPh}_3) \) is more stable than trans-\( \text{Mo}==\text{C}==\text{O}(\text{PPh}_3\text{CH}_2\text{CH}_2\text{PPh}_3) \), but \( \text{trans-ibo-Mo}==\text{C}==\text{O}(\text{PPh}_3\text{CH}_2\text{CH}_2\text{PPh}_3) \) is more stable than \( \text{cis-ibo-Mo}==\text{C}==\text{O}(\text{PPh}_3\text{CH}_2\text{CH}_2\text{PPh}_3) \). Provide an explanation for the relative stabilities of these isomers. (See Kuchynka, D. J.; Kochi, J. K. *Organometallics* 1989, 8, 677-684.)

15.35 The conversion of \( \text{ferrocenyl} ==\text{C}==\text{O}(\text{PMe}_3\text{CH}_2\text{CH}_2\text{PMe}_3) \) to \( \text{ferrocenyl} ==\text{C}==\text{O}(\text{PMe}_3\text{CH}_2\text{CH}_2\text{PMe}_3) \) by action of \( \text{BF}_3\) is thought to take place by passing through an intermediate containing a phosphonium ligand. Draw structures of the reactant, the intermediate, and the product. (See Nakazawa, H.; Ohni, M.; Miyoshi, K.; Yokida, H. *Organometallics* 1989, 8, 639-644.)

15.36 Metal-phosphine complexes are ubiquitous in organometallic chemistry. There are also metallacalixarene phosphoranes \( (\text{L}==\text{M}==\text{PR}_3) \), phosphides \( (\text{L}==\text{M}==\text{PR}_3) \), and phosphines \( (\text{L}==\text{M}==\text{PR}_3) \). Give specific examples of each.

15.37 When \( \text{CO} \) becomes coordinated to \( \text{B}==\text{H} \), its stretching frequency increases, but when \( \text{CO} \) becomes coordinated to \( \text{NOCO} \), its stretching frequency decreases. Explain.

15.38 Does the CO stretching frequency increase or decrease when

a. \( \text{L}==\text{M}==\text{CO} \) becomes more electron withdrawing?

b. \( \text{CO} \) of \( \text{L}==\text{M}==\text{CO} \) becomes coordinated to a Lewis acid.

15.39 Suppose you were directing a research student who came to you and stated that he or she had isolated a compound that was either (a) or (b): (a) \( \text{C}==\text{O} \); (b) \( \text{C}==\text{O} \). Give specific examples of each.

15.40 Using Fig. 15.33, predict the number of unpaired electrons in

- a. \( \text{Cp}_2\text{Cr} \)
- b. \( \text{Cp}_2\text{Fe} \)

15.41 Organometallic chemistry seems especially prone to the development of descriptive words and phrases. Although much of this language is sometimes considered jargon and is not allowed to enter the formal literature, it is common in oral usage. See if you can define the following terms:

- a. open-faced sandwich
- b. muenstersandwich
- c. club sandwich
- d. ringwrecker
- e. molecular bread jump
- f. piano stool molecules

15.42 The synthesis of a neutral homoleptic uranium complex, \( \text{UR}_3 \), has finally been achieved. Why do you think \( \text{U}==\text{M}==\text{O} \) was chosen for this synthesis?

15.43 The complexes of Fig. 15.38 are commercially available. Starting with complexes which contain only carbonyl ligands, suggest syntheses for the following:

- a. \( \text{Cp}_2\text{V}==\text{O} \)
- b. \( \text{Cp}_2\text{Fe}==\text{O} \)
- c. \( \text{Cp}_2\text{Ni}==\text{O} \)
- d. \( \text{Cp}_3\text{Mo}==\text{O} \)

15.44 The average bond dissociation energy for ferrocene is large (302 kJ mol\(^{-1}\)), Table 15.9 as you might expect, but it is even larger for vanadocene (392 kJ mol\(^{-1}\)). Can you suggest any reasons that vanadocene is more reactive even though it is more stable?

15.45 The reaction of \( \text{Fe}==\text{CO} \), with \( \text{Li}==\text{OH} \) in methanol at -78 °C gives a mixture of \( \\text{[Fe(CO)H] }==\text{O} \) and \( \\text{[Fe(CO)H] }==\text{O} \) as shown by infrared spectroscopy. When \( \text{LiOH} \) is used, however, the sole product is \( \\text{[Fe(CO)H] }==\text{O} \). Explain. (See Lee, S. W.; Tucker, W. D.; Richmond, M. G. *Inorg. Chem.* 1990, 29, 3053-3056.)

15.46 Predict the product of the following nucleophilic addition:

\[ \text{CH}_2==\text{CH}==\text{CH}_2 + \text{CH}_2==\text{CH}==\text{CH}_2 \rightarrow \text{CH}_2==\text{CHCH}==\text{CH}==\text{CH}_2 \]

15.47 Discuss the difference between formulating \( \text{Cr}==\text{C}==\text{H}_2 \) as dibenzenechromium (a) and as 

- a. \( \text{C}==\text{H}_2 \text{chromium} \)
- b. \( \text{C}==\text{H}_2 \text{chromium} \)

15.48 When one mole of \( \text{Pc}==\text{P}==\text{P}==\text{C}==\text{H}_2 \) is treated with two moles of \( \text{BF}_3\), ethylene is quantitatively released and the \( \text{BF}_3 \) is completely consumed. The product consists of a single compound, which is monomeric in dichloromethane solution. Formulate the product and describe the bonding in it. (See Flashek, M.; Nöth, H.; Pete, W.; Wallbridge, M. G. H. *Inorg. Chem.* 1974, 13, 490-492.)

15.49 Van der Sluys, W. G.; Burns, C. J.; Sattelberger, A. P. *Organometallics* 1989, 8, 219-221.
to a lower oxidation state and with the assistance of AlCl$_3$, benzene is coordinated to chromium:

$$3\text{CrCl}_3 + 2\text{Al} + \text{AlCl}_3 + 6\text{C}_6\text{H}_6 \rightarrow 3[\text{Cr}(\eta^6-\text{C}_6\text{H}_6)]_2[\text{AlCl}_4]$$

(15.78)

The cation can be reduced to dibenzenechromium with sodium dithionite, Na$_2$S$_2$O$_4$. The dibenzene complexes of Cr, Mo, and W are all air sensitive and those of Mo and W are especially so. Dibenzenechromium is a black solid that melts at 280 °C.

The success of the Fischer-Hafner method depends upon the particular arene and on the skill of the experimentalist. Several decades ago Timms introduced a chemically innovative approach for making a variety of organometallic complexes. It is based on the premise that if you wish to synthesize a zerovalent complex, it is logical to begin with metal atoms rather than with salts that must be reduced. Highly active metal atoms can be created by vaporizing metals under vacuum with resistive heating and then condensing the atoms on low-temperature walls of a specially designed vessel (Fig. 15.41). A ligand, benzene for example, can be introduced into the vessel where it will react with the metal atoms to form a complex.

$$\text{M(s)} \rightarrow \text{M(g)} \rightarrow \text{M(} \eta^6-\text{C}_6\text{H}_6\text{)}_2$$

(15.79)

Fig. 15.41 An inexpensive apparatus constructed from a modified rotating evaporator used to vaporize metals for condensation with ligands. [Adapted from Markle, R. J.; Pettijohn, T. M.; Lagowski, J. J. Organometallics 1985, 4, 1529-1531. Used with permission.]

The rings of the dibenzene chromium, molybdenum, and tungsten complexes are eclipsed and have a small rotational barrier. Unlike ferrocene, these complexes have labile rings which can be displaced:

$$\text{CrCO}_3 \rightarrow 2$$

(15.80)

The benzene rings can be removed completely by reaction with a more active ligand:

$$\text{Cr}(\eta^6-\text{C}_6\text{H}_6)_2 + 6\text{PF}_3 \rightarrow \text{Cr(} \text{PF}_3\text{)}_6 + 2\text{C}_6\text{H}_6$$

(15.81)

There are a number of heteroatom six-membered aromatic rings which are analogous to benzene in that they can donate six electrons to a metal. These include phosphabenzene, borabenzene anion, borazine, and arsabenzene, shown in Fig. 15.42.

Cycloheptatriene is a six-electron donor that can form complexes similar to those of benzene but differing in the localization of the $n$ electrons in $\text{C}_7\text{H}_6$. The alternation in bond length in the free cycloheptatriene is retained in the complexes (Fig. 15.43). Furthermore, in $\text{C}_7\text{H}_6\text{Mo(CO)}_3$, the double bonds are located trans to the carbonyl groups, providing an essentially octahedral environment for the metal atom.

$$\text{Cycloheptatriene and Tropylium Complexes}$$

Fig. 15.42 Complexes of phosphabenzene, borabenzene anion, borazine, and arsabenzene. These six-membered rings are analogous to benzene, i.e., they are six-electron donors and are aromatic.


Ligands are described with a variety of adjectives, some not used in this chapter. Using other sources, try to determine what is meant by:

- an ancillary ligand
- an amphoteric ligand
- a sterically hindered ligand

Suggest reasonable syntheses for:

- \( \text{Co} \left( \text{PPh}_3 \right)_2 \left( \text{CO} \right)_8 \)
- \( \text{Co} \left( \text{PMe}_3 \right)_2 \left( \text{CO} \right)_8 \)
- \( \text{Ni} \left( \text{PPh}_3 \right)_2 \left( \text{CO} \right)_8 \)
- \( \text{Ni} \left( \text{PMe}_3 \right)_2 \left( \text{CO} \right)_8 \)
- \( \text{Ni} \left( \text{PPh}_3 \right)_2 \left( \text{CO} \right)_8 \)

Bond lengths and angles have been determined by gas phase electron diffraction for two other complexes. A typical C—P—C bond angle in a PMe, complex is 102°, but the cone angle for this complex is analogous to CIHT and \( 2\text{C}(\text{CO})_3 \). Indentify which set of data (I or II) belongs to each complex.

Determine the number and symmetry designations of the infrared-active C—O stretching modes in the following derivatives of MeCO,:

- \( \text{MeCO} \left( \text{PMe}_3 \right)_2 \)
- \( \text{MeCO} \left( \text{PPh}_3 \right)_2 \)
- \( \text{MeCO} \left( \text{PPh}_3 \right)_2 \)
- \( \text{MeCO} \left( \text{PMe}_3 \right)_2 \)
- \( \text{MeCO} \left( \text{PPh}_3 \right)_2 \)

Substitution reactions of polynuclear metal carbonyls with tertiary phosphines often induce the formation of bridging carbonyls. Provide an explanation.


Tropylium salts, such as (C₆H₅)Br, are not used directly for organometallic synthesis because of their explosive power.

Cycloheptatriene complexes can be oxidized (hydride ion abstraction) to form cycloheptatrienyl (sometimes called tropylium) complexes:

The tropylium ring is planar with equal C—C distances. Like benzene and the cyclopentadienide anion, the tropylium cation is an aromatic, six-electron species.

In accord with the Huckel rule of 4n+2 electrons, both cyclobutadiene and cyclooctatetraene (cot⁻²) are nonaromatic. Cyclooctatetraene contains alternating bond lengths and has a tub-shaped conformation:

\[ 2K + C_{8}H_{6} \rightarrow 2K^+ + (C_{8}H_{6})^2^- \]  
(15.83)

Thus cyclobutadiene, which was nonexistent at the time, was shown to be stabilized by complexation. Oxidation of the complex liberates free cyclobutadiene which was trapped by ethyl propionate to give a cycloadduct. The experiments established that...
Organometallic chemistry, as its name implies, has links to both organic chemistry and inorganic chemistry. The ties to organic chemistry, at least in compounds that were more or less laboratory curiosities, have burgeoned into indispensable components of the petroleum chemicals industry. Transition metal organometallic chemistry is largely an extension of the coordination chemistry of strongly bonded ligands, but classical chemistry anticipates the polyhedral chemistry of boranes with extreme delocalization in molecular orbitals (Chapter 16). The concept of isolobal fragments also ties the two disciplines together, with fragments as seemingly disparate as $\text{CH}_2\text{CH}_2\text{P}$ and $\text{P}=$ $\text{C}=$ $\text{R}$.

![Energy barriers (in kJ mol$^{-1}$) for three separate types of rotational motion involving a bridging vinylcarbyne ligand. The values were obtained by line shape analysis of variable-temperature proton NMR spectra.](image)

**Fig. 15.58**

A final example of stereoelectronic nonrigidity, illustrating the application of sophisticated NMR line shape analysis for obtaining rotational barriers, is provided by a cyclopentadienyl diron complex containing a bridging vinylcarbyne (Fig. 15.58). Barriers for three distinct types of rotational motion involving the bridging ligand have been obtained: (1) rotation of the entire vinylcarbyne ligand (44.3 kJ mol$^{-1}$), (2) rotation of the dimethylamino group (45.6 kJ mol$^{-1}$), and (3) rotation of the aryl group (54.3 kJ mol$^{-1}$).

### Problems 7.31

1. A cyclopentadienyl phosphorus compound, (Me$_2$C$_2$)$_2$(H$_2$P)$_2$, has been identified spectroscopically. Is this an organometallic compound? Explain your answer. By electron counting, draw conclusions about the hypervalency of the cyclopentadienyl group. How many electrons does phosphorus need in order to obey the effective atomic number rule?

2. Although 18 valence electrons are found in (FeH$_2$O)$_2$, the effective atomic number rule is violated. Explain.

3. Formulate neutral, 18-electron complexes of chromium which contain only a. cyclopentadienyl and nitrovinyl ligands
b. cyclopentadienyl, carbonyl, and nitrovinyl ligands

4. Postulate geometries for bis(triphenylphosphine)gold. Which of these obey the 18-electron rule? What is the geometry of [Fe(CO)$_2$]? Why is it different from that of the tris(triphenylphosphine) complex?

5. Predict the metal-metal bond order for neutral complexes having the formula [(OC)$_2$M$_2$P$_2$](C$_2$H$_4$). When N = V, Cr, and Mn.

6. Complexes of CS are known, but homoatomic tail ligands the same examples such as Fe(CS)$_2$ have not been synthesized. Why do you think efforts to prepare these complexes have failed?

7. a. Complexes containing Ph$_3$PCH$_2$CH$_2$Ph$_3$, sometimes known as diphos, are abundant. Using the 18-electron rule as guide, draw structures of

   i. (OC)$_2$W(PPh$_3$CH$_2$Ph$_3$)
   ii. (OC)$_2$W(PPh$_3$CH$_2$Ph$_3$)
   iii. (OC)$_2$W(PPh$_3$CH$_2$Ph$_3$)
   iv. (OC)$_2$W(PPh$_3$CH$_2$Ph$_3$)
   v. (OC)$_2$W(PPh$_3$CH$_2$Ph$_3$)

   b. It has not been possible to synthesize [OC$_2$W$_2$(PPh$_3$CH$_2$Ph$_3$)$_2$], but [OC$_3$W$_2$(PPh$_3$CH$_2$Ph$_3$)$_2$] is known. Provide an explanation.

8. Postulate a monometallic manganese complex that obeys the 18-electron rule and contains only the ligands

   a. hydroxyl, methoxy, and cyclopentadienyl
   b. thiolate, pyrylium, and phosphino
   c. alkyl, acrylate, and nitrovinyl
   d. chlorobispyridyl, amino, and isocyanide

9. Trimetallic complexes containing ethylene bridges are well known. Assume that the 18-electron rule in effect and postulate a structure for [Me$_3$P$_3$H$_2$Co$_3$].

10. Ditertiary and dialkyl complexes have prepared Fe$_3$O$_2$, Ps$_2$PCH$_2$C$_2$(R)$_3$(R)$_3$. $\text{SCOMe}_2$(PPh$_3$)Co, which obeys the 18-electron rule? Confirm it does and draw its structure. What is the oxidation state of iron in this compound?

11. Both Fe$_2$P$_2$ and Fe$_2$P$_2$Me$_2$ have been widely used as ligands. Compare their resonance toward O$_2$ and H$_2$O. Which of these two ligands is generally considered to be the better n-donor $\pi$ acceptor? Why?

12. Prefixes abound in organometallic nomenclature. The complex Fe(CO)$_2$(aldehyde)$_2$-
Reactions of Organometallic Complexes

The earliest methods of replacing one or more carbonyl ligands from a complex relied on brute force (heat or light) to break the $\text{M}—\text{CO}$ bond. The idea was that once the gaseous CO had dissociated, it would escape easily from solution and thus have minimal chances of recombining with the metal. The departure of CO from a complex leaves a vacant coordination site and in general an unstable metal fragment which is minimal chances of recombining with the metal. The departure of CO from a complex leaves a vacant coordination site and in general an unstable metal fragment which is electron deficient. The fragment can then react with a nucleophile such as a phosphine, $\text{R}_3\text{P}$, to produce a substituted metal carbonyl. The entire dissociative process can be described as follows:\(^{129}\)

$\text{L}_2\text{M}—\text{CO} \xrightarrow{\text{actinocene, } \text{An} = \text{actinide metal)).}$

(a) Interaction of $f$ orbital of the metal with a ligand $e_g$ orbital. (b) Interaction of $d$ orbital of the metal with a ligand $e_g$ orbital. [From Brennan, J. G.; Green, J. C.; Reddell, C. M. J. Am. Chem. Soc. 1988, 110, 2373-2377. Used with permission.]

(c) Molecular orbital diagram for actinocene, An = actinide metal. Fig. 15.45

$cyclobutadiene could exist, however briefly, and led eventually to its low temperature isolation.

The earliest methods of replacing one or more carbonyl ligands from a complex relied on brute force (heat or light) to break the $\text{M}—\text{CO}$ bond.\(^{129}\) The idea was that once the gaseous CO had dissociated, it would escape easily from solution and thus have minimal chances of recombining with the metal. The departure of CO from a complex leaves a vacant coordination site and in general an unstable metal fragment which is electron deficient. The fragment can then react with a nucleophile such as a phosphine, $\text{R}_3\text{P}$, to produce a substituted metal carbonyl. The entire dissociative process can be described as follows:\(^{129}\)

1. $\text{L}_2\text{M} — \text{CO} \xrightarrow{\text{actinocene, } \text{An} = \text{actinide metal)).}$
2. $\text{L}_2\text{M} + \text{R}_3\text{P} \rightarrow \text{L}_2\text{M}—\text{PR}_3$

Of course some complexes lose CO more readily than others. For example, it is rather easy to displace all four CO groups of $\text{Ni}$(CO)$_4$L with L ($L = \text{R}_3\text{P}$) in stepwise fashion:

$\text{Ni}$(CO)$_4$ + $\text{L}$ $\rightarrow$ $\text{Ni}$(CO)$_3$L $\rightarrow$ $\text{Ni}$(CO)$_2$L$_2$ $\rightarrow$ $\text{Ni}$($\text{CO}$)$_3$L$_2$ $\rightarrow$ $\text{Ni}$L$_4$\(^{18}$

The task is more much more difficult for $\text{Fe}$(CO)$_4$, which has a large energy of activation for substitution and requires higher temperatures. At these temperatures side reactions are significant and yields of substituted products are low:

$\text{Fe}$(CO)$_4$ + $\text{L}$ $\rightarrow$ $\text{Fe}$(CO)$_3$L $\rightarrow$ $\text{Fe}$(CO)$_2$L$_2$ $\rightarrow$ $\text{Fe}$($\text{CO}$)$_3$L$_2$ $\rightarrow$ $\text{Fe}$L$_4$\(^{18}$

Notice that Eq. 15.89 shows only two CO ligands being displaced. Each time CO is replaced by $\text{R}_3\text{P}$, the complex becomes more electron rich and the remaining CO groups receive more $\pi$ electron density. This means that in general the $\text{M}—\text{CO}$ bond strength increases and CO becomes more resistant to dissociation. Of course the steric requirements of the phosphine may limit the degree of substitution as well (see cone angles, page 688).

The thermal and photolytic reactions described above usually give a mixture of products and therefore are not as popular as they once were. Reactions have now been developed which give a good yield of the particular product of interest. For example, if one wishes to prepare $\text{W}$(CO)$_5$PR$_3$, one would not heat W(CO)$_6$ with PR$_3$ at high temperatures but irradiate the reaction mixture with ultraviolet light because both of these methods would give mixtures of $\text{W}$(CO)$_5$PR$_3$, $\text{W}$(CO)$_5$($\text{PR}_3$)$_2$, and perhaps facial or meridional trisubstituted products as well. A preferable approach would be to first prepare W(CO)$_5$thf by photolysis of W(CO)$_6$ and then without isolation of this complex, displace the thf with the phosphine in a subsequent room-temperature reaction:

$\text{W}$(CO)$_5$ + thf $\xrightarrow{\text{actinocene, } \text{An} = \text{actinide metal).}}$ $\text{W}$(CO)$_5$thf + CO

$\text{W}$(CO)$_5$thf + PR$_3$ $\rightarrow$ $\text{W}$(CO)$_5$PR$_3$ + thf

Tetrahydrofuran is a sufficiently poor ligand that it seldom displaces more than one CO group in the photolysis step and thus the reaction yields the monosubstituted product exclusively.

Another twist is to add Me$_2$NO which attacks the carbon of a coordinated CO, leading to eventual loss of CO$_2$ and formation of an unstable trimethylamine complex. The phosphine easily displaces the amine to form the final product:

$\text{OC}_2\text{H}_4\text{W}$(CO)$_5$ + $\text{Me}_2\text{NO}$ $\rightarrow$ $\text{CO}_2$ + $\text{Me}_2\text{NCO}$ + $\text{OC}(\text{CO})_2\text{PR}_3$ + $\text{OC}(\text{CO})_2\text{Me}_2\text{N}$ \(^{18}$

The preparation of pure Fe(CO)$_5$PR$_3$ and trans-Fe(CO)$_5$PR$_2$O have long been frustrating because thermal and photolytic methods give mixtures of products which are not easy to separate. The monosubstituted complex may now be prepared by several routes, one of which involves cobalt(I) chloride as a catalyst:

$\text{Fe}$(CO)$_5$ + PR$_3$ $\rightarrow$ $\text{Fe}$(CO)$_5$PR$_3$ + CO

The exact role of the catalyst in this reaction is unknown.\(^{132}\) Alternatively, the reaction may be catalyzed by polyaluminum inorganic anions, such as $\text{[Fe(CO)]}_{n}^-$ or $\text{[Fe(CO)]}_{n}^-$.
Fig. 15.55 Observed (a) and simulated (b) variable temperature proton NMR spectra of Os(CO)$_3$(η$^2$CH$_2$CH$_3$C≡CCH$_3$CH$_2$). The spectrum at -65 °C, characteristic of two equivalent ABX$_2$ spin systems, is produced when the movement of the alkyn in the metal surface is slowed sufficiently that it is fixed in one position on the NMR time scale. At +82 °C the alkyn molecule is moving rapidly on the metal surface giving an averaged spectrum in which all methylene protons are equivalent. [From Rosenberg, E.; Bracker-Novak, J.; Gellert, R. W.; Alme, S.; Gobetto, R.; Osella, D. J. Organomet. Chem. 1999, 565, 183-187. Reproduced with permission.]

methylene protons, which are diastereotopic and therefore nonequivalent). As the temperature is increased, the multiplet signals broaden and collapse into a single quartet as a result of the free movement of the alkyn. By simulating the observed spectra (Fig. 15.55b), it was possible to determine rate constants and an energy of activation (60 ± 2 kJ mol$^{-1}$) for the process.

A different type of dynamic process involving a polymeric metal system has been identified in [(CH$_3$)$_2$C=C(CH$_3$)$_2$Ru$_4$S$_4$]$^{2-}$, which has a distorted cubane-like structure with three Ru--Ru bonds in the crystalline state (Fig. 15.56). By following its methyl and ring proton resonances over a temperature range from +70 to -43 °C (Fig. 15.57), the complex is shown to undergo a dynamic process involving the metal-metal bonds. At the low-temperature limit, the spectrum contains features predicted for the static structure: two lines of equal intensity for the methyl protons.
A successful method for producing the trans disubstituted complex is to create $[\text{HFe(CO)}_3]^-$ and allow it to react with PR$_3$ in refluxing ethanol.$^{134}$

\[
\text{Fe(CO)}_3^{\text{trans}} \rightarrow \text{Fe(CO)}_2^+ \text{C} \text{H} \text{Fe(CO)}_3^- + \text{CO} \quad (15.94)
\]

\[
[\text{HFe(CO)}_3]^+ + 2\text{PR}_3 + \text{BuOH} \rightarrow \text{trans-Fe(CO)}_3(\text{PR})_3 + \text{CO} + \text{H}_2 + \text{BuOH}^+
\]

(15.95)

The counting is quite important to the outcome of this reaction. Ion pairs, which form between alkali metal ions and the complex, induce CO lability which aids in the substitution process.$^{133}$ Large charge-delocalized cations such as PPN$^+$ are much less effective in forming ion pairs. The substitution process shown in Eq. 15.95 occurs readily when the counterion is Na$^+$ but fails when it is PPN$^+$. Another good example of this effect can be seen by comparing Na[Co(CO)$_4$]$_2$ and PPN[Co(CO)$_4$].$^{133}$ The former is readily substituted by $^{13}$CO, phosphines, and phosphites, while the latter is inert with respect to substitution.

**Ligand Cone Angles**

It is intuitively obvious that the space occupied by a ligand can influence not only how many will fit around a metal atom but also the effectiveness of overlap between metal and ligand orbitals. If ligands are too crowded, repulsion between them forces metal-ligand distances to increase, weakening the metal-ligand bond, and enhancing the overall lability of the complex. Though steric effects have been long discussed in the literature, only after Tolman introduced the concept of the cone angle in 1970 did inorganic chemists have a quantitative means of expressing these ideas.$^{135}$ It should be clear that for a ligand such as Ph$_3$P, the C–P–C bond angle does not give a satisfactory measure of its space requirements. It is the volume of space taken up by the three phenyl groups on phosphorus that is crucial and a simple bond angle does not reflect this information. From a study of zerovalent nickel complexes, Na$_2$L$_2$(L = phosphine or phosphite), Tolman observed that the binding ability of a ligand depended strongly on its steric needs. He concluded that he needed a way of measuring the cone created by the phosphorus ligand. Not all good ideas require an expensive piece of equipment. With a block of wood, a nail, a space-filling model of each ligand, and a protractor for measuring angles, he was able to do what was required. The measuring device is shown in Fig. 15.46a and the cone angle, defined as the apex angle of a right cyclindrical cone, is outlined in Fig. 15.46b. The distance from the center of the phosphorus atom to the tip of the cone, 228 pm, was chosen on the basis of the nickel-phosphorus bond distance. Cone angle values for a number of ligands are shown in Table 15.10.

Ligands such as CO are sterically undemanding and as many as required by the 18-electron rule can easily arrange themselves around a metal atom. When bulky phosphines are part of the coordination sphere, however, it becomes increasingly difficult to satisfy the 18-electron rule simply because there is not enough space for the required number of ligands. It is not difficult to replace three CO groups of Mo(CO)$_6$ with three phosphines having modest cone angles. When PPh$_3$, which has a cone angle of 160°, is chosen, however, it is only possible to replace three CO groups with two phosphines. The result is that a 18-electron species is sterically stabilized. We saw earlier (Eq. 15.31), that H$_2$ may be added to Mo(CO)$_5$(PR)$_3$ to give an 18-electron complex, and this illustrates an important point, namely that complexes containing bulky ligands may have vacant coordination sites, but they are available to only the smallest donors. Often this idea can be used to advantage in designing syntheses for organometallic complexes.

A further example of large ligands blocking out smaller ones to give low coordination numbers is provided by the work of Otsuka.$^{136}$ Phosphines with small cone angles such as PEt$_3$ (122°) allow isolation of [H(Mo(CO)$_5$)$_2$]$_2$, which obeys the 18-electron rule, but ligands with cone angles greater than 160° make it possible to isolate complexes with just two ligands, e.g., PPh$_3$ [H(Mo(CO)$_5$)$_2$]$_2$. It is also observed that bulky ligands avoid being cis to one another.$^{141}$ In a series of octahedral WC(O)$_2$L$_2$ (L = phosphine) complexes, the percentage of trans isomers isolated from a substitution reaction increases as the cone angle of the phosphine increases (Table 15.11). Electronic factors favor cis arrangements, but steric factors become dominant as the cone angle increases. Attempts to synthesize Fe(CO)$_3$(PR)$_3$ have failed because the large cone angle of the phosphine ligand prevents coordination of more than one of them.

One of the most important classes of reactions in organometallic chemistry is oxidative addition. In these reactions a coordinately unsaturated complex in a relatively low oxidation state undergoes a formal oxidation by two units (loss of two

---

139 The recent synthesis of [Ph$_3$P]$_2$[U(μ-η:η:η:η)]$_2$(H) and (H) shows that a coordination number of 2 may be induced with somewhat smaller cone angles (PPh$_3$, 145°).
Fig. 15.52 Proton NMR spectra of (η⁵-C₅H₅)₂(η⁵-C₅H₅)₂Ir from -27 to +62 °C. The separate resonances observed at low temperature for the two types of Cp rings gradually broaden and collapse, giving a single line at 62 °C. [From Cotton, F. A. In Dynamic Nuclear Magnetic Resonance Spectroscopy; Jeckson, L. M., Cotton, P. A., Eds.; Academic: New York, 1975; Chapter 10. Used with permission.]

Fig. 15.53 Migration of iron in terracarbonyltricarbonylalleneiron(0).

In organometallic clusters, ligands frequently appear to move over the surface of the metal framework. The iridium complex, Os₃(CO)₁₂H₂-CH₂CH=CH₂, in Fig. 15.54 provides an example in which the alkynyl moves over the face of the metal triangle at elevated temperatures but remains fixed at low temperatures. Variable temperature proton and carbon NMR studies show that the alkynyl movement is accompanied by exchange of the bridge and terminal carbonyl ligands. In addition, axial and radial carbonyl groups are undergoing exchange. The variable temperature proton NMR spectra are shown in Fig. 15.55a. At -65 °C we see a spectrum characteristic of two equivalent Al₂X₃ spin systems (the AB spins are the...
Table 15.10

<table>
<thead>
<tr>
<th>L</th>
<th>α</th>
<th>L</th>
<th>α</th>
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<td>P(μ-CF₃C₆H₄)₂</td>
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<td>PhHPhH</td>
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Equation 15.99:

ML₂ + X—Y \(\rightarrow\) L₂M X—Y

Equation 15.100:

ML₂ + O₂ \(\rightarrow\) L₂M O₂

Table 15.11

<table>
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<tr>
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</tr>
<tr>
<td>PhH</td>
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<td>100</td>
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* Lubert, C. M. Fundamental Transition Metal Organometallic Chemistry, Brooks/Cole: Monterey, CA, 1993. For all but PhH-Phi, which is from the authors' laboratories. (impal = Me₂N(CH₂)₃NMe₂)
**Time scales for structural techniques**

<table>
<thead>
<tr>
<th>Technique</th>
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<tr>
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</tr>
<tr>
<td>Neutron diffraction</td>
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</tr>
<tr>
<td>X-ray diffraction</td>
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</tr>
<tr>
<td>Ultraviolet</td>
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<td>Visible</td>
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<tr>
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<td>Electron spin resonance</td>
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<tr>
<td>Nuclear magnetic resonance</td>
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<td>Quadrupole resonance</td>
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<td>Mössbauer (iron)</td>
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<td>$10^{-3}$ to $10^{-2}$</td>
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<tr>
<td>Experimental separation of isomers</td>
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</table>

*Time scale depends on chemical system under investigation.*

---

**Table 15.12**

**Spectroscopic methods using ultraviolet, visible, or infrared light are generally much faster than molecular vibrations or interconversions, and the spectra reflect weighted averages of the species present (cf. the broad absorption bands in the visible spectra of transition metal complexes, Chapter 1). The remaining spectroscopic methods are slower, and the time period of the interaction may be compared to that of the lifetimes of individual molecular configurations. The nature of interconversions between configurations can be studied by such techniques.**

Nuclear magnetic resonance techniques have proved to be particularly valuable in the study of fluxional molecules. The most common experimental procedure involves analyzing the changes in NMR line shapes that occur with variations in temperature. The simplest dynamic process is one involving two molecular configurations that have equal probability. If the interconversion process between them is slow on the NMR time scale, as might be the case at a low temperature, two separate sets of equal-intensity resonances, one for each configuration, will be observed in the spectrum. If we can raise the temperature of the sample sufficiently so that the process becomes rapid on the NMR time scale, the result will be a single set of spectral lines, and they will appear at the midpoint of the two sets observed at lower temperature. At this high-temperature limit, the molecule is undergoing changes so rapidly that NMR cannot distinguish the two separate molecular configurations, only an average. As an example of a system of this type, consider $[n]_1 \cdot \mathrm{C}_2 \mathrm{H}_2 \cdot [n]_2 \cdot \mathrm{C}_2 \mathrm{H}_2 \cdot [n]_3$. The crystal structure of the molecule shows two monohapto and two pentahapto cyclopentadienyl rings. At $62^\circ C$, the NH NMR spectrum consists of a single line (Fig. 15.51), consistent with a dynamic process that renders the four ligands equivalent. As the temperature is lowered, the signal broadens and gradually splits into two lines which sharpen into equal-intensity singlets at $27^\circ C$. At this point, the process which interconverts monohapto and pentahapto ligands is occurring slowly enough that both conformations are observable in the spectrum. However, even at this temperature, the monohapto rings are involved in a dynamic process that averages the signals for the three types of ring protons. Instead of separate resonances in a $1:2:2$ ratio, only a single fairly sharp line is observed due to rapid migration of the metal from one site to another within each ring. When the temperature is decreased further, this process also is slowed so that the peak for the monohapto ligands broadens and then collapses, eventually remerging in the expected pattern for three nonequivalent ring protons at $-80^\circ C$. Similar NMR behavior has been observed for $[\mathrm{C}_2 \mathrm{H}_2 \cdot \mathrm{Sc}]_3$, showing that at $30^\circ C$ an $m$-exchange occurs between two $\pi$ and one $\eta^1$ ring. Separate peaks in a $2:1$ ratio for the two types of rings are observed at $-30^\circ C$, with individual resonances for the monohapto ring protons becoming apparent as the temperature is decreased further.

Fluxional processes involving acyclic unsaturated hydrocarbon ligands, such as alkenes and alkenes, are also common. For the $m$-complex formed between trimethylsilane and tetracarbonyliron (Fig. 15.53), the proton magnetic resonance spectrum below $-60^\circ C$ shows three peaks in the ratio $1:2:2$, representing the three $\pi$ hydrogen atoms, three trans hydrogen atoms, and six hydrogen atoms in a plane perpendicular to the carbon-iron bond. With an increase in temperature, the spectrum collapses to a single line (Fig. 15.52). consistent with a dynamic process that renders the four ligands equivalent. As the temperature is lowered, the signal broadens and then collapses, eventually remerging in the expected pattern for three nonequivalent ring protons at $-80^\circ C$. Similar NMR behavior has been observed for $[\mathrm{C}_2 \mathrm{H}_2 \cdot \mathrm{Sc}]_3$, showing that at $30^\circ C$ an $m$-exchange occurs between two $\pi$ and one $\eta^1$ ring. Separate peaks in a $2:1$ ratio for the two types of rings are observed at $-30^\circ C$, with individual resonances for the monohapto ring protons becoming apparent as the temperature is decreased further.

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---


d^4 to d^6 (with formal loss of two electrons), the relative stability of coordination number 4 compared to 5 or 6, and the strength of new bonds created (M—X and M—Y) relative to the bond broken (X—Y) all must be considered. Oxidation of the metal is easier for electron-rich systems than for electron-poor ones; hence oxidative addition is more likely for low-valent metals. The ease of oxidation increases from top to bottom within a triad [Co(I) < Rh(I) < Ir(I)] and the tendency toward five-coordination decreases from left to right across a transition series [Os(II) > Ir(III) > Pd(II)].

Cleavage of the H—H bond by transition metal complexes suggests that similar reactions may be possible with C—H and C—C bonds. In fact it has been shown for a number of years that coordinated triphenylphosphine can undergo intramolecular cyclometallation.

\[
\begin{align*}
\text{(Ph3P)2FeCl} & \rightarrow \text{(Ph3P)2FeCH} \\
\text{(CH3O)2P} & \rightarrow \text{(CH3O)2P} \\
\text{Fe} & 
\end{align*}
\]

This reaction is also called orthometallation because it is the ortho carbon of the phenyl group that participates. Although most common with phenyl groups of phosphines or phosphites, examples involving alkyl groups are also known.

The recognition that H—H is capable of nonclassical coordination to a metal, which may be regarded as an interaction involving incomplete rupture of the H—H bond, was preceded by the discovery that C—H bonds can interact with metal atoms without bond cleavage. It was first observed that in the structures of some complexes a hydrogen atom attached to a phenyl ring was abnormally close to the metal atom. This was viewed at the time as a form of hydrogen bonding. A subsequent neutron diffraction study of \[
\text{[Fe(Ti\text{H}_3Cl)}_3\text{]}(\text{POMe}_3)_2
\]
revealed a strong C—H • • • Fe interaction.

Studies of a number of polymetallic complexes also provided evidence for C—H coordination. Particularly notable was a beautiful NMR study by Calvert and Shapley of a trisodium complex, which was shown to exist as an equilibrium mixture of two structures, one of which included a C—H—Os linkage.

The preceding examples of C—H coordination are all intramolecular in nature. Of greater interest, especially with commercial goals in mind, are intermolecular reactions involving hydrocarbons. Functionalizing the alkane constituents of petroleum under mild conditions is a major challenge in organometallic chemistry and one that

Of added significance in this work was the fact that a methyl C—H bond is broken, which has positive implications for activation of alkanes by transition metals (page 694).

As more and more examples of a carbon-hydrogen bond acting as a ligand were confirmed, the term agostic was coined to describe the interaction. Agostic, as originally proposed, referred to "covalent interactions between carbon-hydrogen groups and transition metal centers in organometallic compounds, in which a hydrogen atom is covalently bonded simultaneously to both a carbon atom and to a transition metal atom." These interactions, like those of B—H—B and W—H—W (page 646), are currently described as three-center, two-electron bonds (see Chapter 14).

As with all other forms of ligand-metal coordination, an agostic interaction requires that a vacant coordination site be available and donation of C—H electron density to a metal contributes toward satisfaction of the 18-electron rule. The cation \[
\text{[Fe(Ti\text{H}_3Cl)}_3\text{]}(\text{POMe}_3)_2
\]
shown above, is an 18-electron system if one counts the C—H bonding pair of electrons. Structural tip-offs indicating the existence of an agostic interaction include C—H bond lengthening by 5-10% relative to a nonbridging C—H bond and M—H distances longer than a terminal M—H distance by 10-20%.

The term agostic has now been extended to generally include M—H—Y systems, in which Y may be B, N, Si, Cl, or F, as well as C. The structure of \[
\text{[FeBH}_3\text{]}(\text{PMMe}_3)_2
\]
reveals one bidentate BH_3 and two monodentate BH_3 ions, each of which possesses one B—H bond attached to titanium in a side-on, agostic manner.

The term agostic is derived from the Greek word *agostikos* and translates "to clasp, to draw towards, to hold to oneself." The term agostic is derived from the Greek word *agostikos* and translates "to clasp, to draw towards, to hold to oneself."
where RX is a halogen, alkyl halide, or hydrogen. In other words, oxidative addition leads to the formation of a metal–metal bond. Unlike the axial oxidative addition, two metal centers are involved simultaneously. The reverse reaction, reductive elimination, may also occur.

\[
\text{[M}_1\text{] Br} \rightarrow \text{[M}_1\text{] H} + \text{H}_2
\]

We can follow our suppositions regarding the formation of an M–M bond upon oxidative addition by watching the change in bond length:

\[
[\text{Pt}_4\text{(pop)}]^{2-} \rightarrow [\text{Br} - \text{Pt}_4\text{(pop)}\text{Pt} - \text{Br}]^{4-}
\]

The greater the overlap of the metal \( d_z^2 \) orbitals, the greater the repulsion in the reduced, \( d^8 \) state, and the stronger the metal–metal bond in the oxidized, \( d^6 \) state. We should expect oxidative addition to be least favored at very long metal–metal distances, and much more strongly favored at those distances corresponding to the normal metal–metal single bond distance, and this is what is found. Conversely, the longer distances favor the reverse, reductive elimination reaction. Indeed, with some bimetallic complexes reversible addition/elimination of \( \text{H}_2 \) can be accomplished, not with molecular dihydrogen, but with a hydrogen donor molecule such as a secondary alcohol:

\[
\text{Me}_2\text{CHOH} + \text{M}_2^+ \rightarrow \text{Me}_2\text{C}=\text{O} + \text{H}^+ + \text{M}^+ + \text{H}^+
\]

Although the reaction in Eq. 15.196 is potentially catalytic, true catalysis has rarely been achieved. However, when \( \text{M}_2^+ \) is \( [\text{Pt}_4\text{(pop)}]^{2-} \), solar-driven catalytic oxidation has been observed. In monomeric \( \text{Pt}(II) \) complexes the HOMO–LUMO transition occurs in the UV region with a peak in the violet. The complex has a yellow, or perhaps yellowish, color. The interaction present in bimetallic complexes, as shown in Fig. 15.50, narrows the HOMO–LUMO gap such that this transition may be shifted into the visible region. The electron may thus be excited by solar radiation:

\[
[\text{Pt}_4\text{(pop)}]^{2-} \rightarrow [\text{Pt}_4\text{(pop)}]^{4+}
\]

The excited diphosphorus complex is now predisposed to react further. The incipient Pt–Pt bond is partially formed and addition of hydrogen is enhanced:

\[
[\text{Pt}_4\text{(pop)}]^{4+} + \text{Me}_2\text{CHOH} \rightarrow [\text{H} - \text{Pt}_4\text{(pop)}\text{Pt} = \text{H}]^{+} + \text{Me}_2\text{C}=\text{O}
\]

Reductive elimination of dihydrogen may then take place to complete the catalytic cycle:

\[
[\text{H} - \text{Pt}_4\text{(pop)}\text{Pt} = \text{H}]^{+} + \text{Me}_2\text{C}=\text{O}
\]

In addition to converting secondary alcohols into ketones, the platinum catalyst also converts toluene and other benzyl hydrocarbons into dimers. The complexes between \( [\text{Ru(bpy)}]^{2+} \) (discussed in Chapter 13) and \( [\text{Pt}_4\text{(pop)}]^{2-} \) are catalytically convert water to hydrogen and oxygen. The excited state platinum complex, \( [\text{Pt}_4\text{(pop)}]^{2+} \), can catalytically convert water to hydrogen and oxygen. The excited state platinum complex, \( [\text{Pt}_4\text{(pop)}]^{2+} \), can catalytically convert secondary alcohols to hydrogen and ketones. An important difference, however, is that the ruthenium excited state species results from the transfer of an electron from the metal to a bpy ligand, while in the platinum excited state species the two unpaired electrons are metal centered. As a consequence, platinum reactions can occur by inner sphere mechanisms (as axially coordinated), a mode of reaction not readily available to the 18-electron ruthenium complex.

Chemists are prone to think in terms of static molecular structures. This viewpoint is initiated by stick-and-ball models and reinforced by regular inspection of molecular structures determined by "instantaneous" methods such as X-ray diffraction. In fact many molecules are stereochemically nonrigid. If the rearrangement leads to configurational isomers which are chemically equivalent, we say that the molecule is fluxional. On the other hand, if the rearrangement gives rise to chemically distinguishable molecules, we simply say that the molecule has undergone a chemical reaction.

Fluxional molecules differ from stereochemically nonrigid molecules in possessing more than a single conformation representing an energy minimum. Several such minima may be present and may be accessible with ordinary thermal energies. As a very simple example, consider symmetric and unsymmetric hydrogen bonds (Chapter 8). If in the symmetric \( \text{H} - \text{F} \) bond the fluorine atoms are considered relatively immobile with respect to each other, the motion of the latter can be considered to be a vibration in a potential well with an average position midway between the fluorines (Fig. 15.51a). In contrast, unsymmetric hydrogen bonds possess two potential wells in which the hydrogen can vibrate (Fig. 15.51b), occasionally being sufficiently excited thermally to jump to the other well. In such a system the hydrogen would be found in one potential well or another by rapid methods such as diffraction.

---

\[\text{Me}_2\text{CHOH} + \text{M}_2^+ \rightarrow \text{Me}_2\text{C}=\text{O} + \text{H}^+ + \text{M}^+ + \text{H}^+\]

\[\text{Me}_2\text{CHOH} + \text{M}_2^+ \rightarrow \text{Me}_2\text{C}=\text{O} + \text{H}^+ + \text{M}^+ + \text{H}^+\]

---

202 Obviously a structure is not determined instantly with X-ray diffraction techniques. Rather the structure is instantaneous in the sense that the same period over which the diffraction waves intersect with the electrons of the molecule is insufficiently short with respect to the frequency of atomic motions.
203 This definition includes all stereochemically nonrigid molecules having identical energy minima and configurations at these minima including molecules such as the pseudooctahedral \( \text{Fe}_6\text{S}_8 \) and \( \text{Fe}_6\text{S}_8\text{O}_{2}\text{C} \) (Chapter 6).
204 For simplicity's sake, both potential wells are shown to be the same depth. In general for a hydrogen bond such as \( \text{O} = \text{H} \rightarrow \text{N} \) this is not true. All of the configurations of a truly fluxional system are energetically equivalent, however, and have equivalent potential wells.
has received a great deal of attention during the past decade. As you know from courses in organic chemistry, alkanes are quite unreactive and their inertness is attributed to high C—H bond energies (typically about 400 kJ mol⁻¹). A plausible sequence for functionalizing hydrocarbons begins with coordination of an alkane:

\[
L_M + R - C - H \rightarrow L_M + \text{hydrocarbon derivatives}
\]

Eq. 15.103 shows formation of a three-center, two-electron bond, presumed to be a first step in C—H activation. The next step (Eq. 15.104) completes the oxidative addition of the alkane to the metal. The process may be thought of as insertion of the metal into the C—H bond. Further reaction with a functionalizing reagent gives the desired organic product (Eq. 15.105). An ultimate goal is to accomplish this process catalytically.

In 1982, Janowicz and Bergman at Berkeley and Hoyano and Graham at Alberta reported the first stable alkane intermolecular oxidative addition products. The Alberta group photolyzed \( \text{Pd} - \text{Me}_3\text{C}_5\text{J}_2\text{R} \) with the loss of H₂, while the Alberta group photolyzed \( \text{Pd} - \text{Me}_3\text{C}_5\text{I}_2\text{R} \) with the loss of CO to give highly reactive iridium intermediates which cleave C—H bonds in alkanes:

\[
\begin{align*}
L_M + R - C - H & \rightarrow L_M + \text{hydrocarbon derivatives} \\
\text{Me}_3\text{C}_5\text{H} & + \text{H}_2 \quad \text{(15.106)} \\
\text{Me}_3\text{C}_5\text{H} & + \text{CO} \quad \text{(15.107)}
\end{align*}
\]

Even methane, under the right experimental conditions, can be activated by an organometallic complex. This is particularly important not only because methane is one of the most abundant hydrocarbons but also because its C—H bond is the strongest among the alkanes (434 kJ mol⁻¹). Success in activating this molecule suggests that all alkane activation barriers are surmountable. The first homogeneous (solution) reaction between methane and an organometallic complex was reported in 1983 and described the exchange of \( \text{H}_2 \) for \( \text{CH}_3 \):

\[
 \text{Me}_3\text{C}_5\text{H} + \text{H}_2 \rightarrow \text{Me}_3\text{C}_5\text{H} + \text{CH}_3 \quad \text{(15.108)}
\]

Somewhat similar reactions with \( \text{Me}_3\text{C}_5\text{H} \) and \( \text{Me}_3\text{C}_5\text{H} \) have also been investigated. It is likely that neither of these two reactions proceeds by oxidative addition because lutetium and thorium are in high oxidation states in the reactants. The activation of methane in solution by an organometallic complex presents some experimental difficulties because any solvent that is likely to be chosen will be more reactive than methane. In addition, insolvability of the complex in liquid methane may preclude reaction with the pure hydrocarbon. These problems were overcome in the case of the reaction of \( \text{CH}_4 \) with the iridium complex of Eq. 15.106 by taking advantage of the fact that the desired hydroxyl methyl complex is thermodynamically more stable than other hydroxyl alkyl complexes. The methyl complex was produced by first creating a hydroxyl cacyclohexyl complex and then allowing it to react with methane.

\[
\text{Me}_3\text{C}_5\text{H} + \text{H}_2 \rightarrow \text{Me}_3\text{C}_5\text{H} + \text{CH}_3 \quad \text{(15.109)}
\]

The reaction \( \text{Me}_3\text{C}_5\text{H} + \text{H}_2 \) represents the presumed reactive intermediate that forms when \( \text{Me}_3\text{C}_5\text{H} \) reacts with the pure hydrocarbon. Another complex to which methane, as well as other hydrocarbons, will oxidatively add is (bis(dicyclohexylphosphino)platinum)chloride.

\[
\begin{align*}
R & + \text{CH}_3 \rightarrow R - \text{CH}_3 \\
& \quad \text{(15.110)}
\end{align*}
\]

The very electron-rich, two-coordinate, 14-electron platinum reactant was not spectroscopically observed, but its existence was inferred from the reaction products. Oxidative addition reactions lead to products that appear to have had a metal atom inserted into a bond, but the term insertion has generally been reserved for reactions which do not involve changes in metal oxidation state. These reactions are enormously important in catalytic cycles (see page 705). Special emphasis in this section

where \(-\) represents the lone pair on the ligating carbon atom. Note that the system must be linear throughout the \(C-N=C-M\) system. We thus have four \(R-C-N=C\) groups on each metal spaced by \((CH_2)_n\) bridges which may vary in length depending upon \(n\).

A second type of bidentate ligand holding the two metal atoms close together is pyrophosphate. It forms from diphosphorous ("pyrophosphorous") acid and, because of the \(P-O-P\) linkage, is often abbreviated "\(pop\)".

Coordination of the pyrophosphate occurs through the phosphorus, which is preferred over the harder oxygen by the soft Pt(II) ion. Thus there is a tautomeric relationship analogous to that in phosphorous acid:

\[
\text{OH} \quad \text{P} \quad \text{OH} \quad \text{(15.192)}
\]

The formulation of the tetakis(\(\mu\)-diphosphito)diplatinate(II) ion is thus \([\text{Pt}(\text{pop})_2]-\). The metal in these complexes is ideally a \(d^8\) species such as Ir\(^{III}\) or Pt\(^{II}\). The van der Waals radii of these metals (Table 8.1) are about 350 pm, so we should expect metal-metal interaction to begin at about this distance and become more significant as the distance decreases. What will this interaction consist of?

Figure 15.50 illustrates the energy levels of a \(d^8\) square planar complex together with the interaction of two filled \(d_{z^2}\) and two empty \(p_z\) orbitals on adjacent metal atoms. As the distance between the two metal atoms decreases, the orbitals along the \(z\) axis will interact more strongly with each other. For both the \(d_{z^2}\) orbitals and the \(p_z\) orbitals, this will give rise to a bonding and an antibonding interaction. Since the \(d_{z^2}\) orbital gives rise to the HOMO and the \(p_z\) orbital to the LUMO, this will decrease the HOMO-LUMO gap with interesting consequences (see below). More important for the present discussion, the increase in energy for the HOMO will destabilize the molecule and make it more reactive. Another way of looking at this enhanced reactivity is to say that if the two electrons were removed from the antibonding \(d_{z^2}\) HOMO, there would be an M-M single bond, stabilizing the molecule. One way to remove the two HOMO electrons without costing energy—indeed, by providing further energy that actually drives the reaction—is to form two new bonds with them.

\[
\text{RX} \quad \text{M} \quad \text{M} \quad \text{RX} \quad \text{(15.193)}
\]
will be given to the insertion of carbon monoxide into a metal-carbon bond and to the
insertion of ethylene into a metal-hydrogen bond.
A classic example of a CO insertion reaction (called migratory insertion for
reasons to be explained later) is found in the work of Noack and Calderazzo. The
reaction of $^{15}$CO with $\text{CH}_3\text{Mn(CO)}_5$ yields $\text{CH}_3\{(\text{CO})_3\text{Mn(CO)}(\text{CO})_4$ as the ex-
clusive product. None of the tagged CO is found in the acetyl group, which establishes
that the reaction is not an intermolecular insertion, i.e., no reaction occurs between
gaseous CO and the M—C bond. Furthermore, none of the $^{15}$CO ends up trans to the
acetyl group. This is an extremely important observation because it establishes that
the CO ligands in the product do not scramble to give a statistical distribution. In other
words, the outcome of the reaction is kinetically, not thermodynamically, controlled.
Although this is an important result, it does not allow a firm distinction to be made
between CO insertion and methyl migration since the product would be the same for
either mechanism. However, additional mechanistic information can be gained by
studying the reverse reaction, i.e., decarbonylation of $\text{CH}_3\{(\text{CO})_3\text{Mn(CO)}(\text{CO})_4$. This result has been
further supported by carbon-13 NMR.

The CO of the acetyl ligand has a choice of four cis positions into which it may
shift, displacing the CO that is already there. One of these positions is occupied by $^{15}$CO.
Thus we would predict that 25% of the product would have no $^{15}$CO and the other 75% would have a $^{15}$CO ligand cis to the methyl group. Experimentally it is found that 25% of
the product is devoid of tagged CO. 25% of the product has $^{15}$CO trans to CH$_3$, and
50% of the product has $^{15}$CO cis to CH$_3$. Therefore CO insertion must be eliminated as
a mechanistic possibility. A methyl migration mechanism, however, is consistent with
these experimental results.

At first glance, these two processes may seem to be indistinguishable. However,
careful consideration of the results of the infrared study will reveal otherwise. The
reaction of $^{15}$CO with $\text{CH}_3\text{Mn(CO)}_5$ yields $\text{CH}_3\{(\text{CO})_3\text{Mn(CO)}(\text{CO})_4$ as the ex-
clusive product. None of the tagged CO is found in the acetyl group, which establishes
that the reaction is not an intermolecular insertion, i.e., no reaction occurs between
gaseous CO and the M—C bond. Furthermore, none of the $^{15}$CO ends up trans to the
acetyl group. This is an extremely important observation because it establishes that
the CO ligands in the product do not scramble to give a statistical distribution. In other
words, the outcome of the reaction is kinetically, not thermodynamically, controlled.
Although this is an important result, it does not allow a firm distinction to be made
between CO insertion and methyl migration since the product would be the same for
either mechanism. However, additional mechanistic information can be gained by
studying the reverse reaction, i.e., decarbonylation of $\text{CH}_3\{(\text{CO})_3\text{Mn(CO)}(\text{CO})_4$. This result has been
further supported by carbon-13 NMR.

The validity of this mechanism has been demonstrated for a number of "CO
insertion" reactions. Thus when chemists use the term CO insertion, they usually
mean alkyl migration. Several things to keep in mind when considering a reaction of
this type are (1) it involves ligands which are cis to one another, (2) in the course of the
reaction a vacant coordination becomes available, and (3) the reverse reaction cannot
occur unless a ligand is first eliminated.

A chiral metal center, as is found in a pseudotetrahedral iron complex with
cyclopentadienyl, carbonyl, triphenylphosphine, and ethyl ligands, has also been used
to address the question of alkyl migration versus carbonyl insertion. Inversion of
One of the great discoveries of organometallic chemistry was the catalyzed polymerization of alkenes at atmospheric pressure and ambient temperature. Vast quantities of polyethylene and polypropylene (over 15 million tons annually) are made by Ziegler-Natta catalysis. Ziegler and Natta received the Nobel prize in chemistry in 1963, and the importance of their work in stimulating interest in organometallic chemistry should not be underestimated.

The Ziegler-Natta catalyst, which is heterogeneous, is made by treating titanium tetrachloride with triethylaluminum to form a fibrous material that is partially alkylated (Et₃AlCl is used as a cocatalyst). Third generation catalysts (introduced about 1980) use a MgCl₂ support for the TiCl₄. The titanium does not have a filled coordination sphere and acts like a Lewis acid, accepting ethylene or propylene as another ligand. The reaction is thought to proceed somewhat after the manner of Wilkinson's catalysts discussed above except that the alkyl group (instead of a hydrogen atom) migrates to the alkene:

\[
\text{CH}_2=\text{CH}_2 \xrightarrow{\text{Tl, } \text{Et}_3\text{AlCl}} \text{CH}_2=\text{CH}_2
\]

The heterogeneous nature of the reaction makes it a difficult one to study, but it has been modeled homogeneously with a lutetium complex which undergoes oligomerization:

\[
(\text{L}^2\text{MeC}_3\text{LuCH}_3 \xrightarrow{\text{HCl}} \text{CH}_2=\text{CH}_2 \xrightarrow{\text{HCl}} \text{CH}_2=\text{CH}_2)
\]

Since homogeneous catalysts tend to offer fast reaction with high selectivity and heterogeneous catalysts offer ease of separation, it is not surprising that efforts have been made to combine the advantageous properties of both. One way to effect this combination is to attach the "homogeneous" catalysts to the surface of a polymer such as polystyrene. Wilkinson's catalyst, for example, can be treated as follows:

\[
\text{CH}_2=\text{CH}_2 \xrightarrow{\text{Tl, } \text{Et}_3\text{AlCl}} \text{CH}_2=\text{CH}_2
\]

A Photodehydrogenation Catalyst ("Platinum Pop")

We have seen in Chapter 11 that the \(d^9\) square planar configuration is particularly stable because four of the mostly metal \(d\) molecular orbitals are stabilized relative to the \(d_{x^2-r^2}\)-derived orbital. Three of the four orbitals (\(d_{x^2}, d_{y^2}\), and \(d_{z^2}\)) may participate in metal-ligand \(\sigma\) bonding, but to a first approximation, the \(d_{x^2-r^2}\) orbital does not interact with any other orbitals in an isolated square planar complex. Suppose, however, we configure the complex so that the \(d_{x^2-r^2}\) is forced into interaction. By bridging two square planar complexes, the two systems are forced to lie parallel (face-to-face) at a fixed distance:

Many possible ligands could span the distance, but if we carefully design the bridge, we can control this metal-metal distance to some extent. Two types of ligands that have been extensively studied are isocyanides and pyrophosphite. Consider, for example, isocyanide ligands of the type:

\[
\text{R}_2\text{C} = \text{N} = \text{C} = \text{R}
\]

Since the \(d_{x^2-r^2}\) orbitals do have some electron density in the \(xy\) plane, there is some interaction with the \(x\) and \(y\) ligands.

configuration is expected for ethyl migration, but retention is expected for carbonyl insertion.\(^\text{155}\)

\[
\text{alkyl migration (inversion of configuration)}
\]

\[
\text{CO insertion (retention of configuration)}
\]

When this reaction is carried out in nitromethane, inversion of configuration is observed, consistent with ethyl migration. In some solvents both stereochemical products are obtained, which may mean that both pathways are operative or that chiral integrity is lost in the intermediate step.

At this point it is fair to ask, what is the driving force for carbonyl insertion? These reactions involve breaking a metal-carbon bond and formation of a carbon-carbon bond. In addition, a bond is formed between the metal and the incoming Lewis base (CO in the foregoing examples, but frequently a phosphine or an amine). The enthalpy change, \(\Delta H\), for the reaction

\[
\text{Mn(CO)}_5\text{CH}_3 + \text{CO} \rightarrow \text{Mn(CO)}_5(\text{COCH}_3)
\]

has been calculated as \(-54 \pm 8 \text{ kJ mol}^{-1}\).\(^\text{156}\) The less energy required to break the M—R bond and the more energy released when the C—C and M—CO bonds are formed, the more favorable will be the reaction. Since gaseous CO is captured, it would be expected that the entropy change would inhibit spontaneity, but even so, the larger negative enthalpy term is dominant. Insertions are not always thermodynamically favorable, however, as is illustrated by the absence of reaction when Mn(CO)_5H is subjected to CO.

\[
\text{Mn(CO)}_5\text{H} + \text{CO} \rightarrow \text{Mn(CO)}_5(\text{COH})
\]

The calculated enthalpy change for this reaction is approximately 20 kJ mol\(^{-1}\). This result is of considerable consequence because it suggests that reduction of CO with a transition metal hydride is not a useful route to organic products (see Fisher-Tropsch catalysis, page 715).

The organometallic chemistry of actinides, ignored in the early development of the field, is currently receiving a great deal of attention.\(^\text{157}\) In many instances the chemistry of this group of elements is unlike that of the transition metals. For example, it has been shown that a thorium hydride, in contrast to the manganese hydride shown above, does undergo CO insertion.\(^\text{158}\)

\[
(\text{\textsuperscript{5}C}_5\text{H}_5)\text{Th} + \text{CO} \rightarrow (\text{\textsuperscript{5}C}_5\text{H}_5)\text{Th-C-C} \quad \text{OR}
\]

A driving force for this reaction is the strong interaction of the oxygen of the inserted CO with the thorium atom.

Of equal importance to carbonyl insertion into a metal-carbon bond is olefin insertion into a metal-hydrogen bond.

\[
\text{M—H} + \text{R}_2\text{C}=\text{CR}_2 \rightarrow \text{M-CR}_2\text{CR}_3\text{H}
\]

Catalytic hydrogenation and hydroformylation are just two of the many important processes in which these reactions are fundamental (see page 711). The first step in the reaction is coordination of the alkene to the metal, followed by rapid insertion into the M—H bond. The transition state involves a four-center planar structure.

The reverse of alkene insertion, \(\beta\) elimination, represents the chief pathway for decomposition of a transition metal alkyl complex (Eq. 15.45). The process begins with deinsertion of the alkyl ligand to yield a metal hydrido alkene complex, which then eliminates the alkene.\(^\text{159}\) The decomposition process can be thwarted by designing alkyl complexes in which \(\beta\) elimination is not possible either because the ligands have no hydrogens on carbon atoms to the metal [e.g., \(\text{PhCH}_2\text{CH}_3\), \(\text{CH}_3\text{CH}_2\text{CH}_3\), or \(\text{CH}_3\text{CCH}_3\)] or the \(\beta\) hydrogen is too far from the metal to allow deinsertion to occur (e.g., \(\text{C}=\text{CH}\)). Note also that \(\beta\) elimination cannot take place unless there is a vacant site for


Alcohols and alkanes are also primary products and are not shown in the simplified Eq. 15.182. The overall reaction is complicated and, as a result, its mechanism has been the subject of considerable debate. The reaction may be viewed as the reductive polymerization of carbon monoxide, with molecular hydrogen as the reducing agent. A variety of heterogeneous catalysts, such as metallic iron and cobalt on alumina, have been used. It is believed that carbon monoxide dissociates on the catalytic surface to give carbides and that these are in turn hydrogenated to give surface carbenes:

\[
\begin{align*}
\text{CO} & \rightarrow \text{C}^\text{II}, \\
\text{C}^\text{II} & \text{H}_2 \\
\text{CH}_3
\end{align*}
\]

(15.183)

Carbene insertion into a metal-hydrogen bond gives a methyl group that can undergo carbene insertion in a propagating manner:

\[
\begin{align*}
\text{H} & \text{CH}_2 \text{CH}_2 \text{CH}_2 \rightarrow \text{CH}_3 \text{CH}_2 \text{CH}_2 \rightarrow \text{CH}_3 \text{CH}_2 \text{CH}_2 \\
\text{CH}_2 & \text{CH}_2 \text{CH}_2 \text{CH}_2 \\
\text{etc.}
\end{align*}
\]

(15.184)

Although it is always somewhat risky to draw conclusions about surface reactions from solution experiments, a number of such studies support the carbide/carbene mechanism proposal. A model compound for the carbide proposal is a butterfly cluster formed from an unusual six-coordinate carbide:

\[
\begin{align*}
\text{Fe} & \text{C}^\text{II}
\end{align*}
\]

(15.185)

The exposed carbide carbon reacts successively with carbon monoxide and methyl alcohol:

\[
\text{Fe} \text{C}^\text{II}
\rightarrow \text{CO} \rightarrow \text{CH}_3 \text{OH}
\]

(15.186)

followed by hydrogenation to yield methyl acetate. Note that a carbon-carbon bond is formed in this reaction. The net synthesis produces an organic oxygenate from synthesis gas, which may also occur in the Fischer-Tropsch reaction.

Support for the propagation step of the Fischer-Tropsch reaction is provided by the homogeneous reaction:

\[
\text{CH}_3 \text{H} + \text{CH}_3 \text{H} \rightarrow \text{CH}_2 \text{CH}_2 \text{CH}_3
\]

(15.187)

The bridging carbones of the bimetallic complex, which parallel the surface carbones of the Fischer-Tropsch catalyst, are involved in C—C bond formation.

Both the Fischer-Tropsch reaction and the Mobil process enable one to convert synthesis gas into hydrocarbons. Since synthesis gas may be obtained from coal, we have in effect a means of converting coal to gasoline. Germany moved its Panzer Korps in World War II with synthetic fuels made from the Fischer-Tropsch reaction, and improved technological developments have enhanced the attractiveness of the process. South African Synthetic Oil Limited (SASOL) currently operates several modern Fischer-Tropsch plants. Many organometallic chemists refer to both the Fischer-Tropsch and Mobil processes as "political processes" because they are heavily subsidized by countries that find it important to be independent of foreign oil.

---

hydrogen to occupy in the deinsertion step. Thus 18-electron complexes with ligands that remain attached to the central metal, such as the dicarbonylcyclopentadienyl-ethyliron(II) complex shown below, are kinetically inert with respect to \( \beta \) elimination.

Organometallic complexes frequently are susceptible to nucleophilic attack by an external reagent. In some instances the attack takes place on the metal center (see substitution reactions, page 686), while in others it occurs on a bound ligand. Already in this chapter we have seen many instances in which coordinated carbon monoxide undergoes nucleophilic attack. Examples include reactions with H\(^+\) to produce a formyl complex (Eq. 15.19), with R\(^-\) to form an acyl complex (Eq. 15.49), and with OH\(^-\) to give a hydroxycarbonyl complex (Eq. 15.24).

\[
M\rightarrow\text{C}=\text{O} + \text{Nu}^- \rightarrow [M\rightarrow\text{C}(\text{Nu})\text{O}]^-
\]  

We have also observed that the carbon atom of a Fischer carbene is subject to reaction with nucleophiles (Eq. 15.52).

Coordinated unsaturated hydrocarbons are particularly susceptible to nucleophilic attack even though as free organic molecules they tend to resist such reactions because they are relatively electron rich. Upon coordination, they yield some electron density to the metal and thereby lose some resistance to reaction with nucleophiles. A metal fragment with good \( \pi \)-accepting ligands and/or a positive charge (i.e., one that is more electrophilic) will therefore be an especially good candidate for activating an unsaturated hydrocarbon toward nucleophilic attack. Of course not all coordinated unsaturated hydrocarbons are equally reactive. The following order of nucleophilic susceptibility in 18-electron cationic complexes has been established: \(^1\)

\[
\begin{align*}
1 & \rightarrow 2 & \rightarrow 3 & \rightarrow 4
\end{align*}
\]

The usefulness of such a series is twofold: (1) if two different unsaturated ligands are found in the same complex, one can predict which ligand will react, and (2) it is possible to estimate how activating a metal fragment must be in order to cause a reaction to occur. Notice that hydrocarbons of even hapticity are more reactive than those with odd hapticity. In addition, acyclic ligands are more reactive than cyclic ones.

Reactions illustrating nucleophilic attack on coordinated olefins and allyls are shown in Eqs. 15.124 and 15.125.

\[
\begin{align*}
\text{Eq. 15.124:} & \quad \text{Eq. 15.125:}
\end{align*}
\]

Oxidation of the complex with \( I_2 \) liberates the derivative of benzene.

\[
\begin{align*}
\text{Eq. 15.126:} & \quad \text{Eq. 15.127:}
\end{align*}
\]

can be altered with the water-gas shift reaction, which can be catalyzed by a variety of heterogeneous and homogeneous catalysts:

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad (15.161)
\]

There are several reasons for wishing to alter the hydrogen concentration. First, hydrogen is a more versatile industrial chemical than water gas. Second, small organic molecules tend to have roughly three to four times as many hydrogen atoms as carbon atoms, so if the \(\text{H}_2/\text{CO}\) mole ratio can be changed to about two, a good feedstock is obtained.

Commercially, the water-gas shift reaction is usually carried out over \(\text{Fe}_3\text{O}_4\). However, current interest centers on homogeneous catalysts. Metal carbonyl complexes such as \([\text{HFe(CO)}_4]^+\), \([\text{Rh(CO)}_2\text{I}_2]^+\), and \([\text{Ru(bpy)}_2(\text{CO})\text{Cl}]^+\) are effective and although all the mechanisms have not been worked out completely, the reactions may be viewed in general terms as beginning with a nucleophilic attack on coordinated carbon monoxide:

\[
\text{M} + \text{CO} \rightarrow \text{M} - \text{CO} \rightarrow [\text{M}-\text{H}]^+ \quad (15.162)
\]

The hydridic hydrogen can then attack water:

\[
[M-H]^+ + \text{H}_2\text{O} \rightarrow \text{M} + \text{OH}^- + \text{H}_2 \quad (15.163)
\]

Alternatively (and equivalently) a water molecule can attack in Eq. 15.162 (freeing an \(\text{H}^+\) ion) followed by attack of a proton on the hydridic ion in Eq. 15.163. A scheme for the reaction catalyzed by \([\text{Ru(bpy)}_2(\text{CO})\text{Cl}]^+\) can be presented as:

\[
[\text{RuL}_2(\text{CO})\text{Cl}]^+ + \text{H}_2\text{O} \rightarrow [\text{RuL}_2(\text{CO})(\text{H}_2\text{O})]^2+ + \text{Cl}^- + [\text{RuL}_2(\text{CO})\text{H}]^+ + \text{H}^+ \quad (15.164)
\]

Displacement of water gives \([\text{RuL}_2(\text{CO})\text{H}]^+\), which undergoes nucleophilic attack to form a hydroxycarbonyl complex. Decarbonylation occurs with hydride formation followed by liberation of hydrogen gas and reformation of the catalyst.

The preferred route to synthesis gas currently is by reforming methane (principal component of natural gas):

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \quad (15.165)
\]

Whatever the source of synthesis gas, it is the starting point for many industrial chemicals. Some examples to be discussed are the hydroformylation process for converting alkenes to aldehydes and alcohols, the "Monsanto process" for the production of acetic acid from methanol, the synthesis of methanol from methane, and the preparation of gasoline by the Mobil and Fischer-Tropsch methods.

The reaction of an alkene with carbon monoxide and hydrogen, catalyzed by cobalt or rhodium salts, to form an aldehyde is called hydroformylation (or sometimes the oxo process):

\[
2\text{RCH}=\text{CH}_2 + \text{CO} + \text{H}_2 \rightarrow \text{RCH}_2\text{CH}=\text{CH}_2 + 2\text{CO} \quad (15.166)
\]

It was discovered by Roelen in 1938 and is the oldest and largest volume catalytic reaction of alkenes, with the conversion of propylene to butyraldehyde being the most important. About 3 million tons of aldehydes and aldehyde derivatives (mostly alcohols) are produced annually making the process the most important industrial synthesis using a metal carbonyl complex as a catalyst.\(^{175}\) The name hydroformylation arises from the fact that in a formal sense a hydrogen atom and a formyl group are added across a double bond. The net result of the process is extension of the carbon chain by one and introduction of oxygen into the molecule.

The most widely accepted mechanism for the catalytic cycle is the following one proposed by Heck and Breslow:

\[
\text{CO} \quad \text{CH}_3 \text{CHO} \quad \text{CH}_3 \text{CHO} \quad \text{H}_2 \quad \text{L} = \text{bpy}
\]

This particular cycle is significant because all of the key intermediates have been isolated.\(^{174}\) Substitution of \(\text{H}_2\text{O}\) for \(\text{Cl}^-\) in \([\text{Ru(bpy)}_2(\text{CO})\text{Cl}]^+\) gives \([\text{Ru(bpy)}_2(\text{CO})\text{H}(\text{H}_2\text{O})]^2+\) which exists in equilibrium with \([\text{Ru(bpy)}_2(\text{CO})\text{OH}]^+\). Carbon monoxide replaces water to give \([\text{Ru(bpy)}_2(\text{CO})\text{Cl}]^+\) which undergoes nucleophilic attack to form a hydroxycarbonyl complex. Decarbonylation occurs with hydride formation followed by liberation of hydrogen gas and reformation of the catalyst.

The preferred route to synthesis gas currently is by reforming methane (principal component of natural gas):

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \quad (15.165)
\]


Hydroformylation\(^{175}\)

\[
\text{CO} \quad \text{CH}_3 \text{CHO} \quad \text{CH}_3 \text{CHO} \quad \text{H}_2 \quad \text{L} = \text{bpy}
\]

\[
\text{H}_2\text{O} \quad \text{H}_2\text{O} \quad \text{H}_2\text{O} \quad \text{H}_2\text{O} \quad \text{H}_2\text{O}
\]

\[
\text{CO} \quad \text{CO} \quad \text{CO} \quad \text{CO} \quad \text{CO}
\]

\[
\text{H}_2 \quad \text{H}_2 \quad \text{H}_2 \quad \text{H}_2 \quad \text{H}_2
\]

\[
\text{L} = \text{bpy}
\]

\[
\text{RuL}_2(\text{CO})\text{H}_2\text{O}
\]

\[
\text{RuL}_2(\text{CO})\text{H}_2\text{O}
\]

\[
\text{RuL}_2(\text{CO})\text{COOH}
\]

\[
\text{RuL}_2(\text{CO})\text{CO}_2\text{H}
\]

\[
\text{RuL}_2(\text{CO})\text{Cl}
\]

\[
\text{RuL}_2(\text{CO})\text{O}
\]


The net result is that benzene has undergone a substitution reaction that is not possible for the free molecule.

Although the coordinated cyclopentadienyl group resists nucleophilic attack, it does react with electrophiles. Ferrocene resembles free benzene in that it reacts with many electrophilic reagents, but it does so at an even faster rate than benzene. The aromatic character of ferrocene was recognized soon after the complex was identified and has led to a rich literature. Among the numerous reactions that have been studied is acylation in the presence of a Friedel-Crafts catalyst.

\[
\text{CH}_3\text{COCI} + \text{AlCl}_3 \rightarrow \text{CH}_3\text{C}^+\text{O} + \text{AlCl}_4^-
\]

The reaction of acetic anhydride with phosphoric acid will generate the same electrophile and offers the advantage that only the monoacyl product results. Acylation of the first ring deactivates the second and the concentration of \(\text{CH}_3\text{C}^+\text{O}\) from the phosphoric acid reaction is too small to produce the diacyl product.

A second example of the reactivity of the ferrocene rings is their condensation with formaldehyde and amines (the Mannich condensation):

\[
\text{Fe}^I(\text{C}_5\text{H}_5)_2 + \text{CH}_2\text{O} + \text{HNMe}_2 \rightarrow \text{Fe}^I(\text{C}_5\text{H}_4\text{CH}_2\text{NMe}_2)
\]

Ferrocene thus resembles the more reactive thiophene and phenol rather than benzene which does not undergo Mannich condensation.

Other reactions typical of aromatic systems, such as nitration and bromination, are not feasible with metalloenes because of their sensitivity to oxidation. However, many of the derivatives that would be produced in these types of reactions can be made indirectly by means of another reaction typical of aromatic systems: metallation. Just as phenyllithium can be obtained from benzene, analogous ferrocene compounds can be prepared:

![Chemical structures and reactions](image)

\footnote{Ferrocene loses an electron rather reluctantly since it involves disrupting an 18-electron configuration, but it does so when subjected to strong oxidizing agents like nitric acid or bromine. Cobaltocene is readily oxidized to the very stable cobaltocenium ion, losing the 19th and only antibonding electron. Nickelocene loses one of its two antibonding electrons to form the relatively unstable nickelocene ion.}

Carbonylate Anions as Nucleophiles

Carbonylate complexes have many useful synthetic applications. Typical reactions involve nucleophilic attack of the metal ion on a positive center (alternatively viewed as an electrophilic attack on the metal). The synthesis of metal alkyl complexes has been referred to earlier (Eqs. 15.46 and 15.47). Other examples include:

\[
\text{RCO} + [\text{Co(O)}]^- \rightarrow \text{RCO}^+ + X^-
\]

\[
\text{Mn(CO)}_3\text{Br} + [\text{Mn(CO)}]^- \rightarrow \text{Mn}_2(\text{CO})_6 + \text{Br}^-
\]

Although the reaction in Eq. 15.135 is of little importance in the manufacture of \(\text{Mn}_2(\text{CO})_6\) (the reactants typically are synthesized from the dimanganese complex), it illustrates a general and useful method of forming metal-metal bonds that can be applied to cases in which the metals are different.
Ethylene is commonly chosen to illustrate homogeneous hydrogenation with Wilkinson's catalyst, but the process is actually very slow with this alkene. The explanation lies with the formation of a stable rhodium ethylene complex, which does not readily undergo reaction with H₂.

Ethylene competes effectively with the solvent for the vacant coordination site created when triphenylphosphine dissociates from Wilkinson's catalyst and thus serves as an inhibitor to hydrogenation.

\[
\text{(Ph}_3\text{P)}_3\text{RhCl} + \text{H}_2\text{C}==\text{CH}_2 \rightarrow \text{(Ph}_3\text{P)}_2\text{RhCl} + \text{Ph}_3\text{P}
\]
$$\text{Mn}(\text{CO})_5\text{Br} + [\text{Re}(\text{CO})_5]^- \rightarrow (\text{OC})_5\text{MnRe(CO)}_4 + \text{Br}^- \quad (15.136)$$

$$\text{HgSO}_4 + 2[\text{Mn}(\text{CO})_5]^- \rightarrow (\text{OC})_5\text{MnHgMn(CO)}_4 + \text{SO}_4^- \quad (15.137)$$

$$\text{PhSnCl}_3 + 3[\text{Co}(\text{CO})_4]^- \rightarrow \text{PhSn}[\text{Co(CO)}_4]_3 + 3\text{Cl}^- \quad (15.138)$$

$$([\text{Ph}_3\text{P})_2\text{NiCl}_2 + 2[\text{Co}(\text{CO})_4]^- \rightarrow (\text{OC})_4\text{CoNi(PPh}_3\text{)}_2\text{Co(CO)}_4 + 2\text{Cl}^- \quad (15.139)$$

Applications of carbonylate reactions in organic synthesis are numerous. Particularly noteworthy are schemes involving tetracarbonylferrate(−II) (referred to as Collman's reagent), which can be isolated as a sodium salt, Na−Fe(CO)_4−1.5 dioxane, and is commercially available. The highly nucleophilic [Fe(CO)_4]− reacts readily with alkyl halides to yield alkyl iron carbonylates:

$$\text{RX} + [\text{Fe(CO)}_4]^- \rightarrow [\text{RFe(CO)}_4]^- + \text{X}^- \quad (15.140)$$

These alkyl complexes do not undergo β elimination (the stable 18-electron complex does not provide the necessary vacant coordination site) and optically active R groups do not undergo racemization. Migratory insertion reactions (page 695) do occur in the presence of Ph_3P or CO to give the corresponding acyl complexes.

$$\text{RX} + [\text{Fe(CO)}_4]^- \rightarrow [\text{RFe(CO)}_3\text{L}]^- \quad (L = \text{Ph}_3\text{P} \text{ or CO}) \quad (15.141)$$

Although the alkyl and acyl products shown in Eqs. 15.140 and 15.141 have been isolated and characterized, they are frequently treated directly to produce aldehydes, carboxylic acids, ketones, esters, or amides.

$$\text{RCOOH} \quad (15.143)$$

$$\text{RCHO} \quad (15.142)$$

$$\text{RCOOR} \quad (15.146)$$

$$\text{RCNR} \quad (15.145)$$

Thus Collman's reagent functions much like a Grignard reagent in its ability to convert alkyl halides into a wide variety of organic compounds.

A rich chemistry has also developed for the chromium dianion, [Cr(CO)_5]^−2. The expected displacement of Cl− occurs when this reagent reacts with an acid chloride:

$$[\text{Cr}(\text{CO})_5]^− + \text{RCCI} \rightarrow [\text{RCr}(\text{CO})_4]^- + \text{Cl}^- \quad (15.148)$$

The acylate complex may be alkylated directly to give an alkoxycarbene or the same end may be achieved by acetylation followed by alkylation:

$$\text{RCCr}(\text{CO})_4 \quad (15.149)$$

$$\text{RCO} \quad (15.150)$$

The resulting transition metal carbenes have been used to synthesize a wide variety of organic compounds such as furanocoumarins, pyrroles, and β-lactams.

Catalysis by Organometallic Compounds

A thermodynamically favorable reaction may be slow at modest temperatures and therefore not of value for synthesis. Increasing the temperature of the reaction may significantly accelerate its rate, but providing the energy to do so is expensive and higher temperatures may induce competing side reactions that will greatly reduce product yields. A more attractive approach to increasing the rate of a reaction is to use a catalyst. Catalysts are classified as homogeneous if they are soluble in the reaction medium and heterogeneous if they are insoluble. Each type has its advantages and disadvantages. Heterogeneous catalysts are easily separated from the reaction products (a very positive feature) but tend to require rather high temperatures and pressures and frequently lead to mixtures of products, i.e., they have low selectivity.

Homogeneous catalysts must be separated from the product (a negative feature) but operate at low temperatures and pressures (a very positive aspect), and usually give good selectivity (another very positive aspect).

Many important chemicals are produced commercially by reactions which are catalyzed by organometallic compounds and this fact provides one of the motivating forces for studying organometallic chemistry. Much of the focus in this section will be on homogeneous catalysis because solution reactions are better understood than the surface reactions of heterogeneous systems. It is also easier to modify an organometallic compound and evaluate the effects of the modification than it is to alter and study a surface.

Although the reaction of hydrogen gas with ethylene is thermodynamically favorable, it does not take place at room temperature and pressure.

\[
\Delta H^\circ = -136 \text{ kJ mol}^{-1} \quad \Delta G^\circ = -101 \text{ kJ mol}^{-1}
\]

However, in the presence of metallic nickel, copper, palladium, or platinum, the reaction is fast and complete. The metal may be deposited on an inert solid support such as alumina or calcium carbonate, but the reaction is with the metal surface and therefore is heterogeneously catalyzed.

The first effective homogeneous catalyst to be discovered for hydrogenation was the square planar 16-electron chlorotris(triphenylphosphine)rhodium(I), \[(Ph,P)_3RhCl\] (Fig. 15.47), which is known as Wilkinson's catalyst. In Chapter 11 we saw that this geometry and electron configuration are an especially favorable combination. These species also have wide possibilities for oxidative addition (page 689). They can become five-coordinate through simple addition of a ligand or six-coordinate through addition combined with oxidation. In either case they become isoelectronic with the next noble gas, i.e., they achieve an 18-electron valence shell configuration.

It is not surprising then that 16-electron square planar complexes have been regarded as very attractive catalyst candidates on the premise that they may oxidatively add two reactant molecules and thereby enhance their reactivity.

Wilkinson's catalyst is thought to behave as follows: In solution one of the phosphine ligands dissociates, leaving \[(Ph,P)_3RhCl\]. This tricoordinate complex is very reactive and has not as yet been isolated, but the closely related \[(Ph,P)_3Rh\]^+ which could form from the dissociation of a chloride ion from Wilkinson's catalyst has been studied and found to have an unusual structure (Fig. 15.48). Unlike most three-coordinate complexes (Chapter 12), it is more T-shaped than triangular. The evidence for dissociation of a \(Ph,P\) ligand from \[(Ph,P)_3RhCl\] is indirect but persuasive: (1) For complexes with less sterically hindered phosphines (e.g., \(Et,P\)), the catalytic effect disappears—apparently steric repulsion forcing dissociation is necessary; and (2) with the corresponding iridium complex in which the metal-phosphorus bond is stronger, no dissociation takes place and no catalysis is observed.

To return to the catalyst, the \[(Ph,P)_3RhCl\] molecule, possibly solvated, can undergo oxidative addition of a molecule of hydrogen to form an alkyl group. This reaction will result from a migration of a hydrogen from the metal to a carbon in the coordinated alkene. Although the hydrogen atom does essentially all of the moving, this reaction is often called an alkene insertion reaction (page 699).

The reactions involved in hydrogenation with Wilkinson's catalyst thus can be represented as follows (\(L = Ph,P, S = solvent molecule\)).

\[
L/L' - Rh - L + S \rightarrow L/L' - Rh - L + L
\]

oxide cages (Fig. 16.36). All are anhydrides that react readily with water to form the corresponding acids:

\[
P_4O_{12} + 6H_2O \rightarrow 4H_3PO_4\]  \hspace{1cm} (16.75)
\[
P_4O_{10} + 6H_2O \rightarrow 4H_4PO_4\]  \hspace{1cm} (16.76)

The \(P_4O_{12}\) molecule reacts to form both phosphoric acid and phosphorous acid. In addition to the discrete cage molecule pictured in Fig. 16.36c, phosphorus pentoxide also exists in several polymeric forms.\(^{113}\)

White phosphorus can be converted readily to its more stable allotropes:

\[
\frac{5P_4}{4P_4 \text{ red or blue}} \rightarrow P_r \hspace{1cm} \text{(red phosphorus)}\]  \hspace{1cm} (16.77)
\[
\frac{5P_4}{4P_4 \text{ red or blue}} \rightarrow P_r \hspace{1cm} \text{(black phosphorus)}\]  \hspace{1cm} (16.78)

Crystalline black phosphorus has a corrugated layer structure.\(^{114}\)

"Red phosphorus" does not appear to be a well-defined substance but differs according to the method of preparation. It probably consists of random chains. The rate of formation is increased by certain substances such as iodine which appear to be incorporated into the product.

The chemistry of phosphorus and sulfur is considerably more complicated than phosphorus-oxygen chemistry.\(^{115}\) Only two phosphorus sulfides, \(P_4S_3\) and \(P_4S_5\), are isoelectronic and isostructural with phosphorus oxides. The former may be prepared by allowing stoichiometric amounts of phosphorus and sulfur to react:

\[
4P + S \rightarrow 4P_3S_3\]  \hspace{1cm} (16.79)

By mixing phosphorus and sulfur in appropriate stoichiometric quantities, \(P_xS_y\) and \(P_4S_5\) may be obtained. Slow oxidation of \(P_4S_3\) with sulfur yields \(P_4S_5\):

\[
4P_3S_3 + S \rightarrow 4P_4S_5\]  \hspace{1cm} (16.80)

Two cage phosphorus sulfides may be synthesized by the formation of sulfide bridges through the action of bistrimethylstibine sulfide.\(^{116}\)

\[
(Me_3Sn)_2S + P_4S_3 \rightarrow (B-P_4S_5) + 2Me_3Sn\]  \hspace{1cm} (16.81)
\[
(Me_3Sn)_2S + P_4S_3 \rightarrow (B-P_4S_5) + 2Me_3Sn\]  \hspace{1cm} (16.82)

The structures of all of these sulfides are known (Fig. 16.37). They are all derived from a tetrahedron of phosphorus atoms with sulfur atoms bridging along various edges. All except \(P_4S_3\) and \(P_4S_5\) retain one or more \(P=P\) bonds. The heavier congeners of phosphorus resemble it in a tendency to form cages. Both arsenic and antimony form unstable tetrameric molecules which readily revert to polymeric structures. Cage molecules as well as polymeric forms are also known for \(As_4\) and \(Sb_4\), and in addition there are a number of sulfides, some of which are known to exist as cages (Fig. 16.38).

By extension of the reactions involved in the formation of cyclopolydisilanes, West and Carberry\(^{117}\) synthesized bicyclic and cage permethylpolysilanes such as:

\[
\text{MeMeSi} \quad \text{SiMeMe}\]  \hspace{1cm} (16.83)
Transition metals, 27-28

Valence bond (VB) theory, 139-153, 391-394, 474

Virulence mechanisms, 266

Vacancy formation, promotion to, 148-149

Valence state values, 191

van der Waals forces, 252, 299.

See also London dispersion forces

van der Waals radii, 290-291, 301, 700. See also London dispersion forces

Van Vleck, J. H., 395

Vaska's complex, 691

Wacker process, 714-715

Wade's rules, 798, 805

Walden inversion, 243

Wadsley diagrams, 218

Water, physical properties of, 360

Water-gas shift reaction, 710

Werner, Alfred, 387, 388, 389, 390, 491, 495

Wilkinson, G., 387, 669

Wilkinson's catalyst, 707

Wurtzite, 96-97

Xenon, 5, 70, 332-336

X-ray diffraction, 233-235, 248, 497, 645

p-Xylene, 5-6

Yatsimirskii, K. B., 117

Zeolites, 3-5, 7, 378, 715, 745-748

Ziegler, K., 718

Ziegler-Natta catalysis, 718

Zinc, 582-587

Zinc blende, 96-97

Zintl salts, 527, 817

ZSM-5, 747-748

Transactinide elements, 599-607, 613-617

Trans effect, 543-545

Transferrins, 937

Transition metal hydrides, acidities of, 643
In order to get branching to form cages (bridgehead silicon atoms) some methyltrichlorosilane is added to the dimethyldichlorosilane in the reaction.

In the limited space allowed here, it has been possible to mention only a few of the many nonmetallic inorganic cages. If we consider those which also include carbon atoms, we have an even larger group from which to choose. One of the more remarkable cages to be synthesized recently is ($\text{-BuCP})_4$ which has a cubane structure. Two molecules of tert-butylphosphacetylene (1) undergo a head-to-tail dimerization to give an intermediate (2) which is thought to dimerize once again or react with two additional molecules of the starting material to give (3) which "zips up" to give the final product (4).

Inorganic Chains, Rings, Cages, and Clusters

Boron Cage Compounds

Reactions of boron halides might be expected to produce borine, $\text{BH}_3$. However, it is impossible to isolate the monomer; all syntheses resulting in diborane, $\text{B}_2\text{H}_6$.\(^{119}\)

$$\text{BHF}_3 + 6\text{NaH} \rightarrow 6\text{NaBF}_4 + 3\text{B}_2\text{H}_6$$  \hspace{1cm} (16.84)

$$2\text{NaBH}_4 + \text{I}_2 \rightarrow \text{B}_2\text{H}_6 + 2\text{NaI} + \text{H}_2$$  \hspace{1cm} (16.85)

$$2\text{KBH}_4 + 2\text{H}_2\text{PO}_4 \rightarrow 2\text{B}_2\text{H}_6 + 2\text{K}_2\text{H}_2\text{PO}_4 + 2\text{H}_2$$  \hspace{1cm} (16.86)

Although $\text{BH}_3$ exists in the form of Lewis acid-base adducts and as a presumed intermediate in reactions of diborane, only trace quantities of the free molecule have been detected. The equilibrium constant for dimerization is approximately $10^3$ and the enthalpy of dissociation of the dimer to the monomer is about +150 kJ mol\(^{-1}\) or slightly more.\(^{120}\)

$$2\text{BH}_3(g) \rightarrow \text{B}_2\text{H}_6(g)$$  \hspace{1cm} (16.87)

Diborane is the simplest of the boron hydrides, a class of compounds that have become known as electron deficient. They are electron deficient only in a formal sense—there are fewer electrons than required for all of the adjacent atoms to be held together by electron pair covalent bonds. The compounds, in fact, are good reducing agents


\(^{120}\) Trimethylboron, unlike $\text{BH}_3$, shows no tendency to dimerize.
agents and show no tendency to accept electrons when offered by reducing agents. A number of approaches have been used to rationalize the bonding in these compounds.

The most successful and extensive work in this area, as we shall see, has been that of William N. Lipscomb. Before proceeding with an examination of the bonding in diborane, it will be helpful to examine its structure (Fig. 16.39). Each boron atom is surrounded by an approximate tetrahedron of hydrogen atoms. The bridging hydrogen atoms are somewhat further from the boron atom and form a smaller H—B—H bond angle than that for the terminal hydrogen atoms.

The earliest attempt at rationalizing the dimerization of borane invoked resonance in a valence bond (VB) context:

\[
\begin{align*}
\text{H}_2\text{B} & \quad \text{H}_2\text{B} \\
\text{H}_2\text{B} & \quad \text{H}_2\text{B}
\end{align*}
\]

Although adequate from a formal point of view, it suffers from the usual unwieldiness of VB terminology when extensive delocalization exists. A second attempt considers the \( \text{B}_3\text{H}_6^+ \) anion as isoelectronic and isostructural with ethylene. Such an ion would have a cloud of electron density above and below the \( \text{B}—\text{H} \) plane. The neutral \( \text{B}_3\text{H}_6 \) molecule could then be formally produced by embedding a proton in the electronic cloud above and below the plane of the \( \text{B}_3\text{H}_6^+ \) ion. Although this may appear to be somewhat farfetched, it is but a simplistic way of describing the bonding model which is currently accepted as best—the three-center, two-electron bond.

Consider each boron atom to be \( \text{sp}^3 \) hybridized. The two terminal \( \text{B}—\text{H} \) bonds on each boron atom presumably are simple \( \sigma \) bonds involving a pair of electrons each. This accounts for eight of the total of twelve electrons available for bonding. Each of the bridging \( \text{B}—\text{H}—\text{B} \) linkages then involves a delocalized or three-center bond as follows. The appropriate combinations of the three orbital wave functions, \( \phi_1, \phi_2, \phi_3 \) (approximately \( \text{sp}^3 \) hybrids), and \( \phi_4 \) (an \( \pi \) orbital) result in three molecular orbitals:

\[
\begin{align*}
\psi_1 &= \phi_1 + \phi_2 + \frac{1}{\sqrt{3}}\phi_3 \\
\psi_2 &= \frac{1}{\sqrt{2}}(\phi_1 - \phi_2 + \frac{1}{\sqrt{3}}\phi_3) \\
\psi_3 &= \phi_4 \\
\end{align*}
\]

Although adequate from a formal point of view, it suffers from the usual unwieldiness of VB terminology when extensive delocalization exists. A second attempt considers the \( \text{B}_3\text{H}_6^+ \) anion as isoelectronic and isostructural with ethylene. Such an ion would have a cloud of electron density above and below the \( \text{B}—\text{H} \) plane. Although this may appear to be somewhat farfetched, it is but a simplistic way of describing the bonding model which is currently accepted as best—the three-center, two-electron bond.
Inorganic Chains, Rings, Cages, and Clusters

Boron Cage Compounds

Fig. 16.41 (a) Qualitative picture of bonding in diborane. (b) A common method of depicting B—H—B bridges.

Bridging B—H—B bond. Two other bonds are of importance in the higher analogues:
(1) the two-center, two-electron B—B bond, best exemplified by the boron subhalides, X₃B—BX₂; and (2) the three-center, two-electron B—B—B bond, which may be formed by overlap of three orbitals from three corners of an equilateral triangle of boron atoms (Fig. 16.42). Like the three-center B—H—B bond, three molecular orbitals will result, of which only the lowest energy or bonding one will be occupied by a pair of electrons.

With this repertoire of bonding possibilities at our disposal, we can construct the molecular structures of various boron-hydrogen compounds, both neutral species and anions. The simplest is the tetrahydroborate or borohydride ion, BH₄⁻. Although diborane is unstable with respect to dimerization, the addition of a Lewis base, H₃O⁺, satisfies the fourth valency of boron and provides a stable entity. Other Lewis bases can coordinate as well.

\[ \text{B}_2\text{H}_6 + 2\text{NaH} \rightarrow 2\text{NaBH}_4 \]  \hspace{1cm} (16.92)

\[ \text{B}_2\text{H}_6 + 2\text{CO} \rightarrow 2\text{H}_3\text{B} \text{CO} \]  \hspace{1cm} (16.93)

\[ \text{B}_2\text{H}_6 + 3\text{R}_2\text{N} \rightarrow 2\text{H}_3\text{BNR}_3 \]  \hspace{1cm} (16.94)

Fig. 16.42 The closed three-center, two-electron B—B—B bond: (a) formation from three boron atomic orbitals; (b) simplified representation.

Although the ammonia adduct of BH₄⁻ is stable, it must be prepared by a method that does not involve B₂H₆, such as:

\[ \text{Me}_3\text{OBH}_3 + \text{NH}_3 \rightarrow \text{H}_3\text{OBH}_3 + \text{Me}_3\text{O} \]  \hspace{1cm} (16.95)

Direct reaction of ammonia and diborane results in the "annimonolate" of diborane, which has been shown to be ionic:

\[ \text{B}_2\text{H}_6 + 2\text{NH}_3 \rightarrow [\text{BH}_3(\text{NH}_3)_2]^+ + \text{BH}_4^- \]  \hspace{1cm} (16.96)

This unsymmetric cleavage:

\[ \text{H}_3\text{B} \text{H}_3 \]  \hspace{1cm} \text{is typical of reactions with small, hard Lewis bases and further examples will be discussed below. Larger bases, such as phosphines, promote symmetric cleavage:}

\[ \text{H}_3\text{B} \text{H}_3 \]  \hspace{1cm} \text{Diborane is very air sensitive, reacting explosively when exposed to air. Although it is said that in extremely pure form, the compound is stable in air at room temperature, these conditions are rarely met. In general, the higher molecular weight boranes are much less reactive. For example, decaborane (B₁₀H₁₄) is quite stable in air. All of the compounds discussed thus far (except diborane and decaborane) contain only two-center, two-electron bonds. A simple boron hydride containing three types of bonds is tetraborane, B₄H₁₀ (Fig. 16.43). It is formed by the slow decomposition of diborane:

\[ 2\text{B}_2\text{H}_6 \rightarrow \text{B}_4\text{H}_{10} + \text{H}_2 \]  \hspace{1cm} (16.97)

In addition to terminal and bridging B—H bonds, this compound contains a direct B—B bond. Tetraborane undergoes both symmetric and unsymmetric cleavage (Fig. 16.44). Larger Lewis bases tend to split off BH₃ moieties, which are either complexed or allowed to dimerize to form diborane:

\[ \text{B}_4\text{H}_{10} + 2\text{Me}_3\text{N} \rightarrow \text{Me}_3\text{NBH}_3 + \text{Me}_3\text{NBH}_3 \]  \hspace{1cm} (16.98)

\[ 2\text{B}_4\text{H}_{10} + 2\text{Et}_3\text{O} \rightarrow 2\text{Et}_3\text{OBH}_3 + \text{B}_4\text{H}_6 \]  \hspace{1cm} (16.99)

\[ 2\text{B}_4\text{H}_{10} + 2\text{Me}_3\text{S} \rightarrow 2\text{Me}_3\text{SBH}_3 + \text{B}_4\text{H}_6 \]  \hspace{1cm} (16.100)

Small, hard Lewis bases such as ammonia and the hydroxide ion result in unsymmetric cleavage, i.e., the splitting off of the BH₄⁻ moiety:

\[ \text{B}_4\text{H}_{10} + 2\text{NH}_3 \rightarrow [\text{H}_2\text{B}(\text{NH}_3)_2]^+ + [\text{B}_2\text{H}_6]^- \]  \hspace{1cm} (16.101)

\[ 2\text{B}_4\text{H}_{10} + 4\text{OH}^- \rightarrow [\text{B}_2\text{O}_6]^2^- + [\text{BH}_4^-]^2^- + 2[\text{B}_2\text{H}_6]^+ \]  \hspace{1cm} (16.102)

\[ \text{Further heating gives borazines (see Eq. 16.34).} \]
Fig. 16.43 Bonding and structure of tetraborane, \( B_4H_0 \). [From Muetterties, E. L. The Chemistry of Boron and Its Compounds, Wiley: New York. 1967. Reproduced with permission.]

Fig. 16.44 Symmetric (a) and unsymmetric (b) cleavage of tetraborane.

The reaction in Eq. 16.102 can be considered as an abstraction of \( BH_1 \) if it is assumed that \([H_2B(OH)_2]^+\) forms and disproportionates:

\[
2[H_2B(OH)_2]^+ \rightarrow [B(OH)_3]^- + [BH_3]^+ \quad (16.103)
\]

Rather than continue to progress from less complex to more complex boron-hydrogen compounds, it will be more convenient to jump to a complex bill highly symmetric borohydride ion, \([B_3H_8]^2-\). It may be synthesized by the pyrolysis of the \([B_3H_6]^2-\) ion:

\[
3[B_3H_6]^2- \rightarrow [B_3H_8]^2- + 2[BH_3]^- + 3H_2 \quad (16.104)
\]

It is not necessary to use \([B_3H_6]^2-\) directly in this reaction; it may instead be formed in situ from diborane and borohydride:

\[
2[BH_4]^2- + 5B_2H_6 \rightarrow [B_3H_8]^2- + 13H_2 \quad (16.105)
\]

The \([B_3H_8]^2-\) ion is a regular icosahedron of atoms, each of the twenty faces being an equilateral triangle (Fig. 16.45a). All of the hydrogen atoms are external to the boron icosahedron and are attached by terminal B—H bonds. The icosahedron itself involves a resonance hybrid of several canonical forms of the type shown in Fig. 16.45b and c. Both two-electron, two-center B—B and two-electron, three-center B—B—B bonding are involved.

An icosahedral framework of boron atoms is of considerable importance in boron chemistry. Three forms of elemental boron as well as several nonmetal borides contain discrete \( B_{12} \) icosahedra. For example, \( \alpha \)-rhombohedral boron consists of layers of icosahedra linked within each layer by three-center B—B—B bonds and between layers by B—B bonds (Fig. 16.46). \( \beta \)-Rhombohedral borons consists of twelve \( B_{12} \) icosahedra arranged icosahedrally about a central \( B_1 \) unit, i.e., \( B_1(12B_{12})_1 \). Tetragonal boron consists of icosahedra linked, not only by B—B bonds between the icosahedra themselves, but also by tetrahedral coordination to single boron atoms.

Several boranes may be considered as fragments of a \( B_{12} \) icosahedron (or of the \([B_3H_8]^2-\) ion) in which extra hydrogen atoms are used to "sew up" the unused valences around the edge of the fragment. For example, decaborane \( 14 \) (Fig. 16.47a) may be considered a \( B_{12} \) framework from which \( B_1 \) and \( B_3 \) (Fig. 16.45) have been removed leaving " dangling " three-center bonds that are completed with hydrogen atoms to form B—H—B bridges.

Other examples of boranes that are icosahedralfragments are hexaborane\( 10 \), which is a pentagonal prism (Fig. 16.47b), pentaborane\( 13 \), similar to the former with 24. The prefix gives the number of boron atoms and the number in parentheses gives the number of hydrogens atoms. Thus decaborane \( 14 \) is \( B_{12}H_{18} \).
**Fig. 16.46** Structure of a rhombohedral boron. The icosahedra are linked within the layer via three-center bonds. This layer is linked to the layer above by B—B bonds arising from the boron atoms marked • and to the layer below by three additional boron atoms not seen on the opposite face.

**Fig. 16.47** Molecular structures of boranes related to $[\text{B}_n\text{H}_{2n-3}]^-$; (a) decaborane(14) formed by removal of atoms $\text{B}_1$ and $\text{B}_2$; (b) hexaborane(10). Note that the pentagonal pyramid is an apical fragment of an icosahedron. (c) Octaborane(12) related to $[\text{B}_n\text{H}_{2n-3}]^-$ by removal of $\text{B}_3$, $\text{B}_4$, $\text{B}_5$, $\text{B}_6$. [From Metcalf, E. L. The Chemistry of Boron and Its Compounds, Wiley: New York, 1967. Reproduced with permission.]

**Fig. 16.48** (a) The structure of the $[\text{B}_n\text{H}_{2n-3}]^-$ anion compared to an idealized dodecahedron. [From Guggenberger, L. J. Inorg. Chem. 1969, 8, 2771. Reproduced with permission.] (b) Molecular structure of $\text{B}_4\text{Cl}_4$ compared to an idealized tetrahedron. [From Metcalf, E. L. The Chemistry of Boron and Its Compounds, Wiley: New York, 1967. Reproduced with permission.]

A deltahedron is a polyhedron with all faces that are equilateral triangles. The deltahedra from $n = 4$ to $n = 12$ are tetrahedron (4), trigonal bipyramid (5), octahedron (6), pentagonal bipyramid (7), bisdisphenoid (dodecahedron) (8), tricapped trigonal prism (9), bicapped square antiprism (10), octadecahedron (11), and icosahedron (12). Most of these are illustrated in Chapters 6 and 12. See also Fig. 16.50.


---

A basal boron atom missing, octaborane(12) (Fig. 16.47c), and nonaborane (15). Although relating borane structures to icosahedra was the first successful means of systematizing the structural chemistry of these cages, further experimental work revealed that the icosahedron of $[\text{B}_6\text{H}_{12}]^-$ was merely the upper limit of a series of regular deltahedra. The $[\text{B}_n\text{H}_{2n-3}]^-$ series, complete from $n = 6$ to $n = 12$. As $n = 4$ structure also exists in the form of $\text{B}_4\text{Cl}_4$ (Fig. 16.48). If all of the vertices of the deltahedron are occupied, as in the $[\text{B}_n\text{H}_{2n-3}]^-$ series, the structure is called a closo (Gr., "closed") structure. It is possible to correlate the structure of a borane or its derivatives with the number of electrons involved in the bonding in the framework of the deltahedron. The number of vertices in the deltahedron will be one less than the number of bonding pairs in the framework. This approach is sometimes called the polyhedral skeletal approach.
For the closo series, the number of framework electrons equals \(2n + 2\). To count framework electrons, one notes that each boron atom has one of its three valence electrons tied up with the exo B—H bond (an exo B—H bond is one extending radially outward from the center of the cluster; see Figs. 16.45 and 16.48) and thus has two to contribute to the framework, giving a total of \(2n\) in this case 24 electrons from the B atoms. No neutral \(\text{B}_n\text{H}_2\) species are known, but we have seen an array of cations corresponding to the \(2n + 2\) rule. The 26 electrons in \([\text{B}_2\text{H}_2]^2-\) are just the number required to fill all of the bonding molecular orbitals in \([\text{B}_2\text{H}_2]^2-\) and correspond to 13 \((n + 1, n = 12)\) electron pairs as expected for an icosahedron.

If we remove a boron atom from a vertex of a closo structure, a cup-like or nest-like structure remains (Fig. 16.49). Such structures are termed nido (Latin, "nest"). We have seen that such structures contain extra hydrogen atoms to "sew up" the loose valencies around the opening. The nido structures obey the framework electron formula \(2n + 4\). Consider \([\text{B}_2\text{H}_2]^2-\) for example. Five exo B—H groups will contribute two electrons each and the four "extra" hydrogen atoms will contribute four electrons for a total of 14 \((2n + 4, n = 5)\). This corresponds to 7 \((n + 2)\) electron pairs and the geometry will be derived from an octahedron \((n - 1\) vertices). The structure is thus a square pyramid nido form derived from the closo octahedron. The extra four hydrogen atoms form bridges across the open edges of the nest (Fig. 16.49).

If we remove two vertex boron atoms, the resulting framework is an arachno (Gr., "spider's web") structure. With two vertices missing, the structure is even more open than the nido case, and the resemblance to the parent closo structure is less apparent. Arachno structures obey the electronic formula \(2n + 6\) (or \(n + 3\) electron pairs). Pentaborane(11), \([\text{B}_5\text{H}_11]^3-\), must therefore have an arachno structure. In the arachno series the extra hydrogen atoms form exo B—H bonds (lying close to the framework) as well as bridges.

The hypno (Gr., "net") series of boranes, with electronic formula \(2n + 8\), has been suggested to augment the closo, nido, and arachno series. Although no neutral boranes fit this scheme, some borane derivatives do. It is also possible to construct units consisting of more than one of the above types. These are called conjuncto (Latin, "joined subunits") structures.

The complete structural relationships among the closo, nido, and arachno species are shown in Fig. 16.50. The diagonal lines connecting the species represent the theoretical redox reactions are in horizontal rows. (From Badger, R. W. Acc. Chem. Res. 1976, 9, 446. Reproduced with permission.)
appearing before the ligand name and separated by a hyphen. The whole term, e.g. μ-
chloro, is separated from the rest of the name by hyphens, as in tricyclo[2.2.1]hepta-2.5-
diene)tricarbonyliron.

Examples:
1. [CoCu(C5H5)2](μ-C2H4)](C5H5)
2. [Cr(NH3)3(μ-OH)Cl]3
3. [Fe(CP)2(μ-Cl)][μ-Cl]
4. [Cr(CN)6(μ-H2)][μ-Cl]2

Metal-metal bonding may be indicated in names by italicized atomic symbols of the
appropriate metal atoms, separated by a long dash and enclosed in parentheses, placed
after the list of central atoms and before the ionic charge.

Examples:
1. [Br2ReReBr2]2-
2. [Mn2(CO)10]3-

Organometallic Species

General. Organometallic entities are usually considered to include any chemical
species containing a carbon-metal bond. The simplest entities are those with alkyl radical
ligands such as diethylzinc. In general, ligands bound by a single carbon atom to metals are
named by the customary substituent group names, though these ligands must be treated as
anions in order to calculate oxidation numbers. In any case, the designation is arbitrary.
Ligands conventionally treated as having metal-donor double bonds (alkylidynes) and
triple bonds (alkylidyne) are also given substituent group (radical) names.

Examples:
1. [Hg(C5H5)2]2-
2. [Hg(C5H5)2]3-
3. [Fe(CP)2(μ-Cl)][μ-Cl]2
4. [Cr(CN)6(μ-H2)][μ-Cl]2

Complexes with unsaturated groups. Since the first reported synthesis of ferrocene,
the numbers and variety of organometallic compounds with unsaturated organic ligands
have increased enormously. Further complications arise because alkenes, alkynes, imides,
and other unsaturated ligand systems such as cyclopentadienyl, C5H5−, diazenes, and other
unsaturated ligand systems are employed.

Examples:
1. [PtCl2(NH3)](C5H5)
2. [Cr(CN)6(μ-H2)][μ-Cl]2
3. [Fe(CP)2(μ-Cl)][μ-Cl]2
4. [Cr(CN)6(μ-H2)][μ-Cl]2

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3. [Fe(CP)2(μ-Cl)][μ-Cl]2
4. [Cr(CN)6(μ-H2)][μ-Cl]2

Complexes with unsaturated groups. Since the first reported synthesis of ferrocene,
Carboranes

Carbon has one more electron than boron, so the C—H moiety is isoelectronic with the B—H moieties. The results may be stated simply: For a regular deltahedron having n vertices, there will be n + 1 bonding molecular orbitals. The electron capacity of these bonding MOs is therefore 2n + 2. This gives the highly symmetric closo structure. If there are two more electrons (2n + 4), one bonding MO and one vertex must be used for these extra electrons rather than for a framework atom, and a nido structure with a missing vertex results. Although the electrons in boranes are delocalized and cannot be assigned to a specific region in a particular structure, the parallel between the extra electrons in s3 in molecules like NH2 is real. The 2n + 6 formula of arachno structures simply extends these ideas by one more electron pair and one more vertex.

Carbon has one more electron than boron, so the C—H moiety is isoelectronic with the B—H or BH2 moieties. Note that an isoelectronic relationship also exists between C and B, or B from the B–H bond. In a formal sense it should be possible to replace a boron atom in a borane with a carbon atom (with an increase of one in positive charge) and retain an isoelectronic system. The best-studied system, C4B10H14, is isoelectronic with [B12H12]4– and may be synthesized readily from decaborane and alkenes and diethyl sulfide as solvent.

The mechanism of isomerization, thought to be intramolecular, has been studied in detail. The horizontal series represent structures having the same number of boron atoms but differing in the total number of framework electrons so as to conform to the closo (2n + 2), nido (2n + 4), and arachno (2n + 6) electronic specifications. In a few cases (see below) the change from one structure to an adjacent one on the same line can be effected by a simple redox reaction, but in most instances this is not so. However, we can probably anticipate more examples of this type of transformation now that the general principles of framework electron count and structure are better understood.

What is the source of the 2n + 2, 2n + 4, and 2n + 6 rules and their correspondence with the closo, nido, and arachno structures? Space does not allow derivation of the molecular orbitals for deltalabula, but the results may be stated simply: For a regular deltahedron having n vertices, there will be n + 1 bonding molecular orbitals. The electron capacity of these bonding MOs is therefore 2n + 2. This gives the highly symmetric closo structure. If there are two more electrons (2n + 4), one bonding MO and one vertex must be used for these extra electrons rather than for a framework atom, and a nido structure with a missing vertex results. Although the electrons in boranes are delocalized and cannot be assigned to a specific region in a particular structure, the parallel between the extra electrons in s3 in molecules like NH2 is real. The 2n + 6 formula of arachno structures simply extends these ideas by one more electron pair and one more vertex.

The monocarboranes, CBnH2, are also known. The carbones conform to the electronic rules given above for boranes and are known in closo, nido, and arachno structures. When applying the formula to the carbones, each C—H group should be regarded as donating a pair of electrons to the framework count. Some carbones provide interesting examples of the possible horizontal transformations of Fig. 16.30 mentioned above. For example:

\[
\text{[C3B10H14]^{2-}} \rightarrow \text{[C3B10H12]^{3-}} + \text{H}_2 + \text{Na} \quad (16.108)
\]

\[
\text{[C3B10H12]^{3-}} \rightarrow \text{[C3B10H10]^{4-}} + \text{H}_2 + \text{Na} \quad (16.109)
\]

Metallocarboranes

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\]

\[
\text{[C3B10H12]^{3-}} \rightarrow \text{[C3B10H10]^{4-}} + \text{H}_2 + \text{Na} \quad (16.109)
\]
a completely systematic treatment. Thus, for a particular diastereoisomer of 
\[ \text{[Co(NH}_2\text{)}_2\text{CH}_2\text{CH}_2\text{NH}_2\text{]}\text{Br}_2 \], the polyhedral symbol is OC-6 and the ligating atom priority numbers are as shown below.

Example:

\[
\begin{array}{c}
\text{H} \\
\text{N} \\
\text{H} \\
\text{N} \\
\text{H} \\
\text{N}
\end{array}
\]

For this case, there are no additional complications, and the configuration index is assigned in the usual way as OC-6-32.

The classic case of diastereoisomerism that arises among chelate ligand derivatives is the tris(didentate) complexes in which the two donor atoms of the identical ligands are different. Glycinate, \( \text{NH}_2\text{CH}_2\text{CO}_2 \), and 2-aminoethanethiolate, \( \text{NH}_2\text{CH}_2\text{CH}_2\text{S} \), illustrate this. For complexes of either ligand, the facial and meridional labels described previously could be applied, but the more systematic configuration indexes are OC-6-22 and OC-6-21.

Examples:


Priming convention. The configuration index is especially useful for bis(tridentate) complexes and for more complicated cases. Bis(tridentate) complexes exist in three diastereoisomeric forms which serve to illustrate the utility of a priming convention. These isomers are represented below, along with their site symmetry symbols and configuration indexes. For Examples 1, 2, and 3, the two ligands are identical and the ligating-atom priority numbers are indicated.

Examples:

1. OC-6-2' 2. OC-6-1' 3. OC-6-1'

Chirality Symbols

Symbols R and S. There are two established and well-used systems for chirality symbols and these differ in fundamental ways. The first, the convention for chiral carbon atoms is applicable to metal complexes and is most often used in conjunction with ligand chirality. However, it can be applied to metal centers and has been useful for pseudotetrahedral organometallic complexes where, for example, cyclopentadienyl ligands are treated as if they were monodentate ligands of high priority.

Skew-line convention for octahedral complexes. The second is the skew line convention and applies to octahedral complexes. Tris(didentate) complexes constitute a general family of structures for which a useful unambiguous convention has been developed based on the orientation of skew lines which define a helix. Examples 1 and 2 represent the delta and lambda forms of a complex, such as \( \text{[Co(NH}_2\text{)}_2\text{CH}_2\text{CH}_2\text{NH}_2\text{]}^+ \).

Examples:

1. Delta 2. Lambda

Chirality symbols based on the priority sequence. The procedure is applied as for tetrahedra, but modified because there is a unique principal axis. The structure is oriented so that the viewer looks down the principal axis with the ligand having the higher priority closer to the viewer. Using this orientation, the priority sequence of ligating atoms in the (horizontal) plane is examined. If the sequence proceeds in a clockwise fashion, the chirality symbol \( \text{C} \) is assigned. Conversely, if the sequence is anticlockwise, the symbol \( \text{A} \) is assigned.

Examples:

1. Chirality symbol = C 2. Chirality symbol = A

Polynuclear Complexes

Polynuclear inorganic compounds exist in a bewildering array of structural types, such as ionic solids, molecular polymers, extended assemblies of oxoanions, both of metals and nonmetals, nonmetal chains and rings, bridged metal complexes, and homo- and heteronuclear clusters. This section treats primarily the nomenclature of bridged metal complexes and homo- and heteronuclear clusters.

Bridging ligands, as far as they can be specified, are indicated by the Greek letter \( \mu \).
bear a striking resemblance to the \( \sigma \) orbitals in the \( \pi \) system of cyclopentadienide anion. Noting this resemblance, Hawthorne suggested that the \([\text{C}_n\text{B}_9\text{H}_{11}]^{2-}\) anion could be considered isoelectronic with \( \text{C}_5\text{H}_5^- \) and should therefore be capable of acting as a \( \pi \) ligand in metallocene compounds. He and his coworkers then succeeded in synthesizing metallacarboranes, launching a new area of chemistry which is still being actively investigated.\(^{116}\)

\[
\begin{align*}
\text{[C}_2\text{B}_9\text{H}_{11}]^{2-} + \text{FeCl}_3 & \longrightarrow [\text{C}_2\text{B}_9\text{H}_{11} \text{Fe}]^{2-} + 2\text{Cl}^- \\
[\text{C}_2\text{B}_9\text{H}_{11}]^{2-} + \text{FeCl}_3 & \longrightarrow [\text{C}_2\text{B}_9\text{H}_{11} \text{FeCl}_3]^{2-} + 2\text{Cl}^- \\
[\text{C}_2\text{B}_9\text{H}_{11}]^{2-} + \text{BrMn(CO)}_5 & \longrightarrow [\text{C}_2\text{B}_9\text{H}_{11} \text{Mn(CO)}_5]^{3+} + \text{Br}^- + 2\text{CO}
\end{align*}
\]

The ferrocene analogues, like ferrocene, are oxidizable with the loss of one electron. In cases for which structures have been determined, they have been found to correspond to that expected on the basis of metallocene chemistry (Fig. 16.53).

In Chapter 15 we observed that the 18-electron rule was adequate for predicting stabilities of small organometallic clusters. In this chapter we have seen that Wade's rules allow us to make predictions about borane structures based on the number of framework electrons. These rules also are adequate for most boranes, metallacarboranes, and other heteroboranes.\(^{106}\) Furthermore, organometallic clusters that are not derived from boranes can be dealt with in a similar fashion. More sophisticated extensions are required for complex larger clusters.\(^{117}\)

Structure Prediction for Heteroboranes and Organometallic Clusters

In the previous section we viewed the \([\text{C}_n\text{B}_9\text{H}_{11}]^{2-}\) anion as a ligand analogous to \( \text{C}_5\text{H}_5^- \). Perhaps a more useful approach is to view \([\text{Fe}(\text{C}_5\text{H}_5)]^- \) as a replacement for a BH fragment, i.e., a species which, like BH, provides three orbitals and two electrons. In other words, we might predict that we can replace the BH unit with any anion that is isoelectronic with it (Chapter 15). Possibilities include (in addition to \([\text{Fe}(\text{C}_5\text{H}_5)]^- \), \( \text{Co(CO)}_5 \), \( \text{Ni(CO)}_4 \), \( \text{AlBr} \), or \( \text{Se(II)} \)) (the transition metal fragments are 14-electron species, four electrons short of 18, and the nontransition metal units are four electrons short of an octet). Similarly, one could imagine a CH unit of a carborane being replaced by a species which can provide three orbitals and three electrons. Fitting this description are \( \text{CO(CO)}_3 \), \( \text{Ni(CO)}_4 \), and \( \text{P} \). In Table 16.2 are listed organometallic fragments and the number of electrons each can provide to a framework structure. You can construct your own table by remembering that each transition metal has two electrons associated with it that are reserved for nonframework bonding.\(^{118}\) Electrons in excess of twelve can be contributed to the framework (thus the 14-electron species contribute two electrons each, and the 15-electron species contribute three electrons, etc.). If there are fewer than twelve electrons in the fragment, the framework must make up the difference (e.g., \( \text{Mn(CO)}_4 \), an 11-electron species, is assigned a framework contribution of -1).

\[\text{Mn(CO)}_4 \]

\(\text{Mn} = \text{Mn,} \; \text{a} = 1 \; \text{and} \; \text{M} = \text{Co,} \; \text{a} = 1 \; \text{are isoelectronic with ferrocene and cobalocenium ion,} \; \text{M} = \text{Fe,} \; \text{a} = 1 \; \text{is isoelectronic with ferrocenium ion; (b) mixed carbollyl-cyclopentadienyl analogue of ferracene,} \; n = 1 \; \text{is isoelectronic with ferrocene-carbonyl compound,} \; \text{M = Mn,} \; \text{Re,} \; (\text{c}) \; \text{mixed carbollyl-carbonyl ion;} \; \text{M = Fe.} \]
Examples:

1. \( \text{Cl} \rightarrow \text{N} \rightarrow \text{X} \rightarrow \text{Cl} \)
2. \( \text{Cl} \rightarrow \text{N} \rightarrow \text{X} \rightarrow \text{Cl} \)

Octahedral coordination systems (OC-6). The configuration index consists of two digits. The first digit is the priority number of the ligating atom trans to the ligating atom of priority number 1. These two ligating atoms define the reference axis of the octahedron. The second digit of the configuration index is the priority number of the ligating atom trans to the ligating atom with the lowest priority number (most preferred) in the plane that is perpendicular to the reference axis.

Examples:

1. \((\text{OC-6} - 22) - \text{trinmminetrinitrocobul(formerly fac-isomer)}\)
2. \((\text{OC-6-2I} > \text{lriumminctrinitrocobal(( formerly /}

Formulae and Names for Chelate Complexes

Designation of the ligating atoms in a polydentate ligand

Donor atom symbol as the index. A polydentate ligand possesses more than one donor site, some or all of which may be involved in coordination. Thus, dihydroxolate anion conceivably may be attached through S or O, and these were distinguished by diolato-S,3\(^{3}\) and diolato-O,6\(^{3}\), respectively.

Examples:

1. \(\text{Ni} \rightarrow \text{S} \rightarrow \text{O} \rightarrow \text{S} \rightarrow \text{O} \)
2. \(\text{Pt} \rightarrow \text{S} \rightarrow \text{O} \rightarrow \text{S} \rightarrow \text{O} \)

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2. \(\text{Pt} \rightarrow \text{S} \rightarrow \text{O} \rightarrow \text{S} \rightarrow \text{O} \)

The kappa convention. As the complexity of the ligand name increases, a more general system is needed to indicate the points of ligation. In the nomenclature of polydentate chelate complexes, single ligation atom attachments of a polyatomic ligand to a coordination center are indicated by italic element symbols preceded by a Greek kappa, \(\kappa\). Monodentate ambident ligands provide simple examples, although for these cases the kappa convention is not significantly more useful than the 'donor atom symbol' convention [above\(^{34}\)]. Nitrogen-bonded NCS [formerly isothiocyanato] is thiocyanato-\(\kappa\) and sulfur-bonded NCS is thiocyanato-\(\kappa\). Nitrogen-bonded nitrite [formerly nitro] is named nitrito-\(\kappa\) and oxygen-bonded nitrite is nitrito-\(\kappa\), i.e., \(\text{O} = \text{N} - \text{O} - \text{Co(NH}_3)_2^{2+}\) is pentaa'mmine-\(\kappa\)nitrito-\(\kappa\)cobalt(III) ion.

For polydentate ligands, a right superscript numeral is added to the symbol \(\kappa\) in order to indicate the number of identically bound ligation atoms in the \(\kappa\)ligand. Any doubling prefixes, such as bis-, are presumed to operate on the \(\kappa\)locant index as well.

Examples [1 and 2] use tridentate chelation by the linear triammine ligand, \(\text{N}_3\text{N}^\text{III}-\text{N}^\text{III}-\text{N}^\text{III}-1,2\text{-ethanediamine}\) to illustrate these rules.

Examples:

1. \(\text{Ni} \rightarrow \text{S} \rightarrow \text{O} \rightarrow \text{S} \rightarrow \text{O} \)
2. \(\text{Pt} \rightarrow \text{S} \rightarrow \text{O} \rightarrow \text{S} \rightarrow \text{O} \)

Stereochemical descriptors for chelated complexes. Stereochemical descriptors can be provided for compounds containing chelated ligands but they involve considerations beyond those described above. The polyhedral symbol is determined as in the case of monodentate ligand derivatives. Also, the priority numbers are assigned to ligation atoms as for monodentate ligands. However, a general treatment for the assignmenl of the configuration index requires the use of priming conventions in order to provide

\[\text{[N}_3\text{N}^\text{III}-\text{N}^\text{III}-\text{N}^\text{III}-1,2\text{-ethanediamine-3Cl},\text{II})\text{Pt(NH}_3)_2^{2+}\text{Cl}_2\text{Pt(NH}_3)_2^{2+}}\]

33 The chief advantage of the kappa convention seems to be that it unambiguously denotes ligation atoms in a complex ligand. This distinguishes the ligation atom in an organic ligand that may have organic descriptors, as in \(\text{N}_3\text{N}^\text{N}^\text{III}-\text{N}^\text{III}-\text{N}^\text{III}-1,2\text{-ethanediamine}\).

34 Any chelating ligand capable of binding with more than one set of donor atoms is described as \text{flexidentate}, cf., Stratton, W. J.; Busch, D. H. \text{J. Am. Chem. Soc.} 1969, 91, 3994.
 framework electrons (€) equal the number of metal valence electrons (M) plus the number of electrons donated by ligands (L) minus twelve (F = M + L - 12).

\[ \text{Framework electrons} = M + L - 12 \]

One of our goals here is to be able to predict the structure of a cage or cluster from its molecular formula. We do this by first finding the number of framework electrons. The structure will then be predicted to be \textit{closo}, \textit{nido}, or \textit{arachno} if the number of framework electrons is \(2n + 2\), \(2n + 4\), or \(2n + 6\), respectively. As an example let us consider \(B_4H_8\) \(\text{Fe(CO)}_7\) \(\text{H}_2\), for which \(n\) equals five. The three \(\text{Fe(CO)}_5\) units contribute two electrons each and the four extra hydrogen atoms contribute one electron each to give a total of 14 framework electrons:

\[ \text{2(Fe(CO)}_5 \text{)} + 4H = 6e^- \]
\[ \text{3BH} = 6e^- \]
\[ \text{Total} = 14e^- \]

Since \(n = 5\), we see that there are \(2n + 4\) framework electrons and we predict a \textit{nido} structure which is found experimentally. The square pyramidal structure (Fig. 16.54) can be thought of as resulting from substitution of two BH units with two \(\text{Fe(CO)}_5\) units in \(B_6H_6\) (Fig. 16.49a).

Let us apply these procedures to the anhydride, \(\text{Rh}_6\text{(CO)}_{12}\), for which \(n\) equals six. Each of the six \(\text{Rh(CO)}_5\) units contribute one electron to the framework, while the four extra CO molecules provide eight electrons:

\[ \text{6Rh(CO)}_5 \text{)} + 4\text{CO} = 6e^- \]
\[ \text{Total} = 14e^- \]

Thus we have 14 framework electrons with the complex fitting the \(2n + 2\) category and predicted to have a \textit{closo} structure (Fig. 15.10). There are two terminal CO groups per rhodium and four bridging carbonyl groups which span alternate triangular faces. Another method for obtaining the number of framework electrons starts by counting the valence electrons of all of the metal atoms and then adds all of the electrons donated by the ligands:

\[ \text{5Rh} \times 6 = 30e^- \]
\[ \text{6CO} \times 2 = 12e^- \]
\[ \text{Total} = 42e^- \]

Twelve of these electrons per rhodium (a total of 72) will be used for nonframework bonding leaving 14 for framework bonding. Thus there are seven bonding pairs in the framework corresponding to \(2n + 2\) electrons and, as above, a \textit{closo} structure is predicted. It is worth noting that the 18-electron rule fails for \(\text{Rh}_6\text{(CO)}_{12}\), while Wade's rules are entirely successful.

There are exceptions to Wade’s rules, even among modest-sized clusters (see Footnote 135). In some cases large transition metals cause geometrical distortion. In others, a kinetically favored structure may not be able to rearrange to a more thermodynamically favored one. In still other instances the assumption that transition metal atoms will use twelve electrons for external ligands is not valid. As with most rules, one should not expect predictions to be foolproof.

The bonding capabilities of transition metal clusters (no nonmetals in the framework), based on molecular orbital calculations, has been nicely summarized by Lauher (Table 16.3). Within this table we see three structures (tetrahedron, butterfly, and square plane) for tetranuclear metal clusters. The tetrahedron is a 60-electron cluster, while the butterfly and square plane clusters have 62 and 64 electrons, respectively. When we go from a tetrahedron to a butterfly, one of the edges of the tetrahedron is lengthened corresponding to bond breaking.

\[ \text{Table 16.3} \]

<table>
<thead>
<tr>
<th>Geometry</th>
<th>No. of metal atoms</th>
<th>Bonding molecular orbitals</th>
<th>Cluster electrons</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomer</td>
<td>1</td>
<td>9</td>
<td>18</td>
<td>Ni(CO)₅</td>
</tr>
<tr>
<td>Dimer</td>
<td>2</td>
<td>17</td>
<td>34</td>
<td>Fe(CO)₅</td>
</tr>
<tr>
<td>Trimer</td>
<td>3</td>
<td>24</td>
<td>48</td>
<td>Os₂(CO)₁₄</td>
</tr>
<tr>
<td>Tetrahedron</td>
<td>4</td>
<td>30</td>
<td>60</td>
<td>Rh₄(CO)₁₂</td>
</tr>
<tr>
<td>Butterfly</td>
<td>4</td>
<td>31</td>
<td>62</td>
<td>Re₄(CO)₁₂</td>
</tr>
<tr>
<td>Square plane</td>
<td>4</td>
<td>32</td>
<td>64</td>
<td>Pt₂(CO)₂Me₂</td>
</tr>
<tr>
<td>Trigonal bipyramid</td>
<td>5</td>
<td>36</td>
<td>72</td>
<td>Os₂(CO)₁₄</td>
</tr>
<tr>
<td>Square pyramid</td>
<td>5</td>
<td>37</td>
<td>74</td>
<td>Fe₂(CO)₁₄</td>
</tr>
<tr>
<td>Bicapped tetrahedron</td>
<td>6</td>
<td>42</td>
<td>84</td>
<td>Os₄(CO)₁₆</td>
</tr>
<tr>
<td>Octahedron</td>
<td>6</td>
<td>43</td>
<td>86</td>
<td>Rh₆(CO)₂₆</td>
</tr>
<tr>
<td>Capped square pyramid</td>
<td>6</td>
<td>43</td>
<td>86</td>
<td>Os₄(CO)₁₆</td>
</tr>
<tr>
<td>Trigonal prism</td>
<td>6</td>
<td>45</td>
<td>90</td>
<td>Rh₆(CO)₁₆</td>
</tr>
<tr>
<td>Capped octahedron</td>
<td>7</td>
<td>49</td>
<td>98</td>
<td>Rh₆(CO)₂₆</td>
</tr>
</tbody>
</table>

\[ ^{135} \text{Lauher, J. W. J. Am. Chem. Soc. 1978, 100, 5305-5315. All framework atoms are transition metals.} \]
These affixes are italicized and separated from the rest of the name by hyphens.

- antiprismo: eight atoms bound into a rectangular antiprism
- antihexagonal: a hexagonal antiprism between two faces
- asym: asymmetrical; often used to designate linear polymeric substances
- cis: two groups occupying adjacent positions, not now generally recommended for precise nomenclature purposes
- close: a cage or closed structure, especially a boron skeleton that is a polyhedron having all faces triangular
- cyclo: a ring structure. Cycle here used as a modifier indicating structure and hence is italicized. In organic nomenclature, 'cyclo' is considered to be part of the parent name since it changes the molecular formula, and therefore is not italicized.
- dodecahedro: eight atoms bound into a dodecahedron with triangular faces
- fac: three groups occupying the corners of the same face of an octahedron, not now generally recommended for precise nomenclature purposes
- hexahedro: twelve atoms bound into a hexahedron (e.g., cube)
- hexagonal: an open structure, especially a boron skeleton, more closed than a kalado-structure, but more open than an ortho-structure
- icosaedro: twelve atoms bound into a triangular icosahedron
- klan: a very open polyhedron structure
- mer: three groups occupying vertices of an octahedron; more open than a klado-structure, more closed than a hexahedro-structure.
- nido: a nest-like structure, especially a boron skeleton that is almost closed
- octahedro: six atoms bound into an octahedron
- pentagonal: ten atoms bound into a pentagonal prism
- quadru: four atoms bound into a quadrilateral (e.g., square)
- sym: symmetrical
- tetrahedro: four atoms bound into a tetrahedron
- trans: two groups directly across a central atom from each other, i.e., in the polar positions on a sphere, not now generally recommended for precise nomenclature purposes
- triangulo: three atoms bound into a triangle
- tripiano: six atoms bound into a triangular prism
- μ (mu): signifies that a group so designated bridges two or more centers of coordination
- A (lambda): signifies, with its subscript, the bonding number, i.e., the sum of the number of skeletal bonds and the number of hydrogen atoms associated with an atom in a parent compound

Parentheses, and separated from the name by a hyphen. The polyhedral symbols for the most common coordination geometries for coordination numbers 2 to 9 inclusive are given in Table 1-7.

### Configuration index

**Definition of index and assignment of priority numbers to ligating atoms.** Having developed descriptors for the general geometry of coordination compounds, it becomes necessary to identify the individual coordination positions. The configuration index is a series of digits identifying the positions of the ligating atoms on the vertices of the coordination polyhedron. The individual configuration index has the property that it distinguishes between diastereoisomers. The digits of the configuration index are established by assigning an order of priority to the ligating atoms as described below.

The procedure for assigning priority numbers to the ligating atoms of a mononuclear coordination system is based on the standard sequence rule developed for enantiomeric carbon compounds by Cahn, Ingold, and Prelog. The ligating atom with highest priority is assigned the priority number 1, the ligating atom with the next highest priority 2, and so on.

### Configuration indexes for particular geometries

**Square planar coordination systems (SP-4).** The configuration index is a single digit which is the priority number for the ligating atom in the ligating atom of priority number 4.

### Table 1-7: List of polyhedral symbols

<table>
<thead>
<tr>
<th>Coordination polyhedron</th>
<th>Coordination number</th>
<th>Polyhedral symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Square planar</td>
<td>2</td>
<td>L-2</td>
</tr>
<tr>
<td>Angular</td>
<td>2</td>
<td>A-2</td>
</tr>
<tr>
<td>Trigonal plane</td>
<td>3</td>
<td>TPR-3</td>
</tr>
<tr>
<td>Trigonal pyramid</td>
<td>3</td>
<td>TPR-3</td>
</tr>
<tr>
<td>Tetrahedron</td>
<td>4</td>
<td>T-4</td>
</tr>
<tr>
<td>Square plane</td>
<td>4</td>
<td>SP-4</td>
</tr>
<tr>
<td>Trigonal bipyramid</td>
<td>5</td>
<td>TBP-5</td>
</tr>
<tr>
<td>Square pyramid</td>
<td>5</td>
<td>SPY-3</td>
</tr>
<tr>
<td>Octahedron</td>
<td>6</td>
<td>OC-6</td>
</tr>
<tr>
<td>Trigonal prism</td>
<td>6</td>
<td>TPR-6</td>
</tr>
<tr>
<td>Pentagonal bipyramid</td>
<td>7</td>
<td>PBPY-7</td>
</tr>
<tr>
<td>Octahedron, face monocapped</td>
<td>7</td>
<td>OCF-7</td>
</tr>
<tr>
<td>Trigonal prism, square face monocapped</td>
<td>7</td>
<td>TPR-7 &amp; OCT-8</td>
</tr>
<tr>
<td>Cube</td>
<td>8</td>
<td>CU-8</td>
</tr>
<tr>
<td>Square antiprism</td>
<td>8</td>
<td>SAPP-8</td>
</tr>
<tr>
<td>Trigonal prism, triangular face bicapped</td>
<td>8</td>
<td>TPR-8</td>
</tr>
<tr>
<td>Trigonal prism, square face bicapped</td>
<td>8</td>
<td>TPR-8</td>
</tr>
<tr>
<td>Trigonal prism, square face tricapped</td>
<td>9</td>
<td>TPR-9</td>
</tr>
<tr>
<td>Hexagonal bipyramid</td>
<td>9</td>
<td>HPBPY-9</td>
</tr>
<tr>
<td>Dodecahedron</td>
<td>8</td>
<td>DD-8</td>
</tr>
<tr>
<td>Hexagonal bipyramid</td>
<td>8</td>
<td>HPBPY-8</td>
</tr>
<tr>
<td>Octahedron, trans-bicapped</td>
<td>8</td>
<td>OCT-8</td>
</tr>
</tbody>
</table>

[Note that the term used to distinguish between the three names of a square planar coordination entity (M) is not included.]

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A-70 IUPAC Recommendations on the Nomenclature of Inorganic Chemistry A-71
Inorganic Chains, Rings, Cages, and Clusters

To do this, two additional electrons must be added to the tetrahedron to keep all electrons paired. In fact this is a general principle: Adding electrons to a closo complex opens the structure, converting it to one of lower symmetry. The butterfly structure results when an edge is removed from the tetrahedron.

If we add two electrons to the butterfly structure, another edge is lengthened (another bond broken) and we end up with a square plane.

These principles apply equally well to heteronuclear clusters which can be illustrated with the trigonal bipyramidal cluster of ruthenium and sulfur, [(η5-cymene)Ru3S2]2+. This 48-electron closo cation (24 electrons from three Ru atoms, 18 electrons from three η5-cymene molecules, and eight electrons from two S atoms) may be reduced reversibly to the 50-electron square pyramidal nido cluster by adding two electrons as shown in Fig. 16.55. Both the closo and nido clusters have been isolated and characterized crystallographically. The average Ru—Ru bond distance in the closo structure is 277.8 pm, corresponding to three Ru—Ru single bonds. The nido structure has two Ru—Ru single bonds (272.3 pm) intact, and one bond severed as shown by the longer Ru—Ru distance (361.2 pm).

As you become more familiar with transition metal clusters (no nonmetals in the framework) you will come to associate closo structures with numbers of electrons. A trimer will have 48 electrons, a tetrahedron will have 60 electrons, a trigonal bipyramid will have 72 electrons, and an octahedron will have 86. Some care is required, however, as can be illustrated with Os2(CO)10; an electron count gives us 46 electrons rather than 48. If, however, we allow for one Os—Os double bond, the electron count is as expected. In accord with this expectation, one osmium—osmium bond is found to be shorter than the other two and the complex shows the reactivity expected for an unsaturated complex.

Fig. 16.55 The Ru3S2 core in [η5-cymene]Ru3S2 (left) and its closo [η5-cymene]Ru3S22+ (right). Two electrons attached to ruthenium as six-electron donors are not pictured. Two-electron reduction converts the complex from a closo to a nido geometry.


Some of the beautiful relationships that exist between closo, nido, and anidino osmium complexes are shown in Fig. 16.56.143 For lack of space we have not touched on many subtleties associated with geometry/bonding/electron counting procedures and the reader is encouraged to consult more advanced sources.144

Metal Clusters145

Some of the beautiful relationships that exist between closo, nido, and anidino osmium complexes are shown in Fig. 16.56.143 For lack of space we have not touched on many subtleties associated with geometry/bonding/electron counting procedures and the reader is encouraged to consult more advanced sources.144

Metal Clusters145

Compounds containing metal-metal bonds are as old as chemistry itself (calomel was known to the chemists of India as early as the twelfth century). The dimeric nature of the mercurous ion was not confirmed until the turn of this century and in the next

143 McPartlin, M. Polyhedron 1984, 3, 1279-1286.
Names for Mononuclear Coordination Compounds with Monodentate Ligands

Sequence of central atom and ligand name. The ligands are listed in alphabetical order, without regard to charge, before the names of the central atom. Numerical prefixes indicating the number of ligands are not considered in determining that order.

Examples:
1. dichloro(diphenylphosphine)dichloro(platinum(II))
2. dichloro(benzyl(triphenylphosphine))platinum(II))

Number of ligands in a coordination entity. Two kinds of numerical prefix are available for indicating the number of each kind of ligand within the name of the coordination entity (see Table 1-1). The simple di-, tri-, etc., derived from cardinal numerals, are generally recommended. The prefixes bi-, tri-, tetra-, etc., derived from ordinals, are used with complex expressions and when required to avoid ambiguity; for example, one would use di(exo)- and tri(methyl)amine to make a distinction from diamine diol.

When the latter multiplicative prefixes are used, enclosing marks are placed around the multiplicand. Enclosing marks are not required with the simpler prefixes di-, tri-, etc. There is no elision of vowels or use of a hyphen in tetraammine and similar names, except for compelling linguistic reasons.

Terminations for names of coordination entities. All anionic coordination entities take the ending -ate, whereas no distinguishing termination is used for cationic or neutral coordination entities.

Charge numbers, oxidation numbers, and ionic proportions. When the oxidation number of the central atom can be defined without ambiguity, it may be indicated by appending a roman numeral to the central atom name. No space is left between this number and the rest of the name. When the latter multiplicative prefixes are used, enclosing marks are placed around the multiplicand. Enclosing marks are not required with the simpler prefixes di-, tri-, etc. There is no elision of vowels or use of a hyphen in tetraammine and similar names, except for compelling linguistic reasons.

Examples:
1. K₂[Fe(CN)₆] potassium hexacyanoferrate(III)
2. [Co(NH₃)₆]Cl₂ hexaaquachromium(III) chloride
3. [CoCl₂(NH₃)₄]Cl₃ pentaaqua(trichloroplatinato)platinum(II) chloride
4. [CoCl₄(NH₃)₂]Cl₂ diammonioaquachromium(II) chloride
5. K₂[PtCl₄(NH₃)] potassium tetrachloroplatinato(II) chloride
6. Na₂[PtCl₆(NH₃)₂] sodium amminebromochloronitrito/Platinum(II) chloride
7. K₂(RuCl₄(NH₃)₂)₂ potassium tetrachloroplatinato(II) chloride
8. K₂[PtCl₆(NH₃)₂] sodium amminebromochloronitrito/Platinum(II) chloride
9. Na₂[PtCl₆(NH₃)₂] sodium amminebromochloronitrito/Platinum(II) chloride
10. [Fe(CN)₆]Cl₂ hexacyani(methanooxy)iron(III) chloride
11. Ru(K₂SO₄)[Ni(NH₃)₆] tetrachloromethanooxyhydrogenosmium(III) chloride
12. [Co(H₂O)₆(NH₃)₂]Cl₃ tetrachloroamminediasococobalt(III) chloride

Stereochemical Descriptors

Different geometric arrangements of the atoms attached to the central atom are possible for all coordination numbers greater than one. The coordination polyhedron (or polyhedron in planar molecules) may be denoted in the name by an affix called the polyhedral symbol. This descriptor clearly distinguishes isomers differing in the geometries of their coordination polyhedra.

Given the same coordination polyhedron, diastereoisomerism can arise when the ligands are not all alike as with the cis and trans isomers of tetrachlorodichloro-chromium(III), diaminoo dichloroplatinum(II), and bis-octahydrazonecobalt(III) (Examples 1-6).

Examples:
1. cis-isomer
2. trans-isomer
3. cis-isomer
4. trans-isomer
5. cis-isomer
6. cis-isomer

Attempts to produce descriptors similar to cis and trans for stereochemically more complicated coordination entities have failed to achieve generality, and labels such as cis and trans are no longer recommended. Nevertheless, a diastereoisomeric structure may be indicated for any polyhedron using a configuration index as an affix to the name or formula. Finally, the characteristics of transition structures can be indicated using chirality symbols.

Polyhedral symbol. The polyhedral symbol indicates the geometrical arrangements of the coordinating atoms around the central atom. It consists of one or more capital italic letters derived from common geometric terms which denote the idealized geometry of the ligands around the coordination center, and an arabic numeral that is the coordination number of the central atom. The polyhedral symbol is used as an affix, enclosed in parentheses after the part of the name denoting the central atom. No positive sign is used.

Stereochemical descriptors and structural prefixes may be found in Table 1-6.

Footnotes:
1. [A list of stereochemical descriptors and structural prefixes may be found in Table 1-6.]
2. [Note that American chemists would not indicate cis and trans for fac and mer when not part of a name, nor hyphenate "trans isomer." See also Footnotes 33 and 34.]
Compounds duction (with $\text{H}_2$ or PhClO$_2$) of perrhenate in the presence of $X^-$, H$_2$PO$_4^-$.

The best-studied binuclear species are $\text{Re}_2$X$_4$ ions. They may be prepared by reduction of class I compounds,

$$2\text{ReO}_7^{2-} + \text{H}_2 + 2\text{Cl}_2 \rightarrow \text{Re}_2\text{Cl}_4 + 2\text{HCl}$$

$m = 1$, Br, I, NCS

The most interesting aspect of these compounds is their structure (Fig. 16.37), which possesses two unusual features. The first is the extremely short Re—Re distance of 224 pm compared with an average Re—Re distance of 275 pm in rhenium metal and 248 pm in Re$_2$Cl$_6$. The second unexpected feature is the eclipsed configuration of the chlorine atoms. One might have supposed that since the short Re—Re bond requires $\text{d}^5$ dsp$^3$ hybrids on each rhenium atom, it would be described as a square planar array (the Re is 50 pm out of the plane of the four Cl atoms). We may take the Re—Cl bonds to involve approximate $\text{d}^{10}$ hybrids on each metal utilizing the $\text{d}_{z^2}$ orbital. The metal $\text{d}_{z^2}$ orbitals lie along the bond axis and may be hybridized to form one orbital directed toward the other rhenium atom and a second orbital directed in the opposite direction. The former can overlap with the similar orbital on the second rhenium atom to form a $\pi$ bond (Fig. 16.38a), while the second hybrid orbital forms an approximately nonbonding orbital.

Fig. 16.38 Multiple bonding between rhenium atoms: (a) Formation of a $\pi$ bond from overlap of $\text{d}^{10}$ orbitals of each rhenium atom. (b) Formation of a $\sigma$ bond from overlap of the $\text{d}_z^2$ orbital of one rhenium atom with a $\text{d}_z^2$ orbital of the other rhenium atom. A second $\sigma$ bond forms in the $y$ plane. (c) Positive overlap from $\text{d}_{z^2}$ orbitals to form a $\sigma$ bond in the eclipsed conformation. (d) Zero overlap occurring in the staggered conformation. (e) Part from Cotton, F. A. Acc. Chem. Res. 1969, 2, 240. Reproduced with permission.)
The $d_{x^2}$ and $d_{y^2}$ orbitals of each rhenium are directed obliquely toward their counterparts on the other rhenium and can overlap to form two $\sigma$ bonds (Fig. 16.58a), one in the $xy$ plane and one in the $yz$ plane. A fourth bond can now form by “sideways” overlap of the remaining two $d$ orbitals, a $d_{z^2}$ on each rhenium, the result being a $\delta$ bond. Overlap of the $d_{xy}$ orbitals can only occur if the chlorine atoms are eclipsed (Fig. 16.58c). If the chlorine atoms are staggered, the two $d_{xy}$ orbitals will likewise be staggered with resulting zero overlap (Fig. 16.58d).

The Re—Cl bonds in the complex may be regarded as dative bonds between the $d^6$ ligands and Re$^{2+}$ (d$^5$) ions. The eight $d$ electrons from the two metals will occupy the two $\sigma$ bonding, two $\pi$ bonding, and one $\delta$ bonding orbitals to form the quadruple bond. Hence the complex is diamagnetic, in accord with the bond order of 4.0. Re$^2+$, with 16 $d$ electrons, and $\delta$ bonding molecular orbitals filled. There are no antibonding orbitals for the quadruple bond.

The $\delta$ bonding molecular orbitals are filled only when the $\pi$ and $\pi^*$ orbitals are empty, and it would be expected that electrons could be added to the $\delta$ bonding molecular orbitals filled (Fig. 16.60c). Both $\delta$ and $\delta^*$ orbitals are nonbonding, however, and it would be expected that electrons could be added to the $\delta^*$ level or removed from the $\delta$ level without too much loss in stability. In keeping with this expectation, Re$_2$Cl$_4$(PMe$_2$Ph)$_2$ (Table 16.60d) and Re$_2$Cl$_4$(PMe$_3$Ph)$_2$ (Table 16.60e) which have occupied antibonding orbitals have been synthesized. In addition, [Re$_2$(CO)$_6$Cl]$_2$ (Table 16.60f) and [Re$_2$(HPO$_3$)$_2$Cl]$_2$ (Table 16.60g)

$$\text{Re}_2\text{Cl}_4 + 2\text{MeCOOH} \rightarrow \text{Re}_2(\text{MeCOOH})_2\text{Cl}_4 + 4\text{H}^+ + \text{Cl}^-$$

$$\text{Re}_2\text{Cl}_4 + 4\text{MeCOOH} \rightarrow \text{Re}_2(\text{MeCOOH})_2\text{Cl}_2 + 6\text{H}^+ + 2\text{Cl}^-$$

$$\text{Re}_2(\text{MeCOOH})_2\text{Cl}_2 + 4\text{PhCOOH} \rightarrow \text{Re}_2(\text{PhCOOH})_2\text{Cl}_2 + 4\text{MeCOOH}$$

$$\text{2MeCOOH} + \text{4MeCOOH} \rightarrow \text{Me}_2(\text{MeCOOH})_2 + 12\text{CO} + 2\text{H}_2$$

Structurally these complexes (Fig. 16.59) are closely related to [Re$_2$Cl$_4$]$^{2-}$, the only difference being (for the rhenium complexes) the addition of ligands to overlap with the metal $d$ hybrid orbitals which were nonbonding in [Re$_2$Cl$_4$]$^{2-}$.

Although Cotton's molecular orbital scheme was largely qualitative, based on an approach involving a combination of atomic orbitals, a variety of theoretical studies

Fig. 16.59. Molecular structures of some carboxylic complexes containing metal-metal bonding: (a) Re—Re = 229 pm, X = Cl, Br, I; (b) Re—Re = 229 pm, X = Br, Cl, L = (1) X; (c) X = Br, Cl, L = (1) X, (2) Me$_2$-NC$_5$H$_4$; (d) X = Br; (e) X = Br, Cl, L = C$\equiv$C-C$_6$H$_5$; (f) X = Cl, Br, I, L = C$\equiv$C-C$_6$H$_5$. Re—Re bond lengths are averages; individual values are known to greater accuracy.


104. Experimental determined electron densities and bond orders are consistent with the quadruple bond picture. Pauling's model has provided an alternative, valence bond treatment of the quadruple bond involving $\alpha$ and $\pi$ hybrid orbitals and four equivalent bond pairs. His model also explains the experimental facts described above and provides a good estimate of the bond length.

The strength of the quadruple bond in dirhenium and dimolybdenum compounds has been a matter of considerable difference of opinion. Early estimates of the bond energy ranged from as low as 300 kJ mol$^{-1}$ (weaker than a C—C single bond) to as high as 1500 kJ mol$^{-1}$ (stronger than any other known bond). Recent studies indicate that for 3$d$ elements the bond energy lies in the 400-1000 kJ mol$^{-1}$ range, while for 4$d$ and 5$d$ elements values fall between 250 and 450 kJ mol$^{-1}$. The relative weakness of these quadruple bonds may seem paradoxical, but we should recognize that comparing them with multiple bonds between small atoms which utilize $p$ orbitals is not valid because $p$ orbitals provide superior overlap and lead to inherently stronger bonds.

The Re$_2$Cl$_4$$^{2-}$, with its quadruple bond, is an example of a complex with all of its bonding molecular orbitals filled (Fig. 16.60c). Both $\delta$ and $\delta^*$ orbitals are nearly nonbonding, however, and it would be expected that electrons could be added to the $\delta^*$ level or removed from the $\delta$ level without too much loss in stability. In keeping with this expectation, Re$_2$Cl$_4$(PMe$_2$Ph)$_2$ (Table 16.60d) and Re$_2$Cl$_4$(PMe$_3$Ph)$_2$ (Table 16.60e) which have occupied antibonding orbitals have been synthesized. In addition, [Re$_2$(CO)$_6$Cl]$_2$ (Table 16.60f) and [Re$_2$(HPO$_3$)$_2$Cl]$_2$ (Table 16.60g)
Coordination number. As defined for typical coordination compounds, the coordination number equals the number of sigma-bonds between ligands and the central atom. Even though simple ligands such as CN⁻, CO, N₂, and P(CH₃)₃ may involve both sigma- and pi-bonding between the ligating atom and the central atom, the pi-bonds are not considered in determining the coordination number.

The sigma-bonding electron pairs in the following examples are indicated by : before the ligand formula.

Examples:

<table>
<thead>
<tr>
<th>Complex</th>
<th>Coordination number</th>
<th>Complex</th>
<th>Coordination number</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(NH₃)₆]Cl²⁻</td>
<td>6</td>
<td>[Fe(CN)₅]²⁻</td>
<td>6</td>
</tr>
<tr>
<td>[Ru(NH₃)(NH₂)Cl]⁺</td>
<td>6</td>
<td>[Ni(CO)₄]¹⁻</td>
<td>4</td>
</tr>
<tr>
<td>[Cr(CO)₆]⁻</td>
<td>6</td>
<td>[Co(CN)₅Cl]⁻</td>
<td>4</td>
</tr>
</tbody>
</table>

Chelation. Chelation involves coordination of more than one sigma-electron pair donor group from the same ligand to the same central atom. The number of such ligating groups in a single chelating ligand is indicated by the adjectives didentate, tridentate, etc. (see Table 1-3 for a list of numerical prefixes). The number of donor groups from a given ligand attached to the same central atom is called the denticity.

Examples:

1. diiminate chelation
2. tricate chelation
3. triiminate chelation
4. tericate chelation

Oxidation number. The oxidation number of a central atom in a coordination entity is defined as the charge it would bear if all the ligands were removed along with the electron pairs that were shared with the central atom. It is represented by a roman numeral.

Examples:

1. Addition of ligands to a central atom: Ni²⁺ + 6H₂O → [Ni(H₂O)₆]²⁺

Coordination nomenclature, an additive nomenclature. According to a useful, historically-based formulation, coordination compounds are considered to be produced by adding

ion rections and so they named on the basis of an additive principle. The name is build up around the central atom name, just as the coordination entity is built up around the central atom.

Example:

1. Addition of ligand to a central atom: Ni²⁺ + 6H₂O → [Ni(H₂O)₆]²⁺

Addition of ligands to a central atom name: hexaammoni(II) ion

This nomenclature extends to more complicated structures where central atoms are added together to form dinuclear, trimuclear, and even polymeric species from some mononuclear building blocks. The persistent centrality of the central atom is emphasized by the root-nuclear.

Bridging ligands. In polymeric species it is necessary to distinguish yet another ligand behavior, the action of the ligand as a bridging group.

A bridging ligand bonds to two or more central atoms simultaneously. Thus, bridging ligands link central atoms together to produce coordination entities having more than one central atom. The number of central atoms joined into a single coordination entity by bridging ligands or metal-metal bonds is indicated by dinuclear, trimuclear, tetranuclear, etc.

Examples:

1. Br₂[Cr(CN)₅]Cl⁻ Cl⁻ • Al³⁺
2. [Cr(NH₃)₅Cl]Cl
3. [Co(OH)(en)NH(NH₂)]Cl⁻ Al³⁺

Formulæ for Mononuclear Coordination Compounds with Monodentate Ligands

Sequence of symbols within the coordination formula. The central atom is listed first. The formally anionic ligands appear next and they are listed in alphabetical order according to the first symbols of their formulae. The neutral ligands follow, also in alphabetical order, according to the same principle. Polydentate organic ligands may be designated in formulæ with abbreviations (Table 1-5).

Uses of enclosing marks. The formula for the entire coordination entity, whether charged or not, is enclosed in square brackets. When ligands are polyatomic, their formulae are enclosed in parentheses. Ligand abbreviations are also enclosed in parentheses. In the special case of coordination entities, the nesting order of enclosures is as given on page A-31. There should be no space between representations of ionic species within a coordination formula.

Examples:

1. [Co(NH₃)₆]Cl²⁻ 2. [Co(NH₃)₅Cl]Cl 3. [Co(NH₃)₅(NH₂)]Cl
4. [Co(NH₃)₅H₂O]Cl 5. K₂[Cr(CN)₅] 6. [Co(NH₃)₅Cl]Cl

Ionic charge and oxidation numbers. If the formula of a charged coordination entity is to be written without that of the counterion, the charge is indicated outside the square brackets as a right superscript, with the number before the sign. The oxidation number of a central atom may be represented by a roman numeral used as a right superscript on the central element.

Examples:

1. [CrO₂]²⁻ 2. [Cr(H₂O)₅]³⁺ 3. [Cr(NCS)₅(NH₂)]³⁻
Fig. 16.60.) which have less than full occupation of the 8 bonding orbitals have been prepared. The characterization of W$_2$C$_2$(OR)$_2$(R) (R = Me, Et) with a W—W double bond completed a series of ditungsten compounds with bond orders of 4, 3, 2, and 1.

There are two metals, Cu(II) and Cr(II), in the first transition series which form acidic complexes similar in structure to the rhodium and molybdenum carbonyl clusters (Fig. 16.58d). Like their Re and Mo analogues, the Cu and Cr complexes are diamagnetic, indicating that spins are paired. They differ significantly from the complexes of the heavier metals, however. The Cu—Cu distance in the Cu(II) (dp) complex is 264 pm, which is actually somewhat longer than the Cr—Cu distance in metallic copper (256 pm). It appears that the Cu-Cu bond in copper(II) acetate is only a weak single bond resulting from pairing the odd electron on each copper atom.

The chromium(II) acetate molecule was long thought to have the same metal-metal bond length as the copper compound and thus have a similar weak bond. However, its structure was redetermined and the Cr—Cr distance was found to be 236.2 pm, which is considerably shorter than that found in metallic chromium (249.8 pm). In fact, the Cr—Cr bond has been estimated to be about 45 kJ mol$^{-1}$, which makes it stronger than the Cu—Cu bond. All of this evidence and orbital symmetry suitability might suggest that the Cr—Cr bond in chromium acetate is a quadruple bond. Still, not everyone is willing to go that far. The problem is that this "quadruple" bond is estimated to be only about as strong as a typical Cr—Cr single bond. It appears that most participants in the debate have chosen to view the bond as a very weak quadruple bond. Aside from this controversy, the chief interest in these complexes (Fig. 16.58d) is in the nature of the substituent ligands, is in sharp contrast to the relative uniformity in the length of quadruple bonds in the heavier congeners (Mo—Mo = 204–218 pm; W—W = 216–230 pm). Among the more interesting metal-metal multiple bonded complexes are the butadiene: trinuclear clusters.

The best-known examples of noncarbonyl clusters containing three metal atoms are the rhodium trihalides [Rh$_3$(X)$_3$] (X = F, Cl, Br) and their derivatives. The basic structural unit is shown in Fig. 16.62a. Each rhodium atom is bonded to the other two rhodium atoms directly by metal-metal bonds and indirectly by a bridging halogen ligand. In addition, it is possible that this name was proposed the same year that the Chicago Bears choreographed the "Superbowl Shuffle"? The alkoxide group, RO$^-$, has two filled $p$ orbitals capable of donating $p$ electron density to the metal centers. Even so, because these $p$ orbitals are ligand centered, the complexes are looked upon as coordinatively unsaturated and containing formal metal-metal triple bonds (o=1). The M=2M bonds are somewhat analogous to carbon-carbon triple bonds. For example, the metal-metal bond can undergo addition reactions:

$$\text{(i-PrO)}_2\text{Mo}=\text{Mo}(\text{i-PrO})_2 + \text{i-PrOO}-\text{i-Pr} \rightarrow -\text{(i-PrO)}_2\text{Mo}=\text{MoO}-\text{i-Pr}_4$$

It is also possible to prepare (t-BuO)$_2$W=CR (R = Me, Et, Ph) compounds in which the isolobality of CR and W(OR)$_3$ is apparent. It is also possible to prepare (t-BuO)$_2$W=CR (R = Me, Et, Ph) compounds in which the isolobality of CR and W(OR)$_3$ is apparent. It is also possible to prepare (t-BuO)$_2$W=CR (R = Me, Et, Ph) compounds in which the isolobality of CR and W(OR)$_3$ is apparent.

Recently, it has been shown that W$_2$(O-i-Pr)$_4$ dimers, existing in equilibrium with W$_2$(O-i-Pr)$_3$, a molecule which may be thought of as an analogue of cyclobutadiene:

$$\text{W}_2\text{Cl}_2\text{Cl}_2 + 2\text{RC} = \text{CR} \rightarrow \text{W}_2\text{Cl}_2\text{Cl}_2$$

The tetratrimer has been shown to be fluxional such that the tungsten-tungsten double and single bonds migrate about the W$_4$ ring. At the same time, the two isopropoxide groups attached to each tungsten undergo proximal/distant exchange (Fig. 16.61). All of these motions were taken together to be known as "The Bloomington Shuffle" after the city in which it was discovered.

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syllables 'for' and 'ous', respectively, from the acid name when it is converted to the anion name.

**Polymer Acids**

**Isopolyacids (homopolyacids).** These materials are generally referred to in the literature as isopolyacids. The name homopolyacids is preferable because the Greek root of homo- implies 'the same', in direct contrast to that of hetero- signifying 'different', whereas the root of iso- implies equality. Detailed nomenclature of those compounds has been presented elsewhere. 

Acceptable abbreviated names may be given to polyoxoacids formally derived by condensation (with evolution of water) of units of the same mononuclear oxoacid, provided that the central atom of the mononuclear oxoacid has the highest oxidation state of the Periodic Group to which it belongs, that is, V4 for sulfur, etc. The names are formed by indicating with numerical prefixes the number of atoms of central element present. It is not necessary to state the number of oxygen atoms.

**Examples:**
1. $\text{H}_2\text{SO}_4$ - dihydrogen tetraoxosulfate(IV)
2. $\text{H}_4\text{MoO}_7$ - tetrhydrogen hexahydrate
3. $\text{H}_6\text{MoO}_{12}$ - hexahydrogen heptamolybdate
4. $\text{H}_7\text{P}_{2}O_{9}$ - trihydrogen cyclo-triphosphate (tricarboxyphosphoric acid)

**Heteropolyacids.** A detailed nomenclature of those compounds has been given elsewhere. Names are developed using coordination nomenclature (Section 1-10).

**Examples:**
1. $\text{H}_3\text{SiW}_4\text{O}_{12}$ - tetrahydrogen hexahydrato(tetramolybdate)(tetraoxosilicato)dodecatungstate(4 -)
2. $\text{H}_3\text{P}_{2}\text{O}_{7}$ - hexahydrogen diperoxophosphate
3. $\text{H}_{10}\text{SiW}_{18}\text{O}_{49}$ - dodecahydroxosilicato(tetramolybdate)(oxo)dodecatungstate(6 -)

Some abbreviated semitrivial names are retained for present use due to long-standing usage. This applies if all the central atoms are the same, if the polyanion contains only oxygen atoms as ligands and only one kind of heteroatom, and if the oxidation state of the central atom corresponds to the highest oxidation state of the Periodic Group in which they occur. In this usage, the Main Groups atoms receive specific abbreviated names for incorporation into the hetero-polyacid name. These are:
- B: boron
- Si: silicon
- Ge: germanium
- P: phosphorus
- As: arsenic

**Examples:**
1. $\text{H}_3\text{SiW}_4\text{O}_{12}$ - tetrahydrogen hexahydrato(tetramolybdate)(tetraoxosilicato)dodecatungstate(4 -)
2. $\text{H}_3\text{P}_{2}\text{O}_{7}$ - hexahydrogen diperoxophosphate
3. $\text{H}_{10}\text{SiW}_{18}\text{O}_{49}$ - dodecahydroxosilicato(tetramolybdate)(oxo)dodecatungstate(6 -)

**Ions Derived from Oxoacids**

**Anions.** The hydrogen nomenclature name described above consists of two parts, the second of which is an anion name. This can stand alone to represent the anion itself. Traditional names are still accepted for the exceptions listed in (Table 1-4). The ending -ic of the acid name becomes -ate in the anion name, and -ous becomes -ite.

**Cations.** The cations considered here are obtained by adding formally one or more hydrogen cations to a neutral molecule of the acid.

**Example:**
1. $\text{(H}_2\text{SO}_4)^{+}$ - trihydroxosousoxoferric acid$^{+}$ (sulfuric acidium cation)

---

Note that an extension of the organic style of nomenclature as in (CH$_3$CO$_2$H)$_n$ - ethanoic acidinium is discouraged because it is based on the word 'acid' and is often not easily adaptable to languages other than English. 

**1-10 COORDINATION COMPOUNDS**

**Coordination entity.** A coordination entity is composed of a central atom, usually that of a metal, to which is attached a surrounding array of other atoms or groups of atoms, each of which is called a ligand. In formulae, the coordination entity is enclosed in square brackets whether it is charged or uncharged.

**Examples:**
1. [Co(NH$_3$)$_4$Cl$_2$]$^{3+}$
2. [PtCl$_2$(CH$_3$CN)$_2$]$^{2-}$
3. [Fe$_3$(CO)$_6$]$^{6+}$

**Central atom.** The central atom is the atom in a coordination entity which binds other atoms or groups of atoms (ligands) to itself, thereby occupying a central position in the coordination entity. The central atoms in [Ni(CO)$_4$], [Cr(NH$_3$)$_6$]$,^{3+}$ and [PtCl$_2$(CH$_3$CN)$_2$]$^{2-}$ are nickel, cobalt, and platinum, respectively.

**Ligands.** The ligands are the atoms or groups or atoms bound to the central atom. The root of the word is often converted into other forms, such as to tetrato, meaning to coordinate as a ligand, and the derived participles, tetrato, ligato.

**Coordination polyhedron.** It is standard practice to think of the ligand atoms that are directly attached to the central atom as defining a coordination polyhedron (or polygon) about the central atom. Thus [Co(NH$_3$)$_4$Cl$_2$]$^{3+}$ is an octahedral ion and [PtCl$_2$(CH$_3$CN)$_2$]$^{2-}$ is a square planar ion. In this way the coordination number may equal the number of vertices in the coordination polyhedron. Exceptions are common among organometallic compounds.

**Examples:**
1. octahedral coordination polyhedron
2. square planar coordination polyhedron
3. tetrahedral coordination polyhedron

Historically, the concepts and nomenclature of coordination compounds were unambiguously for a long time, but complications have arisen more recently. According to tradition, every ligating atom or group was recognized as bringing one lone-pair of electrons to the central atom in the coordination entity. This sharing of ligand electron pairs became synonymous with the verb 'to coordinate.' Further, in the inevitable electron bookkeeping that ensues upon consideration of a chemical compound, the coordination entity was dissected (in thought) by removal of each ligating atom or group. Thus in [Co(NH$_3$)$_4$Cl$_2$]$^{3+}$, each NH$_3$ becomes a ligand and the derived participle, ligato.


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Note that an extension of the organic style of nomenclature as in (CH$_3$CO$_2$H)$_n$ - ethanoic acidinium is discouraged because it is based on the word 'acid' and is often not easily adaptable to languages other than English.
each rhenium atom in the triangular array is coordinated by two more halide ligands above and below the plane defined by the three rhenium atoms. Each Re(III) has a $d^8$ configuration which would lead to a paramagnetic complex if only metal-metal single bonds were present. The complexes are diamagnetic, however, which implies that each Re atom is doubly bonded to its rhenium neighbors.

In the solid state the halides retain this basic unit, but further bridging between rhenium atoms by chloro ligands results in a polymeric structure (Fig. 16.62b). Likewise, dissolving the halides in solutions of the hydrohalic acids leads to formation of dodecahalotrirhenate(III) ions, $[\text{Re}_3\text{X}_6^3]$ (Fig. 16.62c), in which additional halide ligands have coordinated to the empty positions present in the Re$_3$X$_6$ units. Other ligands (such as R$_3$P, Me$_2$SO, or MeCN) can also coordinate to these positions. The Re$_3$ cluster is persistent in many chemical transformations. The bond length is 243-250 pm, which is indicative of strong bonding although weaker than in $[\text{Re}_5\text{X}_{12}]^2$.

Although common among carbonyl clusters, far fewer examples of tetranuclear clusters are found among the halides and oxides. One example noted previously is W$_4$(OR)$_4$, which forms by dimerization of W$_2$(OR)$_2$. The tetrameric W$_4$(OR)$_4$ has also been synthesized. Whereas W$_2$(OR)$_2$, and W$_2$(OR)$_4$, may be viewed as unsaturated, W$_4$(OR)$_4$ is saturated, containing W—W single bonds (Fig. 16.63).

Quadruply bonded dinuclear compounds also can dimerize to give tetrameric molecules:

$$2\text{Mo}_2\text{Cl}_6 \rightarrow \text{Mo}_4\text{Cl}_{12} + \text{KCl}$$

The resulting four-membered ring is not square, and it appears from bond length measurements that there are alternating single and triple Mo—Mo bonds.

Tetranuclear cluster units (rhomboidal Mo$_4$), connected by oxygen atoms and forming infinite chains, are found in Ba$_4$Mo$_4$O$_{16}$. Each rhenium atom in the triangular array is coordinated by two more halide ligands above and below the plane defined by the three rhenium atoms. Each Re(III) has a $d^8$ configuration which would lead to a paramagnetic complex if only metal-metal single bonds were present. The complexes are diamagnetic, however, which implies that each Re atom is doubly bonded to its rhenium neighbors.

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In the solid state the halides retain this basic unit, but further bridging between rhenium atoms by chloro ligands results in a polymeric structure (Fig. 16.62b). Likewise, dissolving the halides in solutions of the hydrohalic acids leads to formation of dodecahalotrirhenate(III) ions, $[\text{Re}_3\text{X}_6^3]$ (Fig. 16.62c), in which additional halide ligands have coordinated to the empty positions present in the Re$_3$X$_6$ units. Other ligands (such as R$_3$P, Me$_2$SO, or MeCN) can also coordinate to these positions. The Re$_3$ cluster is persistent in many chemical transformations. The bond length is 243-250 pm, which is indicative of strong bonding although weaker than in $[\text{Re}_5\text{X}_{12}]^2$.

Although common among carbonyl clusters, far fewer examples of tetranuclear clusters are found among the halides and oxides. One example noted previously is W$_4$(OR)$_4$, which forms by dimerization of W$_2$(OR)$_2$. The tetrameric W$_4$(OR)$_4$ has also been synthesized. Whereas W$_2$(OR)$_2$, and W$_2$(OR)$_4$, may be viewed as unsaturated, W$_4$(OR)$_4$ is saturated, containing W—W single bonds (Fig. 16.63). Quadruply bonded dinuclear compounds also can dimerize to give tetrameric molecules.

$$2\text{Mo}_2\text{Cl}_6 \rightarrow \text{Mo}_4\text{Cl}_{12} + \text{KCl}$$

The resulting four-membered ring is not square, and it appears from bond length measurements that there are alternating single and triple Mo—Mo bonds. Tetranuclear cluster units (rhomboidal Mo$_4$), connected by oxygen atoms and forming infinite chains, are found in Ba$_4$Mo$_4$O$_{16}$.
centrated sulfuric acid, are trivial. Later these names were superseded because they were found to be inconvenient and names reflecting chemical information. In this case the acid property (as, for example, with sulfuric acid), were coined. Names for the various derivatives of the parents were developed from these names. This semisystematic approach has limitations, and has also led to ambiguities and inconsistencies.

**Formulas**

In a formula, the hydrogen atoms which give rise to the acid property are cited first, then comes the central atom, and finally the atoms or groups of atoms surrounding the central atom. These last are cited in the following order: oxygen atoms which are bound to the central atom only, followed by other atoms and groups of atoms ordered according to coordination nomenclature rules, that is, ionic ligands precede neutral ligands. Within each class, the order of citation is the alphabetical order of the symbols of the ligating atom.

Examples:

1. H₂SO₃
2. H₂SO₄
3. H₃SO₄ or (HO₂)₂PO₄(OH)₂
4. H₄P₃O₁₀
5. H₂PO₄ or (HO₂)₃PO₄(OH)
6. HSO₃⁻

**Traditional Names**

History. Some traditional names (a selection is in Table 1-4) were introduced by Lavoisier. Under his system, oxoacids were given a two-word name, the second word being 'acid'. In the first word, the endings -ous or -ic were added to the stem of the name, intended to indicate the content of oxygen, which is known today to be related to the oxidation states of the central atom. Unfortunately, these endings do not describe the same oxidation states in different families of acids. Thus sulfuric acid and phosphoric acid refer to oxidation states IV and VI, whereas chlorous acid and chloric acid refer to oxidation states III and V.

An extension of this system became necessary as more related acids were recognized. The prefixes hypo- (very low oxidation state) and per- (very high oxidation state) were introduced. The prefix per- should not be confused with the syllable in the ligand name peroxo-. Finally, it became necessary to use other prefixes, ortho-, pyro-, and meta-, to distinguish acids differing in the 'content of water'. These traditional names do not provide specific information on the number of oxygen atoms, or the number of hydrogen atoms, whether acidic or not. The use of prefixes is not always consistent; for instance, hypo- has been associated with the -ous ending (hypothionous acid) and with the -ic ending (hypophosphoric acid). In the case of sulfuric acids, two classes of acid occur, one with the stem 'sulfur' and the other with the stem 'thio'. Moreover, in substitutive nomenclature found to be inconvenient and names reflecting chemical information, in this case the acid property (as, for example, with sulfuric acid), were coined. Names for the various derivatives of the parents were developed from these names. This semisystematic approach has limitations, and has also led to ambiguities and inconsistencies.

<table>
<thead>
<tr>
<th>Acid nomenclature</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfurous acid</td>
<td>H₂SO₃</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>Sulfonic acid</td>
<td>H₃SO₄</td>
</tr>
<tr>
<td>Hypothionous acid</td>
<td>H₂PO₄</td>
</tr>
<tr>
<td>Hypophosphoric acid</td>
<td>H₃PO₄</td>
</tr>
<tr>
<td>Hypothionous acid</td>
<td>H₂SO₃</td>
</tr>
<tr>
<td>Hypophosphoric acid</td>
<td>H₃PO₄</td>
</tr>
</tbody>
</table>

Allowed traditional names for acids and their derived anions. It is recommended that retained traditional names be limited to very common compounds having names established by a long practice. Systematic names should be used for all other cases. A list of these traditional names which are retained for present use is given in Table 1-4.

The use of -ous, -ic, per-, hypo-, ortho-, meta- should be restricted to those cases in which their indicated meaning is correct for the oxidation states of the central atom. For example, in substituting nomenclature rules, that is, ionic ligands precede neutral ligands. Within each class, the order of citation is the alphabetical order of the symbols of the ligating atom.
Clusters of six molybdenum, niobium, or tantalum atoms have been known for many years, predating the work with rhenium. There are two types: In the first, an octahedron of six metal atoms is coordinated by eight chloride ligands, one on each face of the octahedron (Fig. 16.64a). This is found in "molybdenum dichloride," Mo$_6$Cl$_8$, better formulated as [Mo$_6$Cl$_8$]Cl$_4$. Each Mo(II) atom can use its four electrons to form four bonds with adjacent molybdenum atoms and can receive dative bonds from the four chloride ligands.

Cotton has pointed out that a metal in a low oxidation state can adopt one of two strategies in forming clusters. It can form multiple bonds to another metal, as in [Re$_2$X$_8$]$^2^-$, or it can form single bonds to several other metal atoms, as in the octahedral clusters. It is interesting that Mo(II) adopts both methods (Fig. 16.65) and that both structures have a cubic arrangement of chloride ions.

The second class of hexanuclear clusters also contains an octahedron of metal atoms, but they are coordinated by twelve halide ligands along the edges (Fig. 16.64b). Niobium and tantalum form clusters of this type. Here the bonding situation is somewhat more complicated: The metal atoms are surrounded by a very distorted square prism of four metal and four halogen atoms. Furthermore, these compounds are electron deficient in the same sense as the boranes—there are fewer pairs of electrons than orbitals to receive them and so fractional bond orders of 1 are obtained.

It has been known for nearly 100 years that posttransition metals dissolve in liquid ammonia in the presence of alkali metals to give highly colored anions. In the 1930s, polyatomic anions (Fig. 16.66a, b) such as Sn$_9^-$, Pb$_2^-$, Sb$_2^-$, and Bi$_3^-$ were identified but not structurally characterized. Attempts at isolating crystals were unsuccessful because they decomposed in solution. This problem was overcome in 1975 by stabilizing the cation of the salt as a cryptate (see Chapter 12), e.g., [Na$_4$(crypt)$_4$]Pb$_2$ and [Na$_4$(crypt)$_4$]Sn$_9$, which reduces the tendency of the salt to convert to a metal alloy.

SALTS OF POLYATOMIC CATIONS, such as Bi$_3^+$ and Te$_5^+$, are obtained from melts and stabilized by large weakly basic anions such as AlCl$_4^-$. Re + BiCl$_4^-$(excess) → Bi$_3$[AlCl$_4$]$_3$ (16.126)

Since these homopolyatomic Zintl anions and cations are devoid of ligands, they are sometimes referred to as "naked" clusters. In general there is a good correlation between electronic structure and geometry as predicted by Wade's rules for these clusters, though some exceptions are known. Thus whereas Sn$_9^-$ and Bi$_9^+$ are isoelectronic, they have different structures, the latter violating the rules. Only a small distortion of the bismuth cation, however, would convert it to the geometry observed for the tin cluster.
the central atom are treated as ligands in coordination nomenclature. The name of the central atom, where not a metal, may be contracted.

Examples:
1. [PF₆]⁻, hexafluorophosphate(V), or hexafluorophosphate(−)
2. [Zn(OH)₄]²⁻, tetrahydroxozincate(2−) or tetrahydroxozincate(II)
3. [SO₄]²⁻, tetraoxosulfate(IV), or tetraoxosulfate(2−)
4. [HF]⁺, dihydrofluorohydrid vested (often named hydroxide/hydroxide)

Even when the exact composition is not known, this method can be of use. The number of ligands can then be omitted, as in hydroxozincate, or oxic tone, etc.

Oxoanions. Although it is quite practical to treat oxygen in the same manner as ordinary ligands and use it in the naming of oxoanions by coordination nomenclature, some names having the suffix -ite (indicating a lower-than-maximum oxidation state) are useful and therefore are still permitted.

Examples:
1. NO₃⁻, nitrite
2. ClO⁻, hypochlorite

A full list of permitted alternative names for oxoacids and derived anions can be found in Table I-4.

Substituent Groups or Radicals

Definitions. The term radical is used here in the sense of an atom or a group of atoms having one or more unpaired electrons.

Systematic names of substituent groups or radicals. The names of groups which can be regarded as substituents in organic compounds or as ligands on metals are often the same as the names of the corresponding radicals. To emphasize the kind of species being described, one may add the word 'group' to the name of the species. Except for certain trivial names, names of uncharged groups or radicals usually end with -yl. Carbonyl is an allowed trivial name for the ligand CO.

Examples:
1. (CH₃)₂CH, methyl or methyl
2. (NO)ₙ, nitrosyl

Certain neutral and cationic radicals containing oxygen (or chalcogens) have, regardless of charge, special names ending in -yl. These names (or derivatives of these names) are used only to designate compounds consisting of discrete molecules or groups. Prefixes thio-, teleno-, and telluro- are allowed to indicate the replacement of oxygen by sulfur, selenium, and tellurium, respectively.

Examples:
1. HO, hydroxyl
2. CO, carbonyl
g. NO₂, nitrite
4. PO, phosphonyl
5. SO, sulfinyl, or thionyl
6. SO₂, sulfonyl, or telluroyl
7. H₂O₂, hydroperoxyl, or perhydroxyl, or hydroperoxyl
8. CrO₂, chromyl
9. UO₂, uranyl
10. ClO₃, chlorate
11. CIₗ, chloryl
12. CIₙ, perchloryl

23 The former names are preferred, but the latter are allowed. The vanadium to be used in any particular case depends on the circumstances. Thus, sulfinyl is used in inorganic, radio-functional nomenclature and sulfenyl is used in organic substitutive nomenclature. (The is, organic chemists tend to speak of methanesulfinyl chloride, MeSOCI₂, while inorganic chemists speak of sulfinyl chloride, SO₂Cl₂.)

Oxoacids and Derived Anions

Introduction

Inorganic chemistry is developing in such a way that names based on function are disappearing and nomenclature is based, preferably on composition and structure, rather than on chemical properties. Chemical properties such as acidity depend on the reaction medium and a compound named as an acid might well function as a base in some circumstances. The nomenclature of acids has a long tradition and it would be unwise to introduce systematic acid names fully and alter drastically the commonly accepted names of important and well-known substances. However, there is no reason to provide trivial names which could have a very limited use for newly prepared inorganic compounds.

Definition of the Term Oxoacid

An oxoacid is a compound which contains oxygen, at least one other element, at least one hydrogen bound to oxygen, and which produces a conjugate base by loss of positive hydrogen ions (hydroxyl). The limits of this class of compound are dictated by usage rather than rules.

Oxoacids have been extensively used and studied and many of them therefore have names established by a long practice. The oldest names, such as 'oil of vitriol' (=...
Infinite Metal Chains

Many highly reduced halides of scandium, yttrium, and zirconium have been found to have infinite metal-metal bonded chains. For example, ZrCl₂, which has infinite metal-metal bonded chains, contains double metal layers alternating with double chlorine layers (Fig. 16.68). It was discovered that the inner Mo₆Cl₂⁺ cube is rotated with respect to the Pb lattice (Fig. 16.67). It appears that this rotation is the result of very strong repulsions between the negatively charged sulfur atoms (or sulfide ions) in one S₆ cube with those in an adjacent cube. Thus, if lead is replaced by a more electropositive metal (e.g., Eu²⁺), the calculated charges on sulfur increase and the turn angle decreases. Since the superconductivity is thought to be dependent upon the overlap of the d orbitals on molybdenum, this property may be “tunable” by appropriate choice of metals.¹⁶³

Synthesis of Metal Clusters

An extremely wide variety of compounds, ranging from metal-only to nonmetal-only to those molecules that are mixed metal/nonmetal, has been encountered in this covered rather recently that many of the Groups III (3) and IV (4) halides, once thought to be binary, are in fact stabilized by the presence of interstitial atoms (introduced unknowingly) such as hydrogen, carbon, or nitrogen. An example is Sc₂Cl₃N, once thought to be Sc₂Cl₆. Its structure reveals an interstitial nitrogen atom and consists of infinite pairs of chains in which Sc₂Cl₃N clusters are connected by shared chlorine atoms (Fig. 16.68a) and by shared metal edges (Fig. 16.68b). By exploiting the stabilizing role of interstitial atoms, systematic syntheses have been developed for many new and interesting substances including over 60 zirconium chloride phases.

In the preceding description of metal clusters, synthetic reactions were given for some, but not for others. The paucity of reactions reflects in part the fact that the synthetic chemistry is not fully systematized—often an attempt to make a quadruply bonded compound, for example, may lead to a doubly bonded one instead. Many years ago Cotton observed that “the student of cluster chemistry is in somewhat the position of the collector of lepidoptera or meteorites, skipping observantly over the countryside and exclaiming with delight when fortunate enough to encounter a new specimen.”¹⁷¹ And more recently, he has stated “... the most common method of synthesis is some sort of thermally-driven process, quite often a pyrolysis, and thus design and selectivity tend to be absent much of the time.”¹⁷² Even so, progress toward rational syntheses continues to be made and, in particular, application of the principles of isolobality are proving to be especially useful.¹⁷³

Fig. 16.68 The structure of ZrCl₂, a reduced metal halide system containing infinite metal-metal bonds, showing double metal atom layers alternating with double chlorine atom layers. [From Corbett, J. D. Acc. Chem. Res. 1983, 16, 239. Reproduced with permission.]
Examples:
1. (O₂⁺)²⁺ dioxygen(1+) ion [dioxygenyl]
2. (O₃⁻)³⁻ tetravalent(2-) ion [This would be "cyclo-tetrasulfur(2-)"] in the known species.]
3. (H₈S₈⁺)⁺ dimercury(2+) ion, or dimercury(I) cation [mercurous]

Cations obtained formally by the addition of hydrons to binary hydrides. The name of an ion derived by adding a hydron to a binary hydride can be obtained by adding the suffix -idc [and adding a numerical prefix as needed]. In many cases, contractions or variations are employed, as exemplified below.

Examples:
1. NH₄⁺ ammonium, or azanium
2. H₂O⁺ oxonium
3. PH₄⁺ phosphonium

Coordination cations. The names of complex cations are derived most simply by using the coordination cation names (see Section 1-10). This is preferred whenever ambiguity might result.

Special cases. There are a few cases where trivial, nonsystematic or semisystematic names are still allowed. Some particular examples are shown.

Examples:
1. NO₂⁺ nitrosyl cation
2. NO₄⁺ nitryl cation
3. HOC(NH₂)⁺ oxalyl cation

Anions
Monatomic [and homopolyatomic] anions are named by replacing the termination of the element name by -ate [and adding a numerical prefix as needed]. In many cases, contractions or variations are employed, as exemplified below.

Examples:
1. H⁻ dioxygen(1-) ion
2. O⁻ oxide
3. S⁻ sulfide
4. I⁻ iodide
5. O₇⁻ divalet(1-) hyperoxide, or supervioxide

Although O⁷⁻ is called superoxide in biochemical nomenclature, the Commission recommends the use of the systematic name dioxido(1-) because the prefix super- does not have the same meaning in all languages. Other common names are not recommended. 15

15 Hydro to represent 'hydrido' or 'hydrogen' is sanctioned by usage in boron nomenclature (see Section 1-10). However, the names used here are of coordination type, and different rules apply. In inorganic nomenclature hydrogen is regarded as a cation in the names of acids unless the name is intended to show that it is combined in an anion [as in the examples] above. [Similarly as the hydrogen is bound the same in H₂CO₃, dihydrogen carbonate (carbonic acid), as it is in HCO₃, the dihydrogen carbonate anion. American chemists generally put spaces between the words.]

Special cases. There are a few cases where trivial, nonsystematic or semisystematic names are still allowed. Some particular examples are shown.

Examples:
1. NO₂⁻ nitrosyl cation
2. NO₄⁻ nitryl cation
3. HOC(NH₂)⁻ oxalyl cation

Coordination anions. The names of complex cations are derived most simply by using the coordination cation names (see Section 1-10). This is preferred whenever ambiguity might result.

Special cases. There are a few cases where trivial, nonsystematic or semisystematic names are still allowed. Some particular examples are shown.

Examples:
1. NO₂⁻ nitrosyl cation
2. NO₄⁻ nitryl cation
3. HOC(NH₂)⁻ oxalyl cation

Anions derived from neutral molecules by loss of one or more hydrons. The names of anions formed by loss of hydrons from structural groups such as acid hydrazyl are formed by replacing the -ic acid, -uric acid, or -oric acid ending by -ate. If only some of the acid hydrons are lost from an acid, the names are formed by adding 'hydrogen', 'dihydrogen', etc., before the name to indicate the number of hydrons which are still present and which can, in principle, be ionized.

Examples:
1. CO₂⁺ carbonyl
2. HCO₃⁻ hydrogencarbonate(1-)
3. SO₄²⁻ sulfate

Anions derived formally by the addition of a hydride ion to a mononuclear hydride are named using coordination nomenclature (see Section 1-10). Even when the central atom is not a metal.

Examples:
1. BH₄⁻ tetrahydroborate(1-)
2. PH₄⁻ tetrahydrophosphorat(1-)

Coordination nomenclature for heteropolyatomic anions. The names of polyatomic anions which do not fall into classes mentioned above are derived from the name of the central atom using the termination -ate. Groups, including monatomic groups, attached to central atoms of more than five elements are usually given a special name.

Examples:
1. (H₂C=NOH)⁺ formaldehyde(1+)
2. (H₂C=NO⁻)⁻ formate(1-)

Note that formate and formic acid are used interchangeably, although they are not identical.

When coordinated in mononuclear complexes, these ions may bind through either end. This has led to the use of the names hydrate, acrylate, -OCN, etc., to distinguish the donor. This usage is discouraged, and the italicized donor symbol, namely, cyanato-O, or cyanate-ν, should be employed.
**Problems 821**

16.1 Draw all of the structural isomers of \( \text{P}_4\text{H}_4 \). Assume that inversion at phosphorus is slow and draw all possible stereoisomers.

16.2 Suggest a structure for \( \text{P}_4\text{H}_4 \) and its union, \( \text{P}_4\text{H}_6^+ \).

16.3 As indicated in the text, silanes are less stable than silikanes largely because a facile decomposition pathway is available to them. Suggest a mechanism for the decomposition of \( \text{SiH}_4 \).

16.4 Compare the relative reactivity of silanes and alkynes toward nucleophilic attack, hydrolysis, and halogenation.

16.5 Methods of successfully synthesizing characterizable organic polysilanes were developed only in the last decade. With the aid of references given in this chapter, present a synthesis for the homopolymer \( \text{Me}(\text{MeSiH})_n \), and the copolymer \( \text{Me}(\text{PhSiH})_m \text{Me}(\text{MeSiH})_n \).

16.6 Draw structures of \( \text{[SiO}_4]^{4-}, \text{[SiO}_4]^{3-}, \text{[SiO}_3]^{2-}, \text{[SiO}_2]^{2-}, \text{[SiO}_2]^{-}, \text{[SiO}_3]^{-}, \text{[SiO}_4]^{-} \) and \( \text{[SiO}_4]^{4-} \). Enclose the repeating units in brackets and show that these empirical formulas are correct. How do the ratios of oxygen to silicon correlate with the degree of polymerization in silicates (i.e., discrete ions compared to chains compared to double chains compared to infinite sheets compared to three-dimensional frameworks)?

16.7 Both noselite and ultramarine contain \( \text{Al}_6\text{Si}_4\text{O}_{10} \) formula units. What is the charge on this unit? In addition, noselite contains a sulfide ion and ultramarine has a persulfide ion. How many sodium ions are present in each overall empirical formula?

16.8 a. Why are some seemingly disparate substances as ical, clay, and graphic slipperily and useful as lubricants?

b. Although the structures of ical and muscovite are rather similar, the latter is much harder and unsuitable as a lubricant. Why? Should these minerals have any properties in common?

16.9 Gem-quality beryls are aquamarine (blue), emerald (green), and golden beryl. Likewise, amethyst is a violet-colored silica, and sapphire (blue) and ruby (red) are aluminas. Yet pure beryls (\( \text{Be}_2\text{Al}_2\text{Si}_6\text{O}_{18} \)), silicas (\( \text{Si}_2\text{O}_5 \)), and aluminas (\( \text{Al}_2\text{O}_3 \)) are colorless. Explain.

16.10 Although olivine is a common rock-forming mineral and quartz is the most common mineral in common, they are never found together. Explain.

16.11 Muscovite and biotite have very similar compositions. Why is one "white mica" and the other "black mica"? In the same vein, talc is white, chrysotile is white, asbestos, crocidolite is blue asbestos, and amosite is a gray asbestos.

16.12 Compared to molybdenum(VII) and tungsten(VI), chromium(VI) does not have an extensive oxidation chemistry. Suggest an explanation.

16.13 In addition to chromate and dichromate, trichromate \( \text{[Cr}_3\text{O}_7]^{3-} \) reacts. Postulate a structure for the trichromate ion. Compare its structure to that of \( \text{[PO}_4]^{3-} \). Trichromate hydrolyzes in water. Predict the hydrolysis products.

16.14 From an inspection of the figures, or even better, from molecular models, determine the geometry of the coordination sphere (cavity) in each of the heteropolyanions discussed in this chapter.

16.15 Write balanced equations showing all of the following conversions:

a. \( \text{V}_2\text{O}_3 \) to \( \text{V}_2\text{O}_5 \)

b. \( \text{H}_2\text{V}_2\text{O}_5 \) to \( \text{V}_2\text{O}_5 \)

16.16 Consider the structure of the ion, \( \text{[Ce}_6\text{Mo}_{12}\text{O}_{40}]^{12-} \). This structure may be thought of as consisting of twelve \( \text{Mo}_6\text{O}_{19} \) octahedra or six \( \text{Mo}_6\text{O}_{19} \) groups. The former suggests 72 oxygen atoms and the latter 54. Yet there are only 42 oxygen atoms in the structure. Explain. How many terminal oxygen atoms per molybdenum are present? How many bridging oxygen atoms are present? What is the coordination number of \( \text{Ce}^{4+} \) and each of kind of oxygen atom? What is the point group of the entire anion?

16.17 Determine the point groups of the cyclic phosphines in Fig. 16.34 and the phosphorus oxides in Fig. 16.35.

16.18 The iminophosphorane, \( \text{P} = \text{B} = \text{N} = \text{H} \), trimerizes to \( \text{[P} = \text{B} = \text{N} = \text{H}]_3 \) which has a Dewar-like structure. Calculate the point group of this anion. Suggest an explanation.

16.19 Boroxines result from the condensation of boronic acids, \( \text{RB(OH)}_2 \). The cyclic trimeric anhydride of methylboronic acid is \( \text{[MeB(OH)}_2]_3 \). Give a balanced equation for the reaction of (MeBO)\(_2\) with water. (See Brown, H. C.; Cole, T. E. *Organoboranes* 1985, 4, 816.)

I-6 SOLIDS

The Red Book has a twelve-page section of recommendations with respect to solid state nomenclature, defects, phases, polymorphisms, etc. Very little of this material is applicable to this book, so the section has been omitted because of space.

I-7 NEUTRAL MOLECULAR COMPOUNDS

Substitutive Nomenclature

Introduction. This is a method of naming, commonly used for organic compounds, in which names are based on that of an individual parent hydride, usually ending in -ane, -ene, or -yne. The hydride name is understood to signify a definite fixed population of hydrogen atoms attached to a skeletal structure.

Examples:
1. NaOH sodium hydroxide, preferred to sodium hydroxyde
2. CaCl₂ calcium chloride, preferred to calcium dichloride

The prefix mono- is always omitted unless its presence is necessary to avoid confusion.

Examples:
1. NO₂ nitric oxide
2. NO₃ nitric oxide
3. N₂O₃ dinitrogen oxide
4. CO carbon monoxide
5. SX₄ diatomic chlorine
6. MnO₂ manganese dioxide
7. CO carbon monoxide
8. Na₂S₄ sodium tetrasulfide

The use of these prefixes does not affect the order of citation, which depends upon the initial letters of the names of the compounds. However, when the name of the constituent itself starts with a multiplicative prefix (as in disulfate, dichromate, triphosphate, and tetraborate), two successive multiplicative prefixes may be necessary. When this happens, and in other cases simply to avoid confusion, the alternative multiplicative prefixes, bis-, tri-, tetrakis-, pentakis-, etc. are used (see Table I-3) and the name of the group acted upon by the alternative prefix is placed in parentheses.

Example:
1. Bi₃[BrF₆]₂ barium bis(tetrafluorobromate)
2. TiI₃ thallium triiodide
3. U₂S₃O₄ uranium bis(sulfate)

Hydride names

Names of mononuclear hydrides. Substitutive nomenclature is usually confined to the following central elements: B, C, S, Ge, Sn, Pb, N, P, As, Sb, Bi, O, S, Se, Te, Po, but it may be extended to certain halogen derivatives, especially those of iodine.

In the absence of any designation, the ending -ane signifies that the skeletal element exhibits its standard bonding number. The prefix mono- is always omitted unless its presence is necessary to avoid confusion. Where the compounds contain elements such that it is not necessary to stress the proportion, for instance, where the oxidation states are usually invariant, then indication proportions need not be provided.

Examples:
1. Na₂SO₄ sodium sulfate, preferred to sodium disulfate
2. CaCl₂ calcium chloride, preferred to calcium dichloride

The prefix mono- is always omitted unless its presence is necessary to avoid confusion.

Examples:
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[Note the difference between d/sulfate, SO₄²⁻, and Wsulfate, an older, unsystematic name for HSO₄⁻.]

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[Note the difference between d/sulfate, SO₄²⁻, and Wsulfate, an older, unsystematic name for HSO₄⁻.]
16.20 Phosphazene, (PNH)_n, can be obtained by the reaction of red phosphorus with ammonia. Write a balanced equation for its production from these two reagents and show a possible structure for this cross-linked polymer.

16.21 Monophosphazenes, RPNH, are well known and may be prepared from the reaction of R'Cl and R'NH_2. Write a balanced equation for this reaction.

16.22 As discussed in the chapter, isomeric phosphazenes are usually planar but can be forced out of this geometry. In contrast, benzene derivatives are strictly planar. Discuss the reasons for the greater flexibility of the phosphazenes.

16.23 Draw all of the possible isomers, excluding those that are N—N bonded, of SP(NH)_3.

16.24 The classical argument concerning the equivalence of the positions on the benzene ring is based on the existence of three (ortho, meta, para) isomers of xylene (dimethylbenzene). How many isomers are there of dimethylborazine?

16.25 Complexes (OC)=Fe(PMe_3)_2 and (OC)=Fe(PPh_3)_2 form from the reaction of Fe(CO)_5 and PMe_3. Suggest structures for these complexes. Would you expect similar reactions with PPh_3? (See Walker, M. L.; Mills, J. L. Inorg. Chem. 1977, 16, 3033.)

16.26 Phosphorus pentoxide is an excellent dehydrating agent. For example, it can be used to remove water from nitric acid. Write a chemical equation for this reaction.

16.27 Suggest a structure for P_4O_10, synthesized from P_2O_5 and P_2O_5.

16.28 Ethyne reacts with oxygen to give carbon dioxide and water. diborane reacts with oxygen to give boron trioxide and water. Write balanced equations for these two reactions. Look up heats of formation for the reactants and products of these reactions and calculate the heats of reactions. Considerable work was expended in evaluating the stability of high-energy fuels in the 1950s. Compare ethyne and diborane fuels.

16.29 It has been suggested that Se^2^- exists in the endo form rather than in a so-called "crowns" form with Se(1) flipped down because of reduced lone-pair repulsions between Se(2), Se(3), Se(6) and Se(7). Sketch these two forms of Se^2^- Add lone pairs to your drawing and indicate how stabilization occurs in the endo form.

16.30 What structures do you predict for the anions, B_2H_5^-, B_2H_5^-, and B_2H_5^-

16.31 Dihalogenides widely used in organic chemistry hydroboration) to convert alkenes into alcohols. Consult an organic book and show reactions for this conversion. What is the advantage of this method?

16.32 Complete the following equations:
   a. [Fe(CO)_5] + excess Me_2NH
   b. B_2H_6 + 2RCl
   c. B_2H_6 + 2NH_3
   d. FeCl_3 + excess Cl_2

16.33 Assuming that the external H—B—H angle in B_2H_6 accurately reflects the interorbital angle:
   a. Calculate the s and p character in these bonds.
   b. Calculate the s and p character remaining for the bridging orbitals.
   c. Compare the value from (b) with the experimental interorbital angles.

16.34 Use Wade's rules to predict the structures of the following:
   a. B_2H_6(CO_3
   b. C_6H_6(P(CO_3
   c. C_6H_6(Me)(C(OH)
   d. C_6H_5As(CO_3

16.35 Use the polyhedral skeletal electron-counting rules and show that they are consistent with the aldoke 1-verx structure shown below. 

16.36 What is the maximum bond order under which you would predict for neutral W_2 (no ligands)?

16.37 What bond angle would you expect for Mo—O—R in an alkoxide complex? How might this bond angle change as a lowering of the p orbitals of oxygen increases?


16.39 Note that the product of Eq. 16.125 contains Mo—Mo pairs that are doubly bridged by chlorine and Mo—Mo pairs that are not. If this molecule contains decreasing single and triple bonds, which bonds are which?

16.40 The structure of NiCl_2(S_2) is isomorphous to that of (η-sym)Ni(S_2). (See Hopfield, D.; Brokaw, J. J.; Todd, J. L. Inorg. Chem. 1979, 18, 904-908.)

16.41 Which of the following do you think would be most likely in view of isolobal considerations and Wade's rules? (See Little, J. L.; Haggard, A.; Kester, J. G.; Fadding, K.; Todd, J. L. Inorg. Chem. 1990, 29, 804-808.)

16.42 In addition to the phosphaazines discussed in this chapter, a large group of heterocyclic compounds known as phospholizines has been characterized. These contain a P—N single bond and may contain phosphorus either in the +3 or +5 oxidation states. Draw structures of [Cl_3P(NMe_3)] and [Cl_3P(NMe_3)]. Phospholizines are stable in Lewis bases. Phenylphospholizines have been stabilized by placing phenylphospholizines between adjacent nitrogen atoms. Give one example of each and draw its structure. (See Borko. J. M.; Hafley. K. C.; Sander. C. A.; Normand, A. D. Inorg. Chem. 1991, 30, 2340-2349.)


16.44 Note that the product of Eq. 16.125 contains Mo—Mo pairs that are doubly bridged by chlorine and Mo—Mo pairs that are not. If this molecule contains decreasing single and triple bonds, which bonds are which?

16.45 The structure of NiCl_2(S_2) is isomorphous to that of (η-sym)Ni(S_2). (See Hopfield, D.; Brokaw, J. J.; Todd, J. L. Inorg. Chem. 1979, 18, 904-908.)

16.46 What is the maximum bond order under which you would predict for neutral W_2 (no ligands)?

16.47 What bond angle would you expect for Mo—O—R in an alkoxide complex? How might this bond angle change as a lowering of the p orbitals of oxygen increases?


16.49 Note that the product of Eq. 16.125 contains Mo—Mo pairs that are doubly bridged by chlorine and Mo—Mo pairs that are not. If this molecule contains decreasing single and triple bonds, which bonds are which?

16.50 The structure of NiCl_2(S_2) is isomorphous to that of (η-sym)Ni(S_2). (See Hopfield, D.; Brokaw, J. J.; Todd, J. L. Inorg. Chem. 1979, 18, 904-908.)

16.51 Which of the following do you think would be most likely in view of isolobal considerations and Wade's rules? (See Little, J. L.; Haggard, A.; Kester, J. G.; Fadding, K.; Todd, J. L. Inorg. Chem. 1990, 29, 804-808.)

16.52 In addition to the phosphaazines discussed in this chapter, a large group of heterocyclic compounds known as phospholizines has been characterized. These contain a P—N single bond and may contain phosphorus either in the +3 or +5 oxidation states. Draw structures of [Cl_3P(NMe_3)] and [Cl_3P(NMe_3)]. Phospholizines are stable in Lewis bases. Phenylphospholizines have been stabilized by placing phospholizines between adjacent nitrogen atoms. Give one example of each and draw its structure. (See Borko. J. M.; Hafley. K. C.; Sander. C. A.; Normand, A. D. Inorg. Chem. 1991, 30, 2340-2349.)

A-52

\[ \text{IUPAC Recommendations on the Nomenclature of Inorganic Chemistry} \]

1-5 NAMES BASED ON STOICHIOMETRY

**Names of Constituents**

*Electropositive constituents.* The name of a monatomic electropositive constituent is simply the unmodified element name. A polyatomic constituent assumes the usual cation name, but certain well established radical names (particularly for oxygen-containing species such as nitrosyl and phosphoryl) are still allowed for specific cases.

**Examples:**
1. **NH₄Cl** ammonium chloride
2. **OF₂** oxygen difluoride
3. **UO₂Cl₂** uranyl dichloride
4. **O₃P** phosphoryl trichloride
5. **NO₃** nitrate

**Monoatomic electronegative constituents.** The name of a monatomic electronegative constituent is the element name with its ending (e.g., -en, -ese, -ic, -ine, -ium, -ogen, -on, -orus, -urn, -ur, -y, -ygen) replaced by the anion designator -ide.

**Examples:**
1. **Cl⁻** chloride
2. **O₂⁻** dianion
3. **S²⁻** dithionate
4. **SO₄²⁻** sulfate
5. **PO₄³⁻** metaphosphate
6. **SiO₄⁴⁻** orthosilicate
7. **H₂PO₄⁻** diphosphate
8. **H₂SO₄⁻** dithionate
9. **HOCl** hypochlorite
10. **H₂O₂⁻** hypohalide
11. **H₂O₃⁻** hypophosphate
12. **H₂PO₃⁻** orthophosphate
13. **H₂SiO₄⁻** metallophosphate
14. **H₃PO₄⁻** phosphinate
15. **H₂SiO₃⁻** phosphite
16. **HCO₃⁻** bicarbonate
17. **HS⁻** thiosulfate
18. **HSO₃⁻** sulfite
19. **H₂CO₃⁻** carbonic acid
20. **H₂SO₃⁻** sulfurous acid
21. **H₂S₂O₃⁻** thiosulfate
22. **H₂S₂O₄⁻** sulfuric acid
23. **H₂S₃O₄⁻** threotillate
24. **H₂S₄O₄⁻** tetrasulfate
25. **H₂S₅O₄⁻** pentathionate
26. **H₂S₆O₄⁻** hexathionate
27. **H₂S₇O₄⁻** heptathionate
28. **H₂S₈O₄⁻** octathionate
29. **H₂S₉O₄⁻** nonathionate
30. **H₂S₁₀O₄⁻** decathionate

**Heteropolyatomic electronegative constituents.** The names of these anions take the termination -ate, though a few exceptions are allowed (see Examples 5-16 below). The ending -ate is also a characteristic ending for the names of anions of oxoacids and their derivatives. The names sulfite, phosphite, nitrate, etc., are general names for oxoanions containing sulfur, phosphorus, and nitrogen surrounded by ligands, including oxygen, irrespective of their nature and number. The names sulfite, phosphite, and nitrate were originally restricted to the anions of specific oxoacids, namely SO₃²⁻, PO₄³⁻, NO₃⁻, but this is no longer the case.

**Examples:**
1. **SO₃²⁻** trisulfate, or sulfite
2. **SO₄³⁻** tetrathiosulfate, or sulfite
3. **NO₃⁻** nitrate

Many names with -ate endings are still allowed, though they are not completely in accord with the derivations outlined above. Some of these are cyanide, dichromate, dichromate, dithionate, fulminate, hydroxide, odoriphosphate, metaphosphate, metasilicate, orthophosphate, perchlorate, periodate, permanganate, phosphinate, and phosphonate. The exceptional cases where the names end in -ide or -ite rather than -ate are exemplified below.

**Examples:**
5. **CN⁻** cyanide
6. **NH₂CN⁻** cyanide
7. **NH₂³⁻** hydroxide
8. **NH₃⁻** amide
9. **NH₂⁻** hydroxyamide
10. **NH₂⁻** hydroxyamide

**Indication of Proportions of Constituents**

Use of multiplicative prefixes. The proportions of the constituents, be they monatomic or polyatomic, may be indicated by numerical prefixes (mono-, di-, tri-, tetra-, etc.) as detailed in Table 1-3. These precede the names they modify, joined by a hyphen.

**Table 1-3**

<table>
<thead>
<tr>
<th>Numerical prefixes</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>mono</td>
<td>1. NH₃</td>
</tr>
<tr>
<td>di</td>
<td>2. NH₂</td>
</tr>
<tr>
<td>tri</td>
<td>3. NH</td>
</tr>
<tr>
<td>tetra</td>
<td>4. N₂</td>
</tr>
<tr>
<td>penta</td>
<td>5. N₃</td>
</tr>
<tr>
<td>hexa</td>
<td>6. N₄</td>
</tr>
<tr>
<td>hepta</td>
<td>7. N₅</td>
</tr>
<tr>
<td>octa</td>
<td>8. N₆</td>
</tr>
<tr>
<td>dodeca</td>
<td>10. N₈</td>
</tr>
</tbody>
</table>

*Although the Latin nomina has been used for a long time, the IUPAC has not recommended its use previously, and Na has been universally called "sodium." In view of the placing of terms like "cyanus" and "furic," the introduction of Liebenian buzzinized names is unexpected.*
Chapter 17

The Chemistry of the Halogens and the Noble Gases

Although the observation of a line in the sun's spectrum as early as 1868 led workers to postulate the existence of an unknown element in the sun's atmosphere, the isolation in 1899 of helium from the mineral cleveite by heating was not recognized as a related phenomenon. The first definitive work was by Lord Rayleigh, who noticed a discrepancy between the density of 'chemical nitrogen' and that of 'atmospheric nitrogen'. The former was obtained by chemically removing nitrogen from various nitrogen oxides, ammonia, or other compounds. The latter was obtained by removal of oxygen, carbon dioxide, and water vapor from air. The difference in density was not great: 1.2372 x 10^{-3} g cm^{-3} for 'atmospheric nitrogen' compared with 1.2505 x 10^{-3} g cm^{-3} for 'chemical nitrogen' under the same conditions. The careful work necessary to establish this difference has often been pointed to, quite rightly, as an example of the importance of precise measurements. Unfortunately, too often the emphasis has been upon the number of significant figures rather than the realization by Rayleigh and Ramsay that the difference was chemically significant. Their arguments concerning the significance of the ratio of specific heats of the noble gases (C_p/C_v = 1.66) and their rebuttal of various arguments advanced by their critics show us a much chemical insight as the gas-density argument, if not more.

Ramsay and Rayleigh succeeded in isolating all of the noble gases except radon and in showing that they were inert to all common reagents. They also discovered the identity of alpha particles and ionized helium.

The Early Chemistry of the Noble Gases

It is often assumed that the noble gases had no chemistry prior to 1908. This is true only if one restricts the definition of a chemical compound to (1) something containing 'ordinary' covalent or ionic bonds and (2) something which may be isolated and placed in a bottle on the reagent shelf. If either of these criteria is dismissed, much important chemistry of the noble gases can be recognized prior to the 1900s.

If an aqueous solution of hydroquinone is cooled while under a pressure of several hundred kilopascals (equal to several atmospheres) of a noble gas [X = Ar, Kr, Xe], a crystalline solid of approximate composition [C_4H_4O_2X]_n is obtained. These solids are β-hydroquinone clathrates with noble gas atoms filling most of the cavities. Similar noble gas hydrates are known (Fig. 17.1). These clathrates are of some importance since they provide a stable, solid source of the noble gases. They have also been used to effect separations of the noble gases since there is a certain selectivity exhibited by the clathrates.

Of particular interest is the effect of noble gases in biological systems. For example, xenon has an anesthetic effect. This is somewhat surprising in that the conditions induced in biological systems are obviously not sufficiently severe to effect chemical combination of the noble gas (in the ordinary sense of that word). It has been proposed that the structure of water might be altered via a clathrate-type interaction.

Although clathrate formation and dipole interactions are perfectly acceptable subjects for chemical discussions, chemists feel more at ease when they can find stable compounds formed from the species being studied. A logical approach would be the

---

1 Several names have been applied to the Group VIIIA (18) elements. The term 'inert' is inapplicable to the group as a whole (it is used above as a specific adjective of neon and argon, not in a group appellation) because at least three members of the family are not inert. The name 'noble gas' implies a reluctance to react rather than complete abstention, thus paralleling the use of this term in describing the chemistry of certain metals such as gold and platinum.

2 One could also draw a comparison between the noble gases and the alkali metals based on their low electron affinities. However, the electron affinities of noble gases appear always to be endothermic whereas the alkali metals have small but finite exothermic electron affinities leading to some chemistry based on acceptance of electrons (Chapter 12).
I-4 FORMULAE

This section contains considerable material on the proper writing of formulae, much of it routine, some of it highly specialized. Most of the indicators of the number of atoms, oxidation states, ionic charge, optical activity, and structures are very similar to those for names and will be discussed in later sections, especially Section I-10.

Free radicals. IUPAC recommends that the use of the word radical be restricted to species conventionally termed free radicals. A radical is indicated by a dot as a right superscript to the symbol of the element or group. The formulae of polyatomic radicals are placed in parentheses and the dot is placed as a right superscript to the parentheses. In radical ions, the dot precedes the charge.

Examples:
1. H^- 2. (CN)^- 3. (HgCN)^+ 4. (O)^2-
5. Br^- 6. [Mn(CO)]^6 7. (SnCl^6)^2-

Structural modifiers. Modifiers such as cis-, trans-, etc., are listed in (Table 1-6; see also page A-69). Usually such modifiers are used as italicized prefixes and are connected to the formula by a hyphen (cis-, trans-, etc.).

Examples:
1. cis-[PdCl(NH_3)_2] 2. trans-[PdCl(NH_3)_2]

Sequence of Citation of Symbols

Priorities

General. The sequence of symbols in a formula is always arbitrary and in any particular case should be a matter of convention. Where there are no overriding requirements, the guidelines summarized in Table I-2 should be used.

Electronegativities and citation order. In a formula the order of citation of symbols is based upon relative electronegativities, the more electronegative constituent(s) being cited first. In the formula of Brønsted acids, acid hydrogen is considered to be an electronegative constituent and immediately precedes the anionic constituents.

Examples:

(i) Assign symbols to the constituents.
(ii) Indicate proportions of constituents.
(iii) Divide constituents into electropositive and electronegative. This requires decisions concerning compound type. There are special rules for acids, polyatomic groups, binary compounds, chain compounds, interstitial compounds, coordination compounds, and adduct compounds (e.g., [H_2O]^-).
(iv) Assemble the formula.
(v) Insert appropriate modifiers (geometrical, etc.).
(vi) Insert oxidation states, charges, etc., if required.

Table 1-2
Assignment of formulae of compounds

| (i) | Assign symbols to the constituents |
| (ii) | Indicate proportions of constituents |
| (iii) | Divide constituents into electropositive and electronegative. This requires decisions concerning compound type. There are special rules for acids, polyatomic groups, binary compounds, chain compounds, interstitial compounds, coordination compounds, and adduct compounds (e.g., [H_2O]^-). |
| (iv) | Assemble the formula. |
| (v) | Insert appropriate modifiers (geometrical, etc.). |
| (vi) | Insert oxidation states, charges, etc., if required. |

Polyatomic ions. Polyatomic ions, whether complex or not, are treated in a similar fashion. The central atom(s) (e.g., in [ICl_4]^-, U in UO_2^2-, Si and W in [SiW_12O_40]^4-) or characteristic atom (e.g., Cl in ClO_4^-, O in OH^-) is cited first and then the subsidiary groups follow in alphabetical order of the symbols in such class.

Examples:

Polyatomic compounds or groups. It is necessary to define the central atom of the compound or group, and this is always cited first. If two or more different atoms or groups are attached to a single atom, the symbol of the central atom is followed by the symbols of the remaining atoms or groups in alphabetical order. The sole exceptions are acids, in the formulae of which hydrogen is placed first. When part of the molecule is a group, such as P=O, which occurs repeatedly in a number of different compounds, these groups may be treated as forming the positive part of the compound.

Examples:
1. PbCl_2 2. POCl_3 or POCl_5 3. H_3PO_4 4. SbCl_5

Coordination compounds. In the formula of a coordination entity, the symbol of the central atom(s) is placed first, followed by the ions and then the neutral ligands. Square brackets are used to enclose the whole coordination entity whether charged or not. This practice need not be used for simple species such as the common oxoanions (NO_3^-, NO_2^-, SO_4^{2-}, OH^-, etc.). Enclosing marks are nested within the square brackets as follows: [I], [[OH]], [[[OH]]], etc.

A structural formula of a ligand occupies the same place in a sequence as would its molecular formula.

Examples:

Abbreviations. These may be used to represent ligands in formulae, and they are cited in the same place as the formulae they stand for. The abbreviations should be lower case. Some commonly used abbreviations are in Table I-3.

Examples:
1. [Ph_3P]_2[PICl_6] 2. [Fe(CN)_5][Fe(CO)_5] 3. [Co(en)_2(NH_3)_2]^{3+}

The commonly used abbreviations for organic groups, such as Me, Ph, Bu, etc., are also acceptable in inorganic formulae. Note that the difference between an anion and its parent acid must be observed. Thus ac is an acceptable abbreviation for acetylacetone (acetone-2,4-dione) then becomes Hacac.

(i) The hydroxide ion is represented by the symbol OH^-, although the recommendations for the formulae of acids would suggest HO-. Example 3 accords with majority practice.

(iv) Note that in this example the cis-trans isomer is not specified.
investigation of the noble gases for possible Lewis basicity. Since the noble gases are isoelectronic with halide ions which can be strong Lewis bases, it seemed reasonable that noble gas adducts of strong Lewis acids might likewise exist:

\[
\begin{align*}
F^+ + BF_3 & \rightarrow BF_3^+ \quad (17.1) \\
Ne + BF_3 & \rightarrow NeBF_3 \quad (17.2) \\
Xe + BF_3 & \rightarrow XeBF_3 \quad (17.3)
\end{align*}
\]

Thorouigh studies of solutions of xenon in boron trichloride and boron tribromide were undertaken. A phase study of the melting point of these systems as a function of composition showed no evidence of compound formation. The Raman spectra of these gases is suggested by two lines of thought. (1) From an acid-base point of view, the strongest Lewis acid is the bare proton, \(H^+\), so if any of the noble gases is capable of exhibiting basic behavior it might be expected to do so with \(H^+\) and \(H_2O\): \(\text{He} + H^+ \rightarrow \text{HeH}^+ \quad (17.4)\)
\(\text{Ar} + H^+ \rightarrow \text{ArH}^+ \quad (17.5)\)

(2) From a simple molecular orbital diagram such as given in Fig. 5.7, it might be supposed that four electrons would result in a net bonding condition but that any number of electrons less than four would result in some bonding though not necessarily in an integral bond order. Spectroscopic evidence for species such as \(\text{HeH}^+\) and \(\text{ArH}^+\) has been obtained from a mixture of hydrogen and noble gases passed through gas discharge tubes. Similar reactions can take place between two noble gas atoms if energy is supplied to remove the necessary electron:

\[
\begin{align*}
\text{He} + \text{He} & \rightarrow \text{He}_2^+ \\
\text{Kr} + \text{Kr} & \rightarrow \text{Kr}_2^+ \\
\text{Ne} + \text{Xe} & \rightarrow \text{NeXe}^+ \\
\text{Ar} + \text{H}^+ & \rightarrow \text{ArH}^+ \quad (17.6)
\end{align*}
\]

Although there had been suggestions that some of the noble gases might form compounds unsuccessful attempts to oxidize krypton and xenon with fluorine in the 1930s essentially put a halt to such speculation, especially in view of the success of valency theory in relating stability to filled octets. This worship of the octet is all the more surprising in view of the fact that compounds with expanded valence shells were already known for over two-thirds of the remaining nonmetals. In the early 1960s Neil Bartlett was studying the properties of platinum hexafluoride, an extremely powerful oxidizing agent. In fact, merely mixing dioxygen with platinum hexafluoride, it is possible to remove one electron from the oxygen molecule and isolate the product:

\[
\text{O}_2 + \text{PtF}_6^- \rightarrow \text{O}_2^-[\text{PtF}_6]^- \quad (17.11)
\]

Bartlett realized that the first ionization energy of dioxygen, 1180 kJ mol\(^{-1}\) (12.2 eV), is almost identical to that of xenon, 1170 kJ mol\(^{-1}\) (12.1 eV). Furthermore, the dioxygen cation should be roughly the same size as \(\text{Xe}^+\) ion, and hence the lattice energies of the corresponding compounds should be similar. He mixed xenon and platinum hexafluoride with the result that an immediate reaction took place with formation of a yellow solid. Based on the volumes of gases that reacted, Bartlett suggested the formulation \(\text{Xe}^+[\text{PtF}_6]^-\). However, the reaction is not so simple as was once thought, and the product has been formulated variously as \(\text{Xe}\left[\text{PtF}_6\right] + \text{Xe}\left[\text{PtF}_6\right] + \text{Xe}\left[\text{PtF}_6\right]\). Despite the experimental difficulties in characterizing the products of the reaction there was no doubt whatever that a reaction had taken place and the myth of inertness was shattered forever.

**The Discovery of Stable, Isolable Noble Gas Compounds**

\[
\begin{align*}
\text{Kr} + \text{Kr} & \rightarrow \text{Kr}_2^+ \\
\text{Ne} + \text{Xe} & \rightarrow \text{NeXe}^+ \\
\text{Ar} + \text{H}^+ & \rightarrow \text{ArH}^+ \\
\text{BF}_3 + \text{Xe} & \rightarrow \text{XeBF}_3 \\
\text{Xe} + \text{BF}_3 & \rightarrow \text{XeBF}_3 \\
\text{HeH}^+ & \rightarrow \text{HeH}^+ \\
\text{ArH}^+ & \rightarrow \text{ArH}^+ \\
\text{BF}_3 + \text{He} & \rightarrow \text{HeBF}_3 \\
\text{BF}_3 + \text{Ar} & \rightarrow \text{ArBF}_3 \\
\text{BF}_3 + \text{Ne} & \rightarrow \text{NeBF}_3 \\
\text{BF}_3 + \text{Kr} & \rightarrow \text{KrBF}_3 \\
\text{BF}_3 + \text{Xe} & \rightarrow \text{XeBF}_3
\end{align*}
\]

Although there were indications that some of the noble gases might form compounds unsuccessful attempts to oxidize krypton and xenon with fluorine in the 1930s essentially put a halt to such speculation, especially in view of the success of valency theory in relating stability to filled octets. This worship of the octet is all the more surprising in view of the fact that compounds with expanded valence shells were already known for over two-thirds of the remaining nonmetals. In the early 1960s Neil Bartlett was studying the properties of platinum hexafluoride, an extremely powerful oxidizing agent. In fact, merely mixing dioxygen with platinum hexafluoride, it is possible to remove one electron from the oxygen molecule and isolate the product:

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\text{Ne} + \text{Xe} & \rightarrow \text{NeXe}^+ \\
\text{Ar} + \text{H}^+ & \rightarrow \text{ArH}^+ \\
\text{BF}_3 + \text{Xe} & \rightarrow \text{XeBF}_3 \\
\text{Xe} + \text{BF}_3 & \rightarrow \text{XeBF}_3 \\
\text{HeH}^+ & \rightarrow \text{HeH}^+ \\
\text{ArH}^+ & \rightarrow \text{ArH}^+ \\
\text{BF}_3 + \text{He} & \rightarrow \text{HeBF}_3 \\
\text{BF}_3 + \text{Ar} & \rightarrow \text{ArBF}_3 \\
\text{BF}_3 + \text{Ne} & \rightarrow \text{NeBF}_3 \\
\text{BF}_3 + \text{Kr} & \rightarrow \text{KrBF}_3 \\
\text{BF}_3 + \text{Xe} & \rightarrow \text{XeBF}_3
\end{align*}
\]
Names are constructed by joining other units to these base components. Affixes are syllables or numbers added to words or roots and they can be suffixes, prefixes, or infixes, according to whether they are placed after, before, or within a word or root. Representative examples are listed in Table I-1, together with their meanings.

### Table I-1

<table>
<thead>
<tr>
<th>Affix</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>-an</td>
<td>General suffix for many polyatomic anions in inorganic nomenclature (including coordination nomenclature) and in organic nomenclature: nitrate, acetate, hexanoate.</td>
</tr>
<tr>
<td>-c</td>
<td>Termination for name of many acids both inorganic and organic: sulfuric acid, benzoic acid.</td>
</tr>
<tr>
<td>-de</td>
<td>Termination for name of certain monocatomic anions: chloride, sulfide.</td>
</tr>
<tr>
<td>-ic</td>
<td>Termination for names of the more electronegative constituent (atom or group) in binary type names: disulfur dichloride; triiodide; cyanide.</td>
</tr>
<tr>
<td>-f</td>
<td>Termination for trivial name of certain hydrides such as CH₄, NH₃.</td>
</tr>
<tr>
<td>-fo</td>
<td>General termination for radicals and substituent groups of all kinds appearing as suffixes in systematic names: dichloroethane, dichloroethylene.</td>
</tr>
<tr>
<td>-i</td>
<td>Termination for prefix indicating a group of the type X(O): phosphonyl (X = P).</td>
</tr>
<tr>
<td>-i</td>
<td>Termination for infixes to indicate replacement of oxygen atoms and/or hydroxyl groups: thio-, nitrido-.</td>
</tr>
<tr>
<td>-o</td>
<td>Suffix for the trivial names of bicyclopentadienylmercurials and their derivatives: ferrocene.</td>
</tr>
<tr>
<td>-oan</td>
<td>Termination indicating a substituted derivative of the type XH₃: dichlorotriphenylphosphine (X = P).</td>
</tr>
<tr>
<td>-oan</td>
<td>Termination for prefix indicating a group of the type X(O): phenyl (X = C).</td>
</tr>
<tr>
<td>-oss</td>
<td>Termination for an oxoanion of a central element in an oxidation state lower than the highest. This nomenclature is not generally recommended: phosphorane [acid].</td>
</tr>
</tbody>
</table>
| -y | Termination for names of certain radicals containing oxygen, hydroxy, oxy-.
| -yl | Common termination for names of radicals: methyl, phosphanyl, uranyl. |


1-3 ELEMENTS, ATOMS, AND GROUP OF ATOMS

Names and Symbols of Atoms

The IUPAC-approved names of the atoms of atomic numbers 1-109 for use in the English language are listed in alphabetical order in the table inside the back cover.

Indication of Mass, Charge, and Atomic Number Using Indexes (Subscripts and Superscripts)

Mass, ionic charge, atomic number, [and molecular formula] are indicated by means of:

- left upper index [superscript] mass number
- left lower index [subscript] atomic number
- right upper index [superscript] ionic charge
- right lower index [subscript] molecular formula

Example:

$\text{S}_2^2^+$ represents a doubly positively ionized [tetrathio cation] composed of sulfur atom(s) of atomic number 16 and mass number 32.

Isotypes

Isotypes of hydrogen. The three isotopes, $^1\text{H}$, $^2\text{H}$, and $^3\text{H}$, have the names 'protium', 'deuterium', and 'tritium', respectively. It is to be noted that these names give rise to the names proton, deuteron, and triton for the cations $^1\text{H}^+$, $^2\text{H}^+$, $^3\text{H}^+$, respectively. Because the name 'protium' is often used in contradictory senses, of isotopically pure $^1\text{H}^+$ ions on the one hand, and of the naturally occurring unidifferentiated isotope mixture on the other, the Commission recommends that the latter mixture be designated generally by the more hydrogen, derived from hydrogen.

Name of an element or elementary substance of definite molecular formula or structure. These are named by adding the appropriate numerical prefix (see above) to the name of the atom to designate the number of atoms in the molecule. The prefix mon is not used except when the element does not normally exist in a monatomic state.

Examples:

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Trivial name</th>
<th>Systematic name</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>atomic hydrogen</td>
<td>monohydrogen</td>
</tr>
<tr>
<td>O</td>
<td>oxygen</td>
<td>dioxygen</td>
</tr>
<tr>
<td>3O₂</td>
<td>ozone</td>
<td>trioxygen</td>
</tr>
<tr>
<td>4P₂</td>
<td>white phosphorus</td>
<td>tetraphosphorus</td>
</tr>
<tr>
<td>S₈</td>
<td>sulfur</td>
<td>polysulfur</td>
</tr>
<tr>
<td>6S₈</td>
<td>o-sulfur, β-sulfur</td>
<td>octasulfur</td>
</tr>
<tr>
<td>7S₈</td>
<td>μ-sulfur (plastic sulfur)</td>
<td>polysulfur</td>
</tr>
</tbody>
</table>

[Not all of these sub- and superscripts will normally be used at one time. Thus we may have $^{16}\text{S}^2^+$, the IUPAC example, or we might have $^{32}\text{S}^2^+$ for the tetrathio cation.$]
The Fluorides of the Noble Gases

Mixing xenon and fluorine and activating the mixture by thermal, photochemical, or similar means result in the production of fluorides:

\[ \text{Xe} + \text{F}_2 \rightarrow \text{XeF}_2 \]  \hspace{1cm} (17.12)

\[ \text{Xe} + 2\text{F}_2 \rightarrow \text{XeF}_4 \]  \hspace{1cm} (17.12)

\[ \text{Xe} + 3\text{F}_2 \rightarrow \text{XeF}_6 \]  \hspace{1cm} (17.14)

The chief difficulties in these reactions (since the proper equipment for handling elemental fluorine at high pressure has not been assembled) are not the syntheses but the separations. All three products tend to form (Fig. 17.2). Xenon difluoride can be obtained either by separating it rapidly before it has a chance to react further (by freezing it out on a cold-finger, for example) or by keeping a high Xe-to-F\(_2\) ratio. The hexafluoride is favored by large excesses of fluorine and low temperatures, but some XeF\(_6\) is present which must be separated. The best production of XeF\(_6\) is obtained using gases at low pressure and a "hot wire," a nickel filament at 700-800 °C. The reactor is cooled in liquid nitrogen. The most difficult compound to prepare pure is xenon tetrafluoride since even optimum conditions for its formation thermally (Fig. 17.2) will result in concomitant formation of XeF\(_2\) and XeF\(_4\). The use of dioxygen difluoride at low temperatures and pressures provide XeF\(_6\) in high yield and purity:

\[ \text{Xe} + 2\text{O}_2\text{F}_2 \rightarrow \text{XeF}_4 + 2\text{O}_2 \]  \hspace{1cm} (17.16)

The chemistry of krypton is much more limited than that of xenon. Apparently only the difluoride forms directly from the elements. Attempts to make helium, neon, and argon fluorides have been unsuccessful. Radon should react even more readily than xenon, but its chemistry is complicated by the difficulty of working with a compound of such exceedingly high radioactivity. Nevertheless, the formation of compounds with fluorine was shown conclusively shortly after the discovery of xenon compounds, but their exact natures were not elucidated. More recently radon chemistry in solution has been studied (see below).

There are currently two approaches to the problem of bonding in noble gas compounds. Neither is completely satisfactory, but between the two they account adequately for the properties of these compounds. The first might be termed a valence bond approach. It would treat the xenon fluorides by means of expanded valence shells through promotion of electrons to the 5d orbitals:

**Ground state:** \[ \text{Xe} = [\text{Kr}] 5s^2 5p^6 5d^10 6s^2 \]

**Valence state:** \[ \text{Xe} = [\text{Kr}] 5s^2 5p^6 5d^10 6p^6 \]

For XeF\(_n\), \( n = 1 \) and two bond form: for XeF\(_2\), \( n = 2 \) and four bond form; and for XeF\(_6\), \( n = 3 \) and six bonds form. Using the arguments of VSEPR theory (see Chapter 6 and further discussion below) the resulting electronic arrangements and structures are as follows:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Electron pairs</th>
<th>Hybridization</th>
<th>Predicted structure</th>
<th>Experimental structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>XeF(_2)</td>
<td>6 ( \text{sp}^3\text{d}^1 )</td>
<td>Linear (TBP)</td>
<td>Linear</td>
<td></td>
</tr>
<tr>
<td>XeF(_4)</td>
<td>6 ( \text{sp}^3\text{d}^2 )</td>
<td>Square (planar)</td>
<td>Square, planar</td>
<td></td>
</tr>
<tr>
<td>XeF(_6)</td>
<td>7 ( \text{sp}^3\text{d}^3 )</td>
<td>Nonoctahedral</td>
<td>Unknown exactly, (capped octahedron?) but not octahedral</td>
<td></td>
</tr>
</tbody>
</table>

![Fig. 17.2](image-url) - Equilibrium pressures of xenon fluorides as a function of temperature. Initial conditions: 125 mmol Xe, 1225 mmol F\(_2\) per liter. At higher Xe to F\(_2\) ratios the XeF\(_2\) diminishes considerably and the remaining two curves shift to the left. [From Selig, H. Inorg. Chem. 1967, 1, 403. Reproduced with permission.]

The use of Gillespie's VSEPR theory has allowed the rationalization of these as well as several other structures of noble gas compounds (Fig. 17.3). One of the signal successes of this approach was the early prediction that XeF\(_2\) was nonoctahedral (see Chapter 6). The most serious objection to it is the required promotion of electrons. This has been estimated to be about 1000 kJ mol\(^{-1}\) (10 eV) or more for xenon, a large amount of energy. Furthermore, d orbitals tend to be diffuse and their importance in nonmetal chemistry in a matter of some controversy (see Chapter 18).

An alternative approach to bonding in noble gas compounds is the molecular orbital approach involving three-center, four-electron bonds. Consider the linear F—Xe—F molecule. A 5p orbital on the xenon can overlap with fluorine bonding orbitals (either pure p orbitals or hybrids) to form the usual trio of three-centered orbitals: bonding, nonbonding, and antibonding (Fig. 17.4). Filling in the four valence electrons (2\( \text{sp}^3\text{d}^1 \) + F\(_2\) + F\(_2\)) results in a filled bonding orbital and a filled nonbonding to a first approximation orbital. A single bond (or bonding MO) is thus spread over the F—Xe—F system. A second p orbital at right angles to the first can form a second three-center F—Xe—F bond (XeF\(_4\)), and the third orthogonal p orbital can form a third three-center bond (XeF\(_6\)). The nature of the p orbitals involved in the bonding allows one to predict that XeF\(_2\) will be linear, XeF\(_4\) square planar, and XeF\(_6\)
IUPAC Recommendations on the Nomenclature of Inorganic Chemistry

The standards of nomenclature in chemistry are proposed by the International Union of Pure and Applied Chemistry (IUPAC). The current edition (the third) for inorganic nomenclature is *Nomenclature of Inorganic Chemistry: Recommendations 1990.* Issued by the Commission on Nomenclature of Inorganic Chemistry. Part I consists of 399 pages and it is to be followed by several other parts of specialized nomenclature. It is possible therefore to include here only a very small fraction as a general guide to good usage. Thus the following material is intended to guide the reader through the process of using good nomenclatural practice, but it is not meant to be a substitute for the *Recommendations* themselves.

The guidelines presented here (or even the unbridged set in the Red Book) should not be viewed as a rigid code but as an evolving attempt to clarify the process of naming. Usage must be by consensus and it is interesting to note that whereas preceding editions of the Red Book were entitled "Rules," the current edition consists of *Recommendations.*

The usage in our book has been as close to IUPAC nomenclature as is consistent with good pedagogy. We have followed the IUPAC Recommendations except in those cases in which they conflict directly with current American usage. Students are not served well by finding one type of nomenclature in the text while being encouraged to read the original literature in which they find a radically different nomenclature. The prime purpose of this book is to illustrate inorganic chemistry rather than the details of nomenclatural technique. The nomenclature has therefore been that which would serve best in teaching inorganic chemistry and help the students in reading the original literature.

This appendix consists of short excerpts from *Recommendations 1990.* Our comments and other additions have been placed in square brackets [ ]. Deletions have not been marked, but every attempt has been made to keep the intent of the original. Otherwise the following are verbatim extracts of the *Recommendations* with the exception of minor editing such as changing (1) numbers in series (Footnotes, Tables, and Examples) to make them continuous and (2) the spelling to conform to American usage, e.g., aluminum (Engl. aluminium), center (Engl. centre), cesium (Engl. caesium), etc. Footnotes not in square brackets are footnotes from the Red Book; footnotes in square brackets have been added by us. The Red Book consists of eleven chapters (with numbered subsections), which are here abstracted as "sections"; cross references have generally been omitted except to these major sections, Section I-1, Section I-2, etc.

We have occasionally placed older, often obsolete names in square brackets after the IUPAC name. In no case are these intended to be recommended alternatives but merely to be useful guides to the older (and sometimes current) literature.

All chapters in the Red Book begin with much interesting historical and philosophical material concerning nomenclature. These make interesting and educational reading, but they have not been reproduced for space reasons.

I-1 GENERAL AIMS, FUNCTIONS, AND METHODS OF CHEMICAL NOMENCLATURE

Methods of Inorganic Nomenclature

Systems of nomenclature

- Binary-type nomenclature. In this system, the composition of a substance is specified by the juxtaposition of element group names, modified or unmodified, together with appropriate numerical prefixes, if considered necessary.

  Examples:
  1. sodium chloride [NaCl] 2. silicon disulfide [SiS₂] 3. uranyl difluoride [UO₂F₂]

- Coordination nomenclature. This is an additive system for inorganic coordination compounds which treats a compound as a combination of a central atom with associated ligands (see Section I-6).

  Examples:
  1. tris(dimethylamino)arsine [As(N(CH₃)₂)₃] 2. potassium pentacarbonitrilomethanolate [K(C₅H₇N)₅]⁻

- Substitutive nomenclature. This system is used extensively for organic compounds, but it has also been used to name many inorganic compounds. It is based on the concept of a parent hydrocarbom modified by substitution of hydrogen atoms by groups (radicals). (See Section I-6.)

  Examples:
  1. bromobutane [C₄H₉Br] 2. diethylamine [C₂H₅N] 3. trichlorophosphate [PCl₃]

I-2 GRAMMAR

Introduction

Chemical nomenclature may be considered to be a language. As such, it is made up of words and it should obey the rules of syntax.

Generally, nomenclature systems use a base on which the name is constructed. This base can be derived from a parent compound name such as [al (from silica) in substitutive nomenclature (mainly used for organic compounds)] or from a central atom name such as cobalt in additive nomenclature (mainly used in coordination chemistry).
The Chemistry of the Halogens and the Noble Gases

Linear molecule with three nonbonding electron pairs at the points of an equilateral triangle

Square planar molecule with two nonbonding electron pairs, one above and one below the plane of the molecule

Distorted octahedron with a nonbonding electron pair either at the center of a face or the midpoint of an edge

Square pyramidal molecule with a nonbonding electron pair protruding from the base of the pyramid

Trigonal pyramidal molecule with a nonbonding electron pair protruding from the apex of the pyramid

Perpendicular planar ion with two nonbonding electron pairs above and below the plane of the perpendicular

Fig. 17.3 Molecular shapes predicted by simple VSEPR theory. Bond angle values represent experimental results where known.

Fig. 17.4 Molecular orbital diagram for F—Xe—F three-center bond.

Structural Data for 14-Electron Species

The number of species isoelectronic with XeF$_6^-$ is quite limited. The anions SbBr$_6^-$, TeCl$_6^-$, and TeBr$_6^-$ are octahedral. Both IF$_6^-$ and XeF$_6^-$ are nonoctahedral. I$_2$ Iodine heptfluoride and rhenium heptfluoride may be considered isoelectronic with these species if they are all considered to have 14 valence shell electrons of approximately equal steric requirements. Both have a pentagonal bipyramidal structure (see Fig. 6.12). Most interestingly, the XeF$_6^-$ anion, formed by the Lewis acid XeF$_4^+$:

\[
\text{M}^+ + \text{F}^- + \text{XeF}_4^- \rightarrow \text{M}^+\text{XeF}_6^-(17.16)
\]

is the first example of a pentagonal planar inorganic ion (Fig. 17.3g). It can be rationalized in terms of five bonding pairs to fluorine atoms in a plane with a lone pair above and below the plane. The lone pair appears to be "locked in" to the axial positions as the molecule is not fluxional, as is the isoelectronic XeF$_6^-$. The molecular structure of XeF$_6^-$ has been a vexing problem. In the solid, XeF$_6^-$ and XeF$_5^-$ ions exist. The former has five bonding and one nonbonding pair and is therefore expected to be a square pyramid with the lone pair occupying the sixth position of the idealized octahedron. Experimentally, this is found to be the case. In the gas phase, however, the structure is much more perplexing, from both an experimental and a theoretical view. Electron diffraction studies indicate that the molecular is a slightly distorted octahedron that is probably "soft" with respect to deformation. There are no measurable dipole moments, ruling out large, static distortions. The model of XeF$_6^-$ is that of a stereochemically nonrigid molecule that rapidly passed from one nonoctahedral configuration to another.

The perfectly octahedral species conform to the expectations based on the simple MO derivation given above. The nonoctahedral fluoride species do not, but this difficulty is a result of the oversimplifications in the method. There is no inherent necessity for delocalized MOs to be restricted to octahedral symmetry. Furthermore, it is possible to transform delocalized molecular orbitals into localized molecular orbitals. Although the VSEPR theory is often couched in valence bond terms, it depends basically on the repulsion of electrons of like spins, and if these are in localized orbitals the results should be comparable.

---

Stereoviews and Stereopsis

Closely related to the use of models is the corresponding one of stereoviews to illustrate molecular perspective. The increased availability of molecular data and the use of computers to generate stereoviews has made their use routine in journal accounts of structure determinations. Unlike models, no matter how useful, stereoviews have the ability to capture the depth of a three-dimensional structure on a two-dimensional sheet of paper. An increased number of stereoviews has been included in this edition.

It is not necessary to view stereoviews three dimensionally: Either half conveys much information by itself. But every effort should be made to learn the “tricks” of stereopsis—the amount of insight to be gained is more than rewarding. And although initial attempts may be frustrating, it is well worth the effort and the process becomes increasingly simple and routine. Furthermore, in addition to being a purely informational routine, it is an aesthetic experience. Don’t be afraid to experiment—each person has different ways of facilitating the process. However, the following generalizations should be helpful.

The basic principle (“secret”) of stereopsis is that one is having the eyes doing something that they would never otherwise do; that is, each eye must look at a different image (as opposed to the same image from a slightly different angle). The common frustration in attempting to look at stereoviews in that first both eyes look at the left image, then both eyes look at the right image, then both eyes... It was to break this coordinated behavior of the human visual system that the old-fashioned and bulky stereoscope was invented. Today, folding viewers can readily do the job (see below). By all means, use such a viewer in your initial attempts. It isolates the eyes from each other. Start with a simple stereoview with lots of visual clues to aid the perspective; the cubic crystal systems of Chapter 4 are good. Have the image to be viewed lying perfectly flat. Put the stereoviewer over the images and try to have the left image, and the right eye at the right image. The way to have the eyes looking parallel so that the left eye is looking at the left image, and the right eye at the right image. This is to have the eyes looking parallel so that the left eye is looking at the left image, and the right eye at the right image. The way to have the eyes looking parallel is to view something “at infinity.” It does not have to be the horizon; it can be a sheet of paper or your hand. Use paper “glue-on’s” or light pencil drawings to indicate the osmyl groups of the molecule.

Once the above has been achieved, it is usually possible for the (human) viewer to become sufficiently adept at the process that the (optical) viewer can be dispensed with. The “trick” is to have the eyes looking parallel so that the left eye is looking at the left image, and the right eye at the right image. The way to have the eyes looking parallel is to focus on anything, let your gaze drop to the stereoview. If you find that you can achieve stereopsis more readily this way, fine: If it works, use it! But please remember that the image you see will be inverted. For most purposes this makes no difference, but if the image is a chiral molecule, the cross-eyed method will give the perception of the other enantiomer from the one portrayed.

Problems

III.1 Construct a chiral $D_2$ model as shown. Through which faces does the $C_3$ axis pass? In viewing the model as an example of $D_2$ symmetry (A = B), where are the secondary $C_2$ axes that place it in a dihedral group? How is it that the $C_2$ group lacks these? Which enantiomer do you have? Do you have any problems constructing the other enantiomer? Does the “trick” for constructing the second enantiomer give you any insight into symmetry operations and chirality?

III.2 Construct a model of buckminsterfullerene, “buckyball,” according to the directions in the reference in Footnote 2.

a. Turn to Chapter 3 and do Problems 3.32 through 3.36 on the basis of the model in your hands. Use paper “glue-on’s” or light pencil drawings to indicate the osmyl groups of any atom groups of the model as an example of stereoviews.

b. Bromination of buckyball yields a derivative with 12 Br molecules adding across double bonds.

$$C_{60} + 12 \text{ Br}_2 \rightarrow C_{60}\text{Br}_{12}$$

The resultant structure has a very high and unusual symmetry, with the remaining 18 double bonds shielded from addition by the bulky bromine atoms. Suggest a structure.

III.3 Turn to Chapter 12 and do Problem 12.28.


As with many inorganic systems, the differences between alternative interpretations is more apparent than real. Favoring the purely octahedral molecule will be reduced promotion energies and reduced steric requirements. If these two constraints are relaxed, a stereochemically active ("hybridized") lone pair is favored, probably as a result of better overlap and stronger bonds.

Gillespie first discussed the problem presented to the VSEPR theory by the perfectly octahedral species such as $\text{SbF}_6^{2-}$, $\text{TeCl}_6^{2-}$, and $\text{TeBr}_6^{2-}$. He pointed out that steric interactions between the large halide ligands will be of considerable importance. The Br—Br distance is approximately equal to the sum of the van der Waals radii and an "seven-coordinate" structure with a large lone pair occupying one position would be unfavorable. He therefore suggested that as a result, the seventh pair of electrons resides in an unhybridized $s$ orbital inside the valency shell. As such it would be sterically inactive except for shielding the valence electrons and loosening them from the nucleus. The somewhat lengthened bond in TeCl$_2^-$, 272 pm, compared with that expected from addition of covalent radii, 250 pm, is consonant with this interpretation (as it also is with a bond order of less than one from a three-center bond). In most fluorides the reduction of steric factors allows the lone pair to emerge to the surface of the molecule, although perhaps less than it would in a four- or five-coordinate molecule; hence these molecules appear less distorted than might have been expected (see also Chapter 6).

There are two essentially isostructural cation/anion pairs that are not iso-electronic: They differ by a pair of electrons that could potentially be stereochemically active lone pairs. These are $\text{BF}_2^+$/BrF and $\text{I}_2^+$/IF$_4^-$. Simple VSEPR theory would predict an octahedron and a square antiprism (or closely related eight-coordinate structure) for the cations. The anions might be expected to be a distorted octahedron ($\text{BrF}_4^-$), the isoelectronic $\text{XeF}_6^2-$, and a distorted square antiprism ($\text{I}_2^+$). However, bromine is smaller than xenon, and even the larger iodine atom apparently reaches its coordination limit with eight fluorine atoms. Thus the anions are also a perfect octahedron and a perfect square. They differ from the corresponding cations only in having longer X—F bonds, as might be expected if steric crowding of the fluorine atoms forces the nonbonding pair of electrons into a shielding, centrosymmetric $s$ orbital.

Other Compounds of Xenon

Attempts to isolate a stable xenon chloride have not been very successful. Two chlorides have been identified, and both are apparently unstable species observable as orbital electrons into a shielding, centrosymmetric octahedron. These are $\text{BrF}_4^-$/$\text{BrF}_5^-$ and $\text{IF}_4^-$/IF$_6^-$. Simple VSEPR theory would not account for the bonding; therefore the structures should be more apparent than real. Favoring the purely octahedral molecule will be reduced promotion energies and reduced steric requirements. If these two constraints are relaxed, a stereochemically active ("hybridized") lone pair is favored, probably as a result of better overlap and stronger bonds. Gillespie first discussed the problem presented to the VSEPR theory by the perfectly octahedral species such as $\text{SbF}_6^{2-}$, $\text{TeCl}_6^{2-}$, and $\text{TeBr}_6^{2-}$. He pointed out that steric interactions between the large halide ligands will be of considerable importance.


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$^{13}$ Use of the $s$ orbital in stereochemically active ("hybridized") orbitals requires raising the energy of these electrons to that of the bonding orbitals. The use of empty, high energy orbitals also requires an increase in average electron energy ("lowering of holes").


$^{15}$ For the determination of the structure of $\text{IF}_6^-$, a discussion of the BrF$_2^+$/BrF and IF$_2^+$/IF$_4^-$ problem, and appropriate earlier references, see Mahjoub, A. R.; Soppet, K. Angew. Chem. Int. Ed. Engl. 1991, 30, 876-878.


3. **Chiral (D₃)** "octahedral" models. By cutting and pasting in such a way as to leave "chelate rings" on the model both A and A' enantiomers can readily be constructed. Note that having chelate rings on both triangle 2 and triangle 7 is redundant. One may be removed or used as a construction flap. If A = B, the model has D₃ symmetry; if A ≠ B, the symmetry is C₃.

4. **Icosahedral models.** Cut out the entire figure drawn with solid lines. Omit the faces marked "O₃ only." Construction is facilitated by bending and gluing the two end sections into the "capping" and "foundation" pentagonal pyramids first. Then the remaining "equatorial" band of ten faces can be wound around and fastened to these "end groups." The complete icosahedron represents the B₆H₁₄ ion or dicarbaclosododecaboranes. Other polyhedral boranes can be formed by removal of the appropriate faces from the complete icosahedron.

5. **Pentagonal dodecahedral models.** This model can be constructed in a similar way by copying, cutting, and gluing the pentagonal drawing.

A similar outline drawing for the construction of buckminsterfullerene has been published. Several other polyhedral models constructed from simple materials have been described in a series of articles.

---

1. Note that this model has been altered somewhat from the general model of Fig. H.1. In previous editions an attempt was made to avoid such changes but with the availability of photocopying machines with size altering adjustments and the student's ubiquitous use of them, we have been less restrictive in this edition offering the student greater flexibility.


3. Yamana, S. J. Chem. Educ. 1988, 65, 1972 (tetragonal pyramid); 1989, 66, 1019 (triangular dodecahedron); 1990, 67, 1029-1030 (interpenetrating trigonal pyramids). These are but three examples. Additional ones may be found from the references in these or by consulting the author indexes of the Journal of Chemical Education between the years 1979 and present.
Sometimes the fluorination occurs with displacement of a by-product:

$$2R_2SiCl + XeF_2 \rightarrow 2R_2SiF + Cl_2 + Xe$$ (17.28)

Even more interesting is the production of the $Xe^+$ cation in anionist pentfluoride as solvent. It was first prepared by reduction of $Xe(II)$. Many reducing agents are suitable, including metals such as lead and mercury, or phosphorus trifluoride, lead monoxide, arsenic trioxide, sulfur dioxide, carbon monoxide, silicon dioxide, and water. Surprisingly, even gaseous xenon may be used as the reducing agent:19

$$Xe + XeF^+ + 2F^- \rightarrow Xe^+ \quad (17.29)$$

Alternatively, one can view this as an acid-base (instead of a redox) reaction of a basic xenon atom undergoing a nucleophilic attack on an acidic xenon cation to form the diatomic cation (cf. the reaction of $Xe + CH_2$, page 827).

As mentioned above, xenon trioxide is an endothermic compound which explodes violently at the slightest provocation. Aqueous solutions are stable but powerfully oxidizing. These solutions are weakly acidic ("xenic acid") and contain molecular $H_2XeO_4^-$ ions. When these solutions are made basic, $H_2XeO_4^-$ ions are formed and alkali hydrogen xenates, $MHXeO_3$, may be isolated from them. Hydrogen xenate ions disproportionate in alkaline solution to yield perxenates:

$$2HXeO_3^{-} + 2OH^- \rightarrow XeO_4^{2-} + Xe + O_2 + 2H_2O \quad (17.30)$$

Xenate solutions may also be oxidized directly to perxenate with ozone. Solid perxenates are rather insoluble and are unusually stable for xenon-oxygen compounds: Most do not decompose until heated above 200 °C. X-ray crystallographic structures have been determined for several perxenates, and they have been found to contain the $XeO_4^{2-}$ anion. Dihydrogen perxenate solutions as shown by the following $E^0$ values:

$$H_2XeO_4^+ \quad [2.9] \quad XeO_4^{2-} \quad [1.17]$$

The nature of the species and the values of the potentials are not as well characterized in basic solution, but the oxidizing power seems to be somewhat less:

$$HXeO_4^- \quad [0.33] \quad XeO_4^{2-} \quad [1.74]$$

Like the fluorides, they are relatively "clean" reagents. Unfortunately, the explosive properties of $XeO_4^2-$ have resulted in less work being done with them.

Xenon forms stable compounds only with the most electronegative elements: fluorine ($\chi = 4.0$) and oxygen ($\chi = 3.5$), or with groups such as OsF$^-$ and UO$^-$ that contain these elements. Reasonably stable, though uncommon, bonds are known between xenon and both chlorine ($\chi = 3.0$) and nitrogen ($\chi = 3.0$). Bis(trifluoromethyl)xenon, $Xe(CF_3)_2$, ($\chi_{CF_3} = 3.3$), is known but decomposes in a matter of minutes.

Xenon hexafluoride can act as a Lewis acid. It reacts with the heavier alkali fluorides to form seven-coordinate anions, which in turn can rearrange to form eight-coordinate species:

$$MF + XeF_6 \rightarrow XeF_5^-(M = Na, K, Rb, Cs) \quad (17.32)$$

$$2M[XeF_5^-] \rightarrow M_2[XeF_6] + XeF_4^-(M = Rb, Cs) \quad (17.33)$$

The octafluoroxenates are the most stable xenon compounds known; they can be heated to 400 °C without decomposition. The anions have square antiprismatic geometry. They, too, present a problem to VSEPR theory analogous to that of $XeF_6^2-$ since they should also have a stereochemically active lone pair of electrons that should lower the symmetry of the anion. If the steric crowding theory is correct, however, the presence of eight ligands alone could force the lone pair into a stereochemically inert $s$ orbital.

Xenon fluorides can also act as fluoride ion donors. Strong Lewis acids react with xenon fluorides to yield the expected compounds, but since both the cationic and anionic species can form fluoride bridges, the stoichiometries may appear strange at times:

$$XeF_6 + PtF_5 \rightarrow XeF_5^2- + PtF_6^- \quad (17.34)$$

$$2XeF_6 + AsF_5 \rightarrow XeF_5^2- + AsF_6^- \quad (17.35)$$

$$XeF_6 + SbF_5 \rightarrow XeF_5SbF_6 \quad (17.36)$$

Even compounds with deceptively simple stoichiometries may be more complex, as in the case of $XeF_7^2-$AsF$_3$, which has both bridged cations and anions:

$$\begin{align*}
\begin{array}{c}
F \\
Xe \\
F
\end{array}
\end{align*}$$

Bartlett's compound (page 827), though still incompletely understood, is thought to be of this type. Krypton difluoride forms analogous compounds such as $KrF_2^+$AsF$_3^-$, $KrF_2^+$SbF$_6^-$, $KrF_2^+$SbF$_5^-$, and $KrF_2^+$SbF$_4^-$, and these together with the parent $KrF_2^+$ were the only known compounds of krypton known until recently.20


Appendix

Models, Stereochemistry, and the Use of Stereopsis

Paper Models

It is convenient for many purposes to have models available for inspection in order to realize fully the three-dimensional aspect of molecular and lattice structures. "Ball-and-stick" models of various stages of sophistication are useful when it is necessary to be able to see through the structure under consideration. Space-filling models of atoms with both covalent and van der Waals radii are particularly helpful when steric effects are important. The space-filling models and the more sophisticated stick models tend to be rather expensive, but there are several inexpensive modifications of the "ball-and-stick" type available. It is extremely useful to have such a set at hand when considering molecular structures.

Simple tetrahedral or octahedral models are useful in connection with basic structural questions (as, for example, the first time you try to convince yourself that the two enantiomers of CHFCIBr or of (Co(en))$_3$$^{3+}$ are really nonsuperimposable). If stick models are not available, such simple models can be constructed in a few minutes from paper. In addition, models having bond angles not normally found in ball-and-stick kits—for example, the icosahedral boranes and carboranes—can also be readily constructed from paper. Paper models are especially useful when large numbers of models are necessary as, for example, in constructing models of the iso- and heteropolyanions.

On the following pages generalized outlines are given for the construction of tetrahedra, octahedra, icosahedra (Fig. H.1) and pentagonal dodecahedra (Fig. H.2). These outlines may be reproduced as many times as desired by means of photocopying machines. Instructions for cutting are as follows:

1. Tetrahedral models. Cut out the four triangles enclosed by the $T_d$ brackets (Fig. H.3) and marked with the vertical lines in the drawing. Glue or tape tabs onto adjacent faces to form the tetrahedron.

2. Octahedral models. Cut out the two sets of eight triangles enclosed by the $O_h$ brackets and marked with the horizontal lines in the drawing. Glue or tape tabs onto adjacent faces to form the octahedron.
Reaction of HCN=NH₂ salts of [AsF₅]⁻ with RₓC≡N adds of AsF₅ with KrF₂, in nonaqueous solvents leads to salts characterized as [H_CNC(—Kr—F)⁺][AsF₅]⁻ and [RₓC≡N(—Kr—F)⁺][AsF₅]⁺ (Rₓ = CF₃, C₂F₅, n-C₃F₇, t-C₄F₉). Krypton fluoride has proven extremely useful as a fluorinating agent. It is 50 kJ mol⁻¹ more exothermic than fluorine, F₂. It may be used to raise metals to unusual oxidation states:²¹

\[
8\text{KrF}_2 + 2\text{Au} \rightarrow 2\text{KrF}^+\text{AuF}_2^- + 6\text{Kr} + \text{F}_2 \quad \text{(17.37)}
\]

\[
\text{KrF}_2^- + \text{F}_2 \rightarrow \text{KrF}_2^- + \text{F}_2 \quad \text{(17.38)}
\]

Bond Strengths in Noble Gas Compounds

As might be expected, xenon does not form any strong bonds, but it does form exothermic compounds with fluorine. Some typical bond strengths are listed in Table 17.1. Bartlett²² has shown that such values might have been expected by extrapolation of known bond energy in related nonmetal compounds.

Since radon is the heaviest member of the noble gas family it has the lowest ionization energy, 1037 kJ mol⁻¹ (10.7 eV), and might be expected to be the most reactive. The radioactivity of this element presents problems not only with respect to the chemist (who can be shielded) but also with respect to the possible compounds (which cannot). On the other hand, this radioactivity provides a built-in tracer since the position of the radon in a vacuum line can be ascertained by the \( \gamma \) radiation of Rn and the first and second daughters will not penetrate the vacuum line.

The Chemistry of Radon

Since radon is the heaviest member of the noble gas family, it is the least stable isotope of astatine has a half-life of only 8.3 hours, and the chemistry of this element presents problems not only with respect to the chemist (who can be shielded) but also with respect to the possible compounds (which cannot). On the other hand, this radioactivity provides a built-in tracer since the position of the radon in a vacuum line can be ascertained by the \( \gamma \) radiation of Rn and the first and second daughters will not penetrate the vacuum line. 

Several trends are noticeable from the data in the table. The bond strengths of the interhalogens are clearly related to the difference in electronegativity between the component halogen atoms, as expected on the basis of Pauling's ideas on ionic character (Chapter 5). Furthermore, the tendency to form the higher fluorides and chlorides depends upon the initial electronegativity of the central atom. Only iodine forms a hexafluoride or a triiodide. Not shown in Table 17.2 except indirectly by computation from the values is the instability of certain lower oxidation states to disproportionation:

\[
\text{SIF} \rightarrow 2\text{I} + \text{IF}_3 \quad \text{(17.39)}
\]

Gain in bond energy = 250 kJ mol⁻¹

This tendency toward disproportionation is common among the lower fluorides of iodine and bromine. The behavior of the four iodine fluorides presents a good picture of the factors important in the relative stabilities. Both IF and IF₃ tend to disproportionate (the former to the extent that it cannot be isolated), not because of weakness in

### Table 17.2

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Bond</th>
<th>Bond energy (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XeF₂, XeF₄, XeF₆</td>
<td>Xe—F</td>
<td>130±4</td>
</tr>
<tr>
<td>XeO₂</td>
<td>Xe—O</td>
<td>84</td>
</tr>
<tr>
<td>KrF₂</td>
<td>Kr—F</td>
<td>50</td>
</tr>
</tbody>
</table>

²² Bartlett, N. Endeavour 1963, 80, 3. It is interesting to note that Bartlett did not use isoelectronic series in his extrapolations. Furthermore, although his extrapolations provide quite reasonable values for XeF₂ and XeO₂, they led to much too high a value for KrF₂.
²³ The \( \gamma \) radiation of \(^{222}\text{Rn}\) and the first and second daughters will not penetrate the vacuum line.
Appendix

Tanabe–Sugano Diagrams

bonding (IF has the strongest bond of any of the interhalogens), but because of the greater number of bonds in the pentafluoride to which they disproportionate. At the other extreme, the heptafluoride, while stable, is a reactive species (it is a stronger fluorinating agent than IF) because of the weaker bond energy (resulting from both steric factors and resistance to the extremely high oxidation state on the part of the iodide). Bromine fluoride likewise disproportionate, but BrF$_3$ and BrF$_5$ are stable. Chlorine forms a monofluoride, trifluoride, and pentafluoride.

The competitive forces tending to stabilize high or low oxidation states can be readily rationalized. The simplistic statement: "The tendency to stabilize high oxidation states in compounds XY$_n$ is favored by high electronegativities of Y (usually fluorine) and low electronegativities of X (the heavier halogens)." is definitely not wrong; but does it explain the relative instability of IF (with the strongest interhalogen bond, see above)?

Consider the following reaction to oxidize a halogen monohalide to a trihalide:

$$X - Y + Y - Y \rightarrow Y - X - Y$$

(17.40)

It is obvious that no great change in bond order occurs in this process and so any enthalpic driving force must result from the quality of the bonds. A simple analysis of ionic resonance energy ($E_{IRE}$) in terms of partial charges, rationalizes the relative stability of the monohalide and the trihalide. Assume that the ionic resonance energy that increases the quality of the bonds may be equated to simple Madelung or coulombic energy:

$$E_{IRE} = \delta_X \delta_Y$$

(17.41)

Case I. $\delta_Y$ is approximately the same in XY and XY$_2$ and $\delta_X = 3\delta_Y$. This is a good approximation for Y = F, an element with high values of both $a$ and $b$, i.e., a high inherent electronegativity but low charge capacity; it becomes saturated with negative charge easily. It is also a good approximation for a large, soft, iodine, $X = I$, which can increase its positive charge to accommodate three fluorine atoms. In this case, clearly, $3\delta_X \gg \delta_X \delta_Y$, and the trihalide is favored.

Case II. $\delta_X$ is similar in XY and XY$_2$, and since $\delta_X = 3\delta_Y$, this becomes an increasingly good approximation as Y becomes larger with lower values of both $a$ and $b$, and the large, soft central atom becomes smaller and harder. In this case the monohalide is favored. Exactly the same result is obtained if the initial electronegativity of the central halogen is assumed to be higher in a higher oxidation state, and $\delta_X$ and ionic resonance energy are lower. The same arguments apply equally well to all of the oxidation states:

$$X - X + 7Y = 2X - Y + 6Y = 2XY + 4Y = 2XY + 2Y = 2XY + 2Y$$

(17.42)

26 See the discussion of the instability of CaX in Chapter 4.
Table F.1 (Continued)

<table>
<thead>
<tr>
<th>Half-reaction</th>
<th>$E^0 (V)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ti}^{3+} + 2e^- \rightarrow \text{Ti}$</td>
<td>+1.60</td>
</tr>
<tr>
<td>$\text{Mn(OH)}_2 + 2e^- \rightarrow \text{Mn} + 2\text{OH}^-$</td>
<td>+1.355</td>
</tr>
<tr>
<td>$\text{Mn}^{2+} + 2e^- \rightarrow \text{Mn}$</td>
<td>+1.182</td>
</tr>
<tr>
<td>$V^{2+} + 2e^- \rightarrow V$</td>
<td>+1.125</td>
</tr>
<tr>
<td>$\text{Te} + 2e^- \rightarrow \text{Te}$</td>
<td>+0.90</td>
</tr>
<tr>
<td>$2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^-$</td>
<td>+0.828</td>
</tr>
<tr>
<td>$2\text{Mn}^{2+} + 2e^- \rightarrow 2\text{Mn}$</td>
<td>+0.762</td>
</tr>
<tr>
<td>$\text{Se} + 2e^- \rightarrow \text{Se}^{2-}$</td>
<td>+0.676</td>
</tr>
<tr>
<td>$\text{S}_8 + 16e^- \rightarrow 8\text{S}^{2-}$</td>
<td>+0.577</td>
</tr>
<tr>
<td>$\text{O}_2 + e^- \rightarrow \text{O}^{2-}$</td>
<td>+0.333</td>
</tr>
<tr>
<td>$\text{Fe}^{3+} + 2e^- \rightarrow \text{Fe}^{2+}$</td>
<td>+0.44</td>
</tr>
<tr>
<td>$2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^-$</td>
<td>pH = 7 +0.418</td>
</tr>
<tr>
<td>$\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}$</td>
<td>+0.236</td>
</tr>
<tr>
<td>$\text{Mn}^{2+} + 3\text{H}_2\text{O} + 2e^- \rightarrow 2\text{Mn}^{2+} + 2\text{OH}^-$</td>
<td>+0.234</td>
</tr>
<tr>
<td>$\text{Sn}^{4+} + 2e^- \rightarrow \text{Sn}$</td>
<td>+0.141</td>
</tr>
<tr>
<td>$\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{HO}_2^- + 4\text{H}^+$</td>
<td>+0.065</td>
</tr>
<tr>
<td>$\text{O}_2 + e^- + \text{H}_2\text{O} \rightarrow \text{HO}_2^- + \text{H}_2\text{O}$</td>
<td>+0.053</td>
</tr>
<tr>
<td>$2\text{Mn}^{2+} + 2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{Mn}^{2+} + 2\text{OH}^-$</td>
<td>+0.146</td>
</tr>
<tr>
<td>$\text{MnO}^- + e^- \rightarrow \text{MnO}^{2-}$</td>
<td>+0.27</td>
</tr>
<tr>
<td>$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$</td>
<td>+0.339</td>
</tr>
<tr>
<td>$\text{Hg}^{2+} + 2e^- \rightarrow 2\text{Hg}$</td>
<td>+0.389</td>
</tr>
<tr>
<td>$2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- + \text{O}_2$</td>
<td>+0.401</td>
</tr>
<tr>
<td>$\text{Cu}^{2+} + e^- \rightarrow \text{Cu}$</td>
<td>+0.318</td>
</tr>
<tr>
<td>$\text{ClO}_2^- + 4\text{H}_2\text{O} + 8e^- \rightarrow 2\text{Cl}^- + 8\text{H}_2\text{O}$</td>
<td>+0.56</td>
</tr>
<tr>
<td>$2\text{Mn}^{2+} + 2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{Mn}^{2+} + 4\text{OH}^- + \text{O}_2$</td>
<td>+0.388</td>
</tr>
<tr>
<td>$\text{I}_2 + 2e^- \rightarrow 2\text{I}^-$</td>
<td>+0.620</td>
</tr>
<tr>
<td>$2\text{O}_2 + 4\text{H}_2\text{O} + 8e^- \rightarrow 2\text{O}_2^- + 8\text{H}_2\text{O}$</td>
<td>+0.695</td>
</tr>
<tr>
<td>$\text{Fe}^{3+} + 2e^- \rightarrow \text{Fe}^{2+}$</td>
<td>+0.773</td>
</tr>
<tr>
<td>$\text{NO}_2^- + \text{H}_2\text{O} + e^- \rightarrow \text{NO}_3^- + \text{H}_2\text{O}$</td>
<td>+0.723</td>
</tr>
<tr>
<td>$\text{Ag}^+ + e^- \rightarrow \text{Ag}$</td>
<td>+0.799</td>
</tr>
<tr>
<td>$2\text{Mn}^{2+} + 2\text{H}_2\text{O} + 4e^- \rightarrow 2\text{Mn}^{2+} + 4\text{OH}^- + \text{O}_2$</td>
<td>pH = 7 +0.618</td>
</tr>
<tr>
<td>$\text{Hg}^{2+} + 2e^- \rightarrow \text{Hg}$</td>
<td>+0.908</td>
</tr>
<tr>
<td>$2\text{Mn}^{2+} + 2\text{H}_2\text{O} + 4e^- \rightarrow 2\text{Mn}^{2+} + 4\text{OH}^- + \text{O}_2$</td>
<td>+0.90</td>
</tr>
</tbody>
</table>

**Reduction of water in basic solution.**

First transition series except Cu (+2 + 0).

See pp 580-587, 594-599.

Reduction of neutral water

Reduction of water (H$_2$O) in acidic solution.

Reduction of water (H$_2$O$^+$) in acidic solution.

Reduction of (oxidation by) O$_2$ in basic solution; the reverse is the oxidation (destruction) of water as solvent.

Strongest oxidizing agent, OF$_2$.
molecular iodine behaves as a Lewis acid towards the iodide ion (as it does to other Lewis bases; see Chapter 9):

\[ \text{I}_2 + \text{I}^- \rightarrow \text{I}_3^- \]  

(17.43)

Similar reactions occur with other halogens, and every possible combination of bromine, chlorine, and iodine exists under appropriate conditions in aqueous solution:

\[ \text{Br}_2 + \text{I}^- \rightarrow \text{IBr}_2^- \]  

(17.44)

The participation of fluorine is less common, but several fluoride-containing trihalide ions have been isolated as crystalline salts (Table 17.3). The triiodide ion presents exactly the same problem to classical bonding theory as does xenon difluoride, and although the triiodide ion was discovered in 1819, only eight years after the discovery of iodine itself, chemists managed to live with this problem for almost a century and a half without coming to grips with it. The explanation offered most often was that the interaction was electrostatic—an ion-induced dipole interaction. The existence of symmetrical triiodide ions as well as unsymmetrical triiodide ions makes this interpretation suspect, and the existence of ions such as \( \text{BrF}_3^- \) and \( \text{IF}_4^- \) makes it untenable.

Two points of view are applicable to these species, as they also are to the nonelectronic noble gas fluorides: (1) a valence bond approach with promotion of electrons to orbitals; and (2) three-center, four-electron bonds. The same arguments, pro and con, apply as given previously, so they will not be repeated here. Independent of the alternative approaches via VB or MO theory, all are agreed that Madelung energy ("ionic character") is very important in stabilizing both the polyhalide ions and the polyhalogen compounds.

The polyiodide ions may conveniently be classified into two groups (\( X_3^\text{−} \)-type ions belong to both groups): (1) those that are nonelectronic with noble gas compounds and have general formulas \( XY_n^- \), where \( n \) is an even number; (11) polyiodide ions, mostly polyiodide ions, \( I_x^- \), where \( x \) can have various values, usually odd.

Group I polyiodide ions generally consist of a central atom surrounded by two, four, six, or eight more electronegative atoms, with linear, square planar, distorted octahedral, and square antiprismatic structures, respectively. These structures obey the VSEPR rules and are closely related to polyhalogen structures, differing by a lone pair in place of a bonding pair. They obey the rules discussed above for polyhalogen and noble gas compounds. The Group II polyiodide ions present some unusual bonding situations, and so it is simplest to start with \( I_2^- \) and the two limiting structures of the \( I_x^- \) ion. The bond length in the iodine molecule is 267 pm. We can imagine that upon the approach of an \( I^- \) anion, the charge cloud of the \( I_x^- \) molecule will distort with a resulting induced dipole. The greater the distortion of the iodine charge cloud, the weaker the original \( I—I \) covalent bond is apt to become, and we might expect that bond to lengthen somewhat. This is the situation in ammonium triiodide: The \( 1—1 \) bond lengths are 382 pm and 310 pm. The "intramolecular" bond (original diiodine bond) has lengthened by 15 pm, while the long "intermolecular" bond is 40 pm longer than a "normal" covalent bond and only about 80-100 pm shorter than a simple van der Waals contact. Further approach by the iodide ion eventually will result in a symmetrical triiodide system. Such is found in tetraphenylarsonium triiodide, \( \text{Ph}_4\text{As}^(+)\text{I}_3^- \), in which the two bond lengths are equal at 290 pm (Fig. 17.7). The question is why both symmetrical and unsymmetrical triiodide ions are found in crystal structures has not been completely resolved. In many ways it parallels the problem of symmetrical and unsymmetrical hydrogen bonding systems, \( \text{F}—\text{H}—\text{F} \), unusual bonding.
boldface, and Brewer and coworkers (italics). As in the case of the energies the purpose of the table is for quick reference and the bond length is given as a typical value that should be accurate for most purposes ±2 pm (0.02 Å).

For special purposes and precise computations, the original sources should be consulted for the value, nature, and source of the bond energies, and for the accuracy, experimental method, and variability of the bond lengths. Space requirements prohibit extensive tabulation of information of this type here.

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### An Overview of Standard Reduction Potentials of the Elements

The following table gives a quick overview and perspective of electrochemical potentials of the elements. For each group of elements, brackets indicate the limiting potentials for half-reactions \([\text{Me}^{+} + ne^{-} \rightarrow \text{Me} \, (\text{metals})]; \text{X}_2 + \text{n}e^{-} \rightarrow 2\text{X}^{(\text{II})} \, (\text{halogens})\) of the elements [e.g., \(\text{Li}^+ / \text{Li}\) and \(\text{Na}^+ / \text{Na}\) for Group IA (1)] for that group. Other selected half-reactions are also listed. Bold-face type in the table indicates important limiting potentials for aqueous solutions (see Chapter 10) and italic type indicates half-reactions in 1 M \(\text{OH}^{-}\). Many elements and oxidation states are omitted here for simplicity's sake. More extensive data may be found in the discussions of the descriptive chemistry of the elements in the text on the pages cited. Potentials in parentheses are estimated values.

<table>
<thead>
<tr>
<th>Half-reaction</th>
<th>(E^0) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3\text{N}_2 + 2e^- \rightarrow 2\text{N}_2^+)</td>
<td>-2.663</td>
</tr>
<tr>
<td>(3\text{N}_2 + 2\text{H}_2\text{O}^+ + 2e^- \rightarrow 2\text{H}_3\text{N}_2 + 2\text{H}_2\text{O})</td>
<td>-2.334</td>
</tr>
<tr>
<td>(\text{Li}^+ + e^- \rightarrow \text{Li})</td>
<td>-2.040</td>
</tr>
<tr>
<td>(\text{K}^+ + e^- \rightarrow \text{K})</td>
<td>-2.936</td>
</tr>
<tr>
<td>(\text{Ba}^{2+} + 2e^- \rightarrow \text{Ba})</td>
<td>-2.906</td>
</tr>
<tr>
<td>(\text{Sr}^{2+} + 2e^- \rightarrow \text{Sr})</td>
<td>-3.199</td>
</tr>
<tr>
<td>(\text{Ca}^{2+} + 2e^- \rightarrow \text{Ca})</td>
<td>-2.088</td>
</tr>
<tr>
<td>(\text{Na}^+ + e^- \rightarrow \text{Na})</td>
<td>-2.714</td>
</tr>
<tr>
<td>(\text{La}^{3+} + 3e^- \rightarrow \text{La})</td>
<td>-2.379</td>
</tr>
<tr>
<td>(\text{Mg}^{2+} + 2e^- \rightarrow \text{Mg})</td>
<td>-2.360</td>
</tr>
<tr>
<td>(\text{Lu}^{3+} + 3e^- \rightarrow \text{Lu})</td>
<td>-2.728</td>
</tr>
<tr>
<td>(\text{Al}^{3+} + 3e^- \rightarrow \text{Al})</td>
<td>-1.677</td>
</tr>
<tr>
<td>(\text{U}^{4+} + 4e^- \rightarrow \text{U})</td>
<td>-1.642</td>
</tr>
</tbody>
</table>

---

1 All potentials are standard reduction potentials with all species at unit activity and fugacity except for those values labeled "pH = 7" which have all species at unit activity except \([\text{H}_2\text{O}^+] = [\text{OH}^-] = 1.00 \times 10^{-7}\).
The Chemistry of the Halogens and the Noble Gases

Fluorine—Oxygen Chemistry

versus $F_2\cdot H\cdot F_2$ (Chapter 8). We might equate the symmetrical arrangement with optimal, very strong bonding. Indeed, in hydrogen bonding systems only the very strongest, $F\cdot H\cdot F$ and $O\cdot H\cdot O$ (and not all of them), exhibit the symmetrical structure. The asymmetrical structure could be attributed to the polarization effects from cations that may produce an imbalance in the triiodide system and make the unsymmetrical form more stable.

The higher polyiodides provide a more complicated picture than the triiodide. The pentaiodide ion, $I_5^-$, is an L-shaped molecule which may be considered to be two iodine molecules coordinated to a single iodide ion. Alternatively, it can be considered to be two unsymmetrical triiodide ions sharing a common iodine atom. There are two bond lengths, 1.2 and 4.5 (282 pm) and 2.3 and 3.4 (317 pm), which correspond very well to the bond lengths in the asymmetrical triiodide (Fig. 17.8c).

The "ternaiiodide" as found in CeI$_5$ has been found to be dimeric, $I_5^2^-$. It consists of another leg added to the $I_3^-$ ion to form a Z arrangement. It can be considered to be a central $I_3^-$ molecule with an asymmetrical triiodide coordinated to each end. The "short" bonds of the triiodide groups (bonds 1.2 and 7.8) are 285 pm and the "long" bonds (2.3 and 6.7) are 300 pm, in fair agreement with the preceding values. The bonds joining these triiodide moieties to the central diiodine "molecule" (3.4 and 3.6) are longer than any encountered thus far: 342 pm (Fig. 17.8b).

The so-called heptaiodide ion is found in (Et$_2$N)$_3$I. No discrete $I_7^-$ ions are present. The structure is an infinite three-dimensional framework of "diiodine molecules" (374 pm) and symmetrical "triiodide ions" (390 pm) coordinated through "very long" bonds (344 pm). A discrete $I_5^-$ ion, also consisting of one $I_3^-$ and two $I_2^-$ units, has recently been characterized in (Ph$_3$P)$_2$I$_3$ (Fig. 17.8c).

Finally, the enneaiodide ion, $I_9^-$, is in a still more complex structure, which has been characterized as $I_5^-$ + $I_2^-$ or $I_3^-$ + $I_3^-$, but is probably best considered as a three-dimensional structure similar to the so-called heptaiodide but of more irregular structure with bond lengths of 267, 290, 318, 324, 343, and 349 pm. Unless the latter is arbitrarily considered too long to be a true bond, the system must be considered to be an infinite polymer. A portion of the structure is shown in Fig. 17.9.

There is no evidence that fluorine ever exists in a positive oxidation state. This is reasonable in view of the fact that there is no element that is more electronegative and capable of taking electron density away from it. Certainly the oxygen compounds of fluorine come the closest to achieving a positive charge on fluorine, and since their chemistry is in some ways comparable to that of the other oxyhalogen compounds it is convenient to include these compounds here.

Few oxygen fluorides are known. The most stable of these is oxygen difluoride. It is usually prepared by the passage of fluorine through aqueous alkaline alkali

$$2F_2 + 2OH^- \rightarrow 2F_2\cdot OH^- + 2F^- + H_2O$$

Thermodynamically $OF_2$ is a slightly stronger oxidizing agent than mixtures of oxygen and fluorine. Thus, it occupies the extreme position in the standard electrode potential table (Appendix F), though this potential may not always be realized as alternative reductive pathways are available. It is relatively unreactive unless activated by an electric discharge or similar high-energy source. In contrast to most molecules containing fluorine, it has a very small dipole moment and thus has one of the lowest boiling points of any inorganic compound, 49 K. Other oxygen fluorides have been suggested of which only $O_2F_2$ has been well characterized. It is an orange-yellow solid.

![Fig. 17.8 Structures of polyiodide ions: (a) The pentaiodide ion, $I_5^-$; (b) the octaiodide ion, $I_8^-$; (c) the heptaiodide ion as found in Ph$_3$I$_3$. Solid lines represent essentially normal covalent bonds, dashed lines represent weakened or partial bonds, and dotted lines represent very long and weak interactions. Distances in pm.](image)

31 Of course since electronegativity is a function of valence state ("hybridization" and "charge"), it is not impossible that fluorine might find itself in a compound with an element in a particular valence state that was more electronegative than fluorine. And, of course, since the distinction between loss of electrons and gain in electrons (which may be two different valence states in the admittedly highly electronegative noble gases) is not always made, there is constant skirmishing in the literature over this.

32 The dipole moments of OF$_2$ is only 0.91 x 10$^{-30}$ C m (0.297 D). This results from the convergence of the electronegativity of the hybridized oxygen and hydrogenated fluorine and the effect of lone pair moments. Similar molecules are NF$_2$, $\mu = 1.763 \times 10^{-30}$ C m (8.535 D), bp = 113 K; NF$_3$, $\mu = 4.53 \times 10^{-30}$ C m (16.16 D), bp = 167.5 K. Dipole moment values are from Nelson, R. D., Jr.; Lide, D. R., Jr.; Maryott, A. A.; Selected Values of Electric Dipole Moments for Molecules in the Gas Phase; NSRDS-NBS 83; Washington, D.C., 1967.
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<td>46 ± 1</td>
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<td>0.235</td>
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<td>232.1 ± 0.1</td>
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**Group VIA (16)**

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**Group VIB (18)**

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<td>Xe—F</td>
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<td>248.9 ± 2.1</td>
<td>59.5 ± 0.5</td>
<td>37.9 ± 1.0</td>
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**Values in boldface type are from Darwent and represent his estimates of the "best value" and uncertainties for the energies required to break the bonds at 0 K. Where values are not available from Darwent, they are taken from Brewer and coworkers for metal halides and dihalides (boldface italics) or from Felcher for transition metal, lanthanide, and actinide halides (italics). These values represent enthalpies of atomization at 298 K. The remaining values are from Cotton (Table 170) and references given in parentheses.**

The table is intended for quick reference for reasonably accurate values for rough calculations. No effort has been made to convert the values from 298 K to 0 K, and in many cases the errors in the estimates are greater than the correction anyway. The accuracy of the values can be graded in a descending scale: (1) those giving ± uncertainties; (2) those giving "exact" values to the nearest 0.1; (3) those expressed as "about" a certain value; (4) those which are almost pure guesses, followed by a question mark. All values are experimental except for a few for which A—A bond energies are not known but would be helpful (as for electronegativity calculations). Estimates for these hypothetical bonds (such as Be—Be) are listed in parentheses. The bond lengths are mainly from two sources: Tables of Interatomic Distances and Configuration in Molecules and Ions (The Chemical Society, Special Publication No. 11, 1958) and Supplement (Special Publication No. 18, 1965) with values given in
that decomposes slowly even at low temperatures and is a powerful oxidizing agent. Little is known of O$_2$F which supposedly forms as a red-brown solid at 77 K but decomposes on warming.

Several workers have investigated the possibility of synthesizing fluorine oxygen acids such as HOF, HOFO, HOFO$_2$, or HOFO$_3$. Despite the various claims to have formed species such as these, it is the present opinion that only one, HOF, has been synthesized, and it is also the only hypohalous acid that has been prepared pure. It may be prepared by passing difluorine over ice (Fig. 17.10):

$$F_2 + H_2O \xrightarrow{25^\circ C} HOF + HF$$

(17.16)

It is difficult to prepare and isolate because of its reactivity towards both water and difluorine (Fig. 17.11):

$$HOF + H_2O \rightarrow HF + H_2O_2$$

(17.47)

$$1HOF + F_2 \rightarrow HF + OF_2$$

(17.48)

Other compounds containing the $-OF$ group are known: CF$_3$OF, O$_2$NOF, F$_2$SOF, O$_2$ClOF, CH$_3$C(OF), and CH$_3$OF. These are all thermodynamically unstable compounds with strong oxidizing properties, though some such as CF$_3$OF and F$_2$SOF are sufficiently inert kinetically that they can be stored in cylinders.

Fig. 17.10 Apparatus for carrying out the reaction of fluorine with cold ice. All parts are made from Kel-F, Teflon, Viton plastics, or Monel metal. Reaction tube B is packed with Raschig rings cut from Teflon spaghetti tubing, and wet with 1-2 mL water that is frozen with dry ice. Traps C and E are filled with dry Teflon Raschig rings. Tube A is held at $-196^\circ C$ with liquid nitrogen, traps B and C at $-40$ and $-50^\circ C$, respectively, with chilled ethanol, trap D at $-78^\circ C$ with dry ice, and traps E and F at $-183^\circ C$ with liquid oxygen. Gases are re-circulated with pump G. The pressure is measured with gauge I, and vacuum pumps and a fluorine cylinder are attached through valve J. The HOF collects in Tube E; the OF$_2$ in Tube A. [From Appelman, E. H.; Jache, A. W. J. Am. Chem. Soc. 1987, 109, 1754-1757. Reproduced with permission.]

The series of acids HOCI, HOClO, HOClO$_2$, and HOClO$_3$ (or HClO, HClO$_2$, HClO$_3$, and HClO$_4$) is well known, arising from the disproportionation of chlorine and related reactions:

$$Cl_2 + 2H_2O \xrightarrow{\text{cold}} HCl + H_2O + Cl^-$$

(17.49)

$$Cl_2 + HOCIO \xrightarrow{\text{brk}} HOCl + CO_2 + Cl^-$$

(17.50)

$$3Cl_2 + 6OH^- \xrightarrow{\text{brk}} 3ClO^- + 3Cl^- + 3H_2O$$

(17.51)

$$4KClO_3 \xrightarrow{\text{moist heat}} 3KClO_4 + KCl$$

(17.52)

Chlorous acid and chlorite salts cannot be formed in this way but must be formed indirectly from chlorine dioxide which in turn is formed from chlorates:

$$KClO_3 \xrightarrow{\text{moist heat}} K_2C_2O_4 + CO_2 + Cl_2$$

(17.53)

In basic solution chlorine dioxide disproportionates with the formation of chlorate and chlorite, and the latter is used to form the free acid:

$$2ClO_2 + 2OH^- \rightarrow ClO_3^- + ClO_2^- + H_2O$$

(17.54)

$$Ba(ClO_2)_2 + H_2SO_4 \rightarrow 2HClO + BaSO_4$$

(17.55)

The heavier halogens form similar series of compounds although less complete. In all probability neither HOBrO or HOIO exists. The periodate ion exhibits a higher


<table>
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<th>$D_0$ (kcal mol$^{-1}$)</th>
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**Group IVA (14)**

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coordination number (resulting from the increase in radius of iodine over chlorine) of 6, \( IO_3^- \), as well as four, \( IO_4^2- \). For many years it proved to be impossible to synthesize the perbromate ion or perbromic acid. The apparent nonexistence of perbromate coincided with decreased stability of other elements of the first long period in their maximum oxidation states. This reluctance to exhibit maximum valence bonding has been correlated with promotion energies and with stabilization through coordination and is well characterized. The dichloroiodate(I) anion, \( IOCl^- \), is a simple example. Other complexes of \( I^+ \) may be prepared, as through the disproportionation of iodine in the presence of pyridine:

\[ \text{I}_2 + 2\text{Py} + \text{Ag}^+ \rightarrow \text{I}^+\text{(Py)}_2 + \text{AgI}. \]  

\[ \text{(17.69)} \]

In addition to the polyhalide ions discussed previously, which were all anionic, there are comparable cationic species known, although they have been studied considerably less. Many pure interhalogen compounds arc thought to undergo autoionization (see Chapter 18) with the formation of appropriate cationic species:

\[ \text{ICIO}_3^- + \text{ICl}_4^- \]

\[ \text{ICIO}_4^- + \text{ICl}_4^- \]

\[ \text{(17.64)} \]

\[ \text{(17.65)} \]

Many of these cationic species have been postulated on the basis of chemical intuition coupled with the knowledge that the pure interhalogen compounds are slightly conducting (see Problem 17.4). Homonuclear halo gen cations can be prepared in highly acidic media. For example when iodine is dissolved in 60\% oleum (\( \text{H}_2\text{SO}_4 \)), it is oxidized (by the \( \text{SO}_3 \) present) to yield a deep blue species. Conductometric, spectrophotometric, cryoscopic, and magnetic susceptibility measurements are all compatible with \( I^+ \). Using stoichiometric amounts of oxidizing agents (such as bis[bis(fluoroaryl)peroxide] or arsenic pentafluoride) allow various polyiodine cations to be prepared:

\[ \text{IO} + \text{FSO}_2\text{OSO}_2\text{F} \rightarrow \text{IO}^+ + 2\text{FSO}_2\text{F} \]

\[ \text{(17.63)} \]

\[ \text{IO}_2 + \text{FSO}_2\text{OSO}_2\text{F} \rightarrow 2\text{IO}^+ + 2\text{FSO}_2\text{F} \]

\[ \text{(17.64)} \]

\[ \text{IO}_3 + \text{FSO}_2\text{OSO}_2\text{F} \rightarrow \text{IO}_2^+ + 2\text{FSO}_2\text{F} \]

\[ \text{(17.65)} \]

\[ \text{IO}_4^+ + 3\text{AsF}_5 \rightarrow \text{IO}_3^- + 2\text{AsF}_6 + \text{AsF}_3 \]

\[ \text{(17.66)} \]

\[ \text{IO}_3 + 3\text{AsF}_5 \rightarrow \text{IO}_2^- + 2\text{AsF}_6 + \text{AsF}_3 \]

\[ \text{(17.67)} \]

\[ \text{IO}_3 + 3\text{AsF}_5 \rightarrow \text{IO}_2^- + 2\text{AsF}_6 + \text{AsF}_3 \]

\[ \text{(17.68)} \]

The use of liquid sulfur dioxide as solvent allows the crystallization of the heastable sulfate salts of these cations including the very interesting tetramolybdate dication, \( \text{[Mo}_4\text{O}_8\text{SO}_4]^2+ \). The latter forms through dimerization of \( \text{I}^+ \) as its bright blue solutions are chilled. Dimerization is accompanied by a color change to red. Although the presence of the monomolybdate, \( \text{[Mo}_3\text{O}_7\text{SO}_4]^- \), has not been demonstrated in the systems discussed above, there are conditions under which it is stabilized through coordination and is well characterized. The dichloroiodate(I) ion, \( \text{ClO}_2^- \), is a simple example. Other complexes of \( \text{I}^+ \) may be prepared as through the disproportionation of iodine in the presence of pyridine:

\[ \text{I}_2 + 2\text{Py} + \text{Ag}^+ \rightarrow \text{I}(\text{Py})_2 + \text{AgI}. \]

\[ \text{(17.69)} \]

\[ \text{[Mo}_4\text{O}_8\text{SO}_4]^2+ + 2\text{Mo}^2+ + \text{Tl}^+ \rightarrow \text{[Mo}_3\text{O}_7\text{SO}_4]^- + \text{H}^+ + \text{H}^+ + \text{Tl}^+ \]

\[ \text{(17.70)} \]
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<td>Cu—Cu(CuI₂)</td>
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The Chemistry of the Halogens and the Noble Gases

Table 17.5
Polyhalogen cations:

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<th>X₂⁺</th>
<th>X⁻</th>
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<tbody>
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<td>Cl⁻</td>
<td>Br⁺</td>
<td>Br⁻</td>
<td>I⁺</td>
<td>I⁻</td>
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</table>

This brief overview has not included all of the polyhalogen cations known, but merely discussed a few typical examples. See Table 17.5 for a listing.

Halides

Although many of the compounds of the halogens discussed thus far have exhibited a halogen in a positive oxidation state, most of the chemistry of this family involves either halide ions or covalent molecules in which the halogen is the most electronegative atom.

The pertinent trends in the Group VIA (17) elements are size and tendency to attract electrons (Table 17.6). It is only when both these factors are considered that the chemistry of these elements can be rationalized. The most obvious trend in the family is the attraction for electrons. The ionization energy decreases from fluorine to iodine as expected. There is an apparent anomaly in the case of the electron affinity of chlorine, which is lower than that of chlorine. The small size of the fluorine atom as expected. In covalent molecules it is exhibited by compounds of fluorine without other halogen analogues, for example, AsF₅, XeF₆, and IF₃. In aqueous solution it is exhibited by the high emf of the fluoride electrode resulting from large hydration energy of the small fluoride ion. This much greater reactivity of fluorine has led to its characterization as a "superhalogen."

Table 17.6
Radii, ionization energy, electron affinity, and electronegativity of the halogens

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<th>Element</th>
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<th>rᵢ</th>
<th>rᵢₑ</th>
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<td>200</td>
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<tr>
<td>I</td>
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<td>210</td>
<td>10.4</td>
<td>3.1</td>
<td>2.52</td>
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Alternatively, the potential energy can be described in terms of which the F — F bond is broken. As shown by the following discussion the interrelation between bond energy, size, electronegativity energy, etc., is complex and attributing everything to one factor is unsound.

The Anomaly of Fluorine

Quite often the first member of a periodic group differs from the remaining members of the group (see Chapter 18). In the case of fluorine, the anomaly is quite pronounced. Politzer has illuminated this odd behavior by documenting the weakening of bonding by fluorine to other elements compared with that expected on the basis of extrapolations from the heavier halogens. For example, we have seen that the electron affinity of fluorine is less than might have been expected from the trend of the other halogens. This trend is extrapolated to fluorine, a value of 440 kJ mol⁻¹ is obtained, 110 kJ mol⁻¹ greater than the experimental values. As a result of the lower electron affinity, ionic compounds of fluorine have bond energies which are slightly more than 100 kJ mol⁻¹ weaker than values extrapolated from the other halogens: LiF (104 kJ mol⁻¹ lower), NaF (105 kJ mol⁻¹ lower), KF (117 kJ mol⁻¹ lower), RbF (104 kJ mol⁻¹ lower), and CsF (130 kJ mol⁻¹ lower). This destabilization can be attributed to forming a full or nearly full electronic charge on the small fluorine atom. The surprising fact pointed out by Politzer is that covalent compounds of fluorine seem to show the same destabilization. In Fig. 17.12 the dissociation energies of the hydrogen halides and of the C — X bonds in the methyl halides are plotted against the reciprocals of their bond lengths. The compounds of the three heavier halogens fall on a straight line which, when extrapolated, predicts values for the fluorine compound that are 113 kJ mol⁻¹ lower. This indicates that even when sharing an electron from another atom fluorine is destabilized by its small size. Finally, the fluorine molecule itself has a notoriously weak bond (155 kJ mol⁻¹ compared with chlorine, 243 kJ mol⁻¹), and it is some 226 kJ mol⁻¹ (= 2 x 113) weaker than the extrapolated value. The weak bond in F₂ has traditionally been interpreted in terms of lone-pair repulsions between the adjacent fluorine atoms. There may be a more general phenomenon in terms of small size, charge capacity, and electron-electron repulsion.

Fig. 17.12 Bond dissociation energies and bond lengths of the hydrogen halides, methyl halides, and halogen molecules. Note that this figure, which is taken directly from Politzer's work, portrays in a different way relationships that are closely related to Fig. 9.7. (From Politzer, P. J. Am. Chem. Soc. 1969, 91, 6235. Reproduced with permission.)

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* Mulliken-Jaffe values in Pauling units.

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* Alternatively, the potential energy can be described in terms of which the F — F bond is broken. As shown by the following discussion the interrelation between bond energy, size, electronegativity energy, etc., is complex and attributing everything to one factor is unsound.

---

* Mulliken-Jaffe values in Pauling units.
Table E.1
(Continued)

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<th>$r$ (pm)</th>
<th>$D_0$ (kcal mol$^{-1}$)</th>
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Group III B (3)

Sc−Be    | 108.4 ± 21             | 55.9 ± 5 | 62.8 ± 5                 | 0.628   |
| Sc−F     | 594.6                  | 110.1    | 307.2 ± 5                | 3.072   |
| Sc−Cl    | 460.6                  | 110.1    | 307.2 ± 5                | 3.072   |
| Sc−Br    | 391.2                  | 91.5     | 331.5 ± 5                | 3.315   |

Lanthanides and actinides (kJ mol$^{-1}$)

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Lanthanides and actinides (kcal mol$^{-1}$)

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So how do we resolve this apparent paradox? Is fluorine a "superhalogen" or a "subhalogen"? Does its bond better than the other halogens or worse than expected? There really is no conflict here; it depends upon what one is using for a reference. In comparison with the heavier halogens, fluorine is by far the most active, the most electronegative, and provides the most strongly exothermic reactions. In this regard the weakening present in any X—F bond is offset by the weak F—F bond, so the overall enthalpy of the reaction is not affected, and the effect of a high electronegativity on Madelung energy and electro negativity terms is dominant. Fluorine has three factors favoring it over the larger halogens, all resulting from its small size: (1) the largest electronegativity, at least for small partial charges; (2) large Madelung energies in polar molecules; and (3) good covalent bonding resulting from the ability to "get in close" to the adjacent atom.8 Except for F in which factors 1 and 2 cannot come into play, fluorine typically forms stronger bonds than chlorine: 

\[ H—F = 565, H—Cl = 428; Li—F = 573, Li—Cl = 464; C—F = 485, C—Cl = 327 \text{ (kJ mol}^{-1}\text{)} \]

Thus fluorine displays all the properties expected of the smallest halogen. The deficit of about 100 kJ mol\(^{-1}\) is simply an example of the law of diminishing returns; At some point decreasing size no longer provides increasing bonding benefits in proportion to further decrease in size. Were it not for the saturation effect coming into play, fluorine would probably be a "super-superhalogen"!

A very similar question that depends entirely upon what one takes as "normal" or standard is the question of the covalent radius of fluorine. One half of the single covalent bond length in difluorine is 143 pm = 2 — 71 pm (so listed in Table 8.1). One can then employ the Schomaker-Stevenson relationship and attribute the shortening (and strengthening) of an M—F bond to ionic-covalent resonance (Madelung energy) and account for the fact that the M—F bond is always shorter than \( r_{\text{ion}} \) + \( r_{\text{coval}} \). Alternatively, one can assume that the bonding in most fluorine compounds is "normal" and that the long (and weak) difluorine bond is the "anomaly" because of the lone pair-lone pair repulsions. The two viewpoints are essentially equivalent. For a careful analysis of the covalent radius of fluorine, see Gillespie and Robinson.9

Because of its superreactivity, the preparation of elemental difluorine was not accomplished until long after the preparation of the other halogens.8 So most chemists accepted the impossibility of producing difluorine in any practical way other than the electrolysis of aqueous HF:

\[ 2HF \rightarrowKF + \text{H}_2 + F_2 \]  

(17.70)

However, Christe\(^8\) has shown that by taking advantage of the difference in stability of a given oxidation state of a transition metal depending on whether it is fully coordinated or not, difluorine gas can be generated chemically. Potassium hexafluorodisilicate(IV) can be prepared by reduction of potassium permanganate:

\[ 2K\text{MnO}_4 + 2KF + 10HF + 3\text{H}_2\text{O} \rightarrow 2\text{KMnF}_3 + 8\text{H}_2\text{O} + 3\text{O}_2 \]  

(17.71)

Although \(\text{K}_2\text{MnF}_4\) is stable (perhaps because of its insolubility), the free Lewis acid \(\text{MnF}_3\) is not. Preparation of the latter is accomplished by using very strong Lewis acids such as \(\text{SbF}_5\), \(\text{TiF}_5\), and \(\text{BF}_3\) (see Chapter 9) which also react slowly in the presence of difluorine gas.

\[ \text{K}_2\text{MnF}_3 + 2\text{SbF}_5 \rightarrow 2\text{KSF}_5 + \text{MnF}_3 + 3\text{F}_2 \]  

(17.72)

Similar reactions can be run using nickel or copper as the transition metal.

It was noted above that discussion of astatine together with the other halogens is inconvenient. Although it is, as expected, the most "metallic" of the halogens, there are few values or experimental data to cite in support of this. (Note for example that such fundamental quantities as experimental ionization energies are unavailable.) Various isotopes of astatine are produced only in trace amounts, with half-lives of a few hours or less, and therefore the chemistry of astatine is essentially the descriptive chemistry obtained by tracer methods; macroscopic amounts are not available. The best known oxidation state of astatine is -I. Astatine may be readily reduced to astatide:

\[ 2\text{At} + \text{SO}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{At}^- + 3\text{H}^+ + \text{H}_2\text{SO}_4 \]  

(17.73)

which forms an insoluble silver astatide precipitating quantitatively with silver iodide as carrier.

Studies of elemental astatine are complicated by the fact that the small amounts of astatine present are readily attacked by impurities that normally would not be considered important. Most studies of astatine involve an excess of iodine which lies the astatine up in all molecules. It behaves much as might be expected from the known behavior of I\(_2\). It is readily extractable into CCl\(_4\) or CH\(_3\)Cl and may be oxidized to positive oxidation states by reasonably mild oxidizing agents. The best characterized positive oxidation state is \(\text{At}^\text{V}\). Astatine ions may be formed by oxidation of \(\text{At}^\text{I}\) by peroxydisulfate, the ceric ion, or periodate:

\[ \text{At}^- + \text{S}_\text{2} \text{O}_8^{2-} \rightarrow \text{At}^\text{V}^- + 3\text{H}^+ + \text{H}_2\text{O} \]  

(17.74)

As such it may be quantitatively precipitated with insoluble iodides such as \(\text{PbI}_2\) and \(\text{BaI}_2\).

It appears that perastatate, \(\text{AtO}_5^{2-}\), has not been prepared. When astatine was treated with very strong oxidizing agents, a negligible amount of the activity precipitated as astatine.
None of these represents the breaking of a hypothetical, isolated N—N bond:

\[ \text{N}^+ - \text{N}^- \quad \rightarrow \quad 2 \cdot \text{N}^\cdot \]

By using N—H and N—F bond energies from NH₃ and NF₃, it is possible to estimate the inherent strength of the N—N bond:

- Total energy of atomization, N₂H₅: 1703 kJ mol⁻¹ (407 kcal mol⁻¹)
- 4N—H bonds (assumed from NH₃): 1544 kJ mol⁻¹ (369 kcal mol⁻¹)
- Difference (equated with N—N): 159 kJ mol⁻¹ (38 kcal mol⁻¹)

Total energy of atomization, N₂F₅: 1305 kJ mol⁻¹ (312 kcal mol⁻¹)
- 4N—F bonds (assumed from NF₃): 1134 kJ mol⁻¹ (271 kcal mol⁻¹)
- Difference (equated with N—N): 172 kJ mol⁻¹ (41 kcal mol⁻¹)

The results of this calculation are gratifyingly congruent, and we feel reasonably confident in a value of about 167 kJ mol⁻¹ (40 kcal mol⁻¹) for the N—N bond. Similar results can be obtained for hydrogen peroxide and dioxogen difluoride to obtain an estimate of about 145 kJ mol⁻¹ (34 kcal mol⁻¹) for the O—O bond.

Although the calculations for N—N and O—O bonds are self-consistent, there is always the possibility that a wider series of compounds would show greater variability. This is especially probable in molecules in which the electronativity of the substituents is believed to affect the bonding by particular orbitals, e.g., overlap by diffuse orbitals. Thus on the basis of observed stabilities the presence of electronegative substituents such as —F and —CF₃ seems to stabilize the P—P bond relative to H₂P—PH₂, although there are not enough data to investigate this possibility quantitatively.


Table E.1 has been compiled from the above sources. The ordering is as follows: hydrogen, Group IA (1), Group IIA (2), Group IIIA (3), transition elements, Group IVA (14), Group VA (15), Group VIA (16), Group VIIA (17), Group VIIIA (18). For a given group (such as IA) the compounds are listed in the following order: halides, chalcogenides, etc. Unless specified otherwise, the bond energies are for compounds representing group number oxidation states, such as Cl₂, S₂, and SF₆. Other compounds are listed in parentheses, such as (TeCl₂) and (PCl₃). Values are for the dissociation energies of molecules A—B and mean dissociation values for AB₂. For molecules such as NH₂, two values are given. H₂N—NH₂ represents the dissociation energy to two amino radicals, and N—N (NH₃) represents the estimated N—N bond energy in hydrazine obtained by means of assumed N—H bond energies as shown above.
Electrochemistry of the Halogens and Pseudohalogens

Pseudohalogens

There are certain inorganic radicals which have the properties of existing either as monomeric anions or as neutral dimers. In many ways these groups display properties analogous to single halogen atoms, and hence the term pseudohalogen or halogenoid has been applied to them. Examples of pseudohalogen behavior may be found in the chemistry of cyanide, thiocyanate, and azide anions. Some typical reactions are:

1. Oxidation of $X^-$ ions to form dipseudohalogens:
   $$2SCN^- + 4H^+ + MnO_2 \rightarrow (SCN)_2 + 2H_2O + Mn^{2+}$$  (17.75)

2. Disproportionation of the free pseudohalogen by a base:
   $$(CN)_2 + 2OH^- \rightarrow CN^- + OCN^- + H_2O$$  (17.76)

3. Precipitation by certain metal ions:
   $$Ag^+ + N_3^- \rightarrow AgN_3$$  (17.77)

4. Formation of complex ions:
   $$Zn^{2+} + 4SCN^- \rightarrow [Zn(SCN)_4]^{2-}$$  (17.78)

5. Formation of acids with hydrogen, $HX$. These acids generally are considerably weaker than the hydrohalic acids, e.g., $pK_a$ for HCN = 9.

The extent to which the various pseudohalogenes resemble halogens is generally quite high, with some remarkable parallels:

$$2I^- + Cu^{2+} \rightarrow I_2 + Cu^+$$  (17.79)
$$2CN^- + Cu^{2+} \rightarrow [CN]_2 + CuCN$$  (17.80)

although, however, there are several exceptions. Thus thiocyanogen, $(SCN)_2$, is stable only at low temperatures, and at room temperature polymerizes to $(SCN)_x$. With respect to division into hard and soft species, most pseudohalogens are composed of several nonmetal atoms, often with multiple bonding, and so are quite polarizable. As such they tend to resemble iodine considerably more than fluorine. Some are ambidentate, however, and can behave as reasonably hard bases by coordination via a nitrogen or oxygen atom (see Chapter 12). Finally, pseudohalogens can be compared with the halogens on the basis of their relative oxidizing power. They tend to resemble iodine and bromine (see below for the values of these elements).\(^{44}\)


Electrochemistry of the Halogens and Pseudohalogens

$$\text{(CN)}_2 + 2H^+ + 2e^- \rightarrow 2HCN \quad E^0 = 0.375 \text{ V}$$  (17.81)
$$\text{(SCN)}_2 + 2e^- \rightarrow 2SCN^- \quad E^0 = 0.77 \text{ V}$$  (17.82)

In summary, the concept of pseudohalogens proves useful in systematizing the chemistry of some of these nonmetallic groups, but it should never be followed blindly.

Simple Latimer diagrams for the halogens are given below. The data are from Bratsch.\(^{45}\)


planar with sp\(^2\) hybridization instead of sp\(^3\). The energies associated with various dissociative steps for methane are:

\[
\begin{align*}
\text{CH}_4 & \rightarrow \text{CH}_3 + \text{H} & \Delta U &= 421.1 \text{ kJ mol}^{-1} (101.6 \text{ kcal mol}^{-1}) \\
\text{CH}_3 & \rightarrow \text{CH}_2 + \text{H} & \Delta U &= 469.9 \text{ kJ mol}^{-1} (112.3 \text{ kcal mol}^{-1}) \\
\text{CH}_2 & \rightarrow \text{CH} + \text{H} & \Delta U &= 415 \text{ kJ mol}^{-1} (99.3 \text{ kcal mol}^{-1}) \\
\text{CH} & \rightarrow \text{C} + \text{H} & \Delta U &= 334.7 \text{ kJ mol}^{-1} (80.0 \text{ kcal mol}^{-1})
\end{align*}
\]

We can associate the greater energy of the second dissociation step with a presumed greater bonding strength of trigonal sp\(^2\) hybrids over sp\(^3\) hybrids. Whether we understand (or at least believe we do) the reasons for each of the quantities listed above or not, it is obvious that none represents the bond energy in methane. However, since the summation of these four experimentally observable processes must be identical to the energy for the nonobservable (but desirable) reaction:

\[
\text{CH}_4 \rightarrow \text{C} + 4\text{H}
\]

the average of these four quantities (411 \text{ kJ mol}^{-1}; 98.3 \text{ kcal mol}^{-1}) can be taken as the mean bond energy for the C—H bond in methane.

The mean bond energy is a useful quantity, but it should be remembered that it is derived from a particular molecule and may not be exactly correct in application to another molecule. Thus if the total bond energy in dichloromethane does not equal two times the average bond energy in methane plus two times the average bond energy in carbon tetrachloride, we should not be surprised. The presence of bonds of one type may have an effect in strengthening or weakening bonds of another type. As a matter of fact, there is no unequivocal way of assigning bond energies for molecules such as dichloromethane by means of thermodynamics. The summation of all of the bond energies may be determined as above for methane, but the assignment to individual bonds must be made by secondary assumptions, e.g., the bond C—H energies are comparable to those in methane. Alternatively, the bond energies in molecules containing more than one type of bond may be assigned on the basis of some other type of information such as infrared stretching frequencies.

One of the most serious problems hindering the assignment of bond energies arises for bonds such as N—N and O—O. The nitrogen triple bond and oxygen double bond may be evaluated directly from the dissociation of the gaseous N\(_2\) and O\(_2\) molecules. Single bonds for these elements present special problems because additional elements are always present. For example, consider the following dissociation energies accompanying splitting of the N—N bond:

\[
\begin{align*}
\text{N}_2\text{H}_4 & \rightarrow 2\text{NH}_3 & D_0 &= 247 \text{ kJ mol}^{-1} (59 \text{ kcal mol}^{-1}) \\
\text{N}_2\text{F}_2 & \rightarrow 2\text{NF}_2 & D_0 &= 88 \text{ kJ mol}^{-1} (21 \text{ kcal mol}^{-1}) \\
\text{N}_2\text{O}_2 & \rightarrow 2\text{NO}_2 & D_0 &= 57.3 \text{ kJ mol}^{-1} (13.7 \text{ kcal mol}^{-1})
\end{align*}
\]
17.1. Consider the formation of \( \text{O}_2^+\text{[PtF}_6^\text{2}^- \text{]. Why is the ionization energy of O}_2^- \text{less than that of O}_2^- \text{? Is it likely that a compound N}_2\text{[PtF}_6^- \text{will form?}

17.2. The absence of interaction between noble gases and the Lewis acids BX, was demonstrated by Raman spectroscopy. Discuss the nature of the evidence and what would have been observed if there had been a significant interaction.

17.3. Show how the \( \text{PH}_4^+ \text{ion (Chapter 8) can be treated as a three-center, four-electron bond.}

17.4. Suggest autoionization possibilities for \( \text{BrF}_3 \text{, ICl} \text{, and BrF}_5 \text{. and probable structures for the ions formed.}

17.5. Pure iodine is purple in color as are its solutions in \( \text{CCl}_4 \text{, and CHCl}_3 \text{, and benzene. Aqueous solutions of KI} \text{, are brown. Solutions of dioxine in acetic acid, dimethyl sulfoxide, and diethyl ether are brown. Suggest an explanation.}

17.6. Suggest syntheses for
a. \( \text{XeO}_4 \text{.}

b. \( \text{HClO}_4 \text{.}

c. \( \text{KBrO}_4 \text{.}

17.7. Suggest probable structures for \( \text{I}_4\text{F} \text{, and I}_4\text{Cl} \text{, and give reasons why the two are probably not isomorphous.}

17.8. The production of pseudohalogens requires mild oxidizing conditions (F.q. 17.5). Why do you suppose that it has never been possible to oxidize the azide ion to hexamitrogen (diazyl)?

17.9. Why are the halogen cations \( \text{Cl}_3^+, \text{Br}_3^+, \text{and I}_3^+ \text{best isolated as salts of AsF}_5\text{, SbF}_5\text{, and similar anions?}

17.10. The melting points of the fluorides MF, MF, and MF, are generally somewhat lower than those of the corresponding oxides, \( \text{M}_2\text{O} \text{, MO}_2 \text{, and MO}_3 \text{, because of the greater lattice energy resulting from the electronegative oxide ion, O}^2^- \text{. Yet all of the following reactions are exothermic. Explain.}^{46}\)

\[
\begin{align*}
\text{Li}_2\text{O} + \text{F}_2 & \rightarrow 2\text{LiF} + \text{O}_2 \quad \Delta G^\text{th} = -602 \text{ kJ mol}^{-1} \\
\text{Mg}_2\text{O} + \text{F}_2 & \rightarrow 2\text{MgF}_2 + \text{O}_2 \quad \Delta G^\text{th} = -740 \text{ kJ mol}^{-1} \\
\text{Fe}_2\text{O}_3 + 3\text{F}_2 & \rightarrow 2\text{FeF}_3 + 3\text{O}_2 \quad \Delta G^\text{th} = -1162 \text{ kJ mol}^{-1} \\
\text{ZrO}_2 + 2\text{F}_2 & \rightarrow \text{ZrF}_4 + \text{O}_2 \quad \Delta G^\text{th} = -740 \text{ kJ mol}^{-1} \\
\end{align*}
\]

17.11. If you ask an organic chemist which element can form the largest number of compounds (not that more than a fraction have been synthesized yet), you will usually get one of two answers: carbon from some, hydrogen from others. If you ask an inorganic chemist, you may get a third answer. What is your answer? Discuss.

17.12. On page 835 it is stated that xenon forms bonds with only the most electronegative elements such as the very active fluorine and oxygen. How can you reconcile this with the formation of the \( \text{Xe}^-\text{Xe}^\text{+} \text{ bond in Xe}^2 \text{? (Hint: Rethink Problem 5.15.)}

17.13. \( \text{Xe} \text{;} \text{obviously will have a fairly high electron affinity (see the ionization energy of atomic xenon), and if it gains an electron, it will dissociate (see Chapter 5). Combine these facts with the choice of SF}_5\text{ as solvent and acid-base theory to provide a self-consistent interpretation.}


17.14. The \( \text{OSeF}_4\text{ and OTeF}_4\text{ groups are very electronegative as shown by the stability of their xenon compounds. If you did not do Problem 5.30 when you read that chapter, do so now.}

17.15. The photoelectron spectra of \( \text{Xe} \text{, F}_2 \text{, XeF}_2 \text{, XeF}_4 \text{, OXeF}_4\text{, and XeF}_6 \text{ are shown in Fig. 17.13. What information can you obtain from these spectra? The appearance of two peaks for \( \text{Xe} \text{ is attributable to the ejection of 3d electrons of different } j \text{ values and is irrelevant to the question being asked.}

17.16. Consider the series of xenon oxyfluorides and their relative acidity. Discuss the reasons for the ordering of these compounds. Can you semi-quantitatively answer?
Although the concept of bond energy seems intuitively simple, it is actually rather complicated when inspected closely. Consider a diatomic molecule A—B dissociating. It might be thought that it would be a relatively simple matter to measure the energy necessary to rupture the A—B bond and get the bond energy. Unfortunately, even if the experiment is feasible the result is generally not directly interpretable in terms of “bond energies” without further work. Among the factors to be considered are the vibrational, rotational, and translational energies of the reactants and products, the zero-point energy, and pressure-volume work if enthalpies are involved. The interested reader is referred to books on thermodynamics (especially Dasent, W. E. Inorganic Energetics; Penguin: Harmondsworth, England, 1970). The following is meant as a brief outline of the problem.

Consider the energy of a diatomic molecule as shown in the figure. The concept of bond energy may be equated with the difference between the bottom of the energy curve and the energy of the completely separated atoms (A(\(\overline{U}\))). However, as a result of the zero-point vibrational energy of the AB molecule, even at 0 K, the energy necessary to separate the atoms A(\(\overline{\overline{U}}\)) is somewhat less (by a quantity of \(\Delta^{\circ}\)). The zero-point energy is greatest in molecules containing light atoms such as hydrogen (25.9 kJ mol\(^{-1}\); 6.2 kcal mol\(^{-1}\) in H\(_2\)) and somewhat less in molecules containing heavier atoms.

There is a corresponding difference between two estimates of the bond distance in a molecule A—B. One, \(r_{\text{c}}\), corresponds to the minimum in the energy distance curve (see figure). The second, \(r_{\text{v}}\), corresponds to the average distance in a molecule vibrating with zero-point energy. Since the curve is not perfectly parabolic the two values are not identical.

If the dissociation is to take place at some temperature, \(T\), other than 0 K, the energy necessary to separate the atoms \(\Delta \overline{U}\) is somewhat less (by a quantity of \(\Delta T\)). The zero-point energy is greatest in molecules containing light atoms such as hydrogen (23.9 kJ mol\(^{-1}\); 6.2 kcal mol\(^{-1}\) in H\(_2\)) and somewhat less in molecules containing heavier atoms.

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17.17. a. Predict the most likely by-products of the reduction of $\text{XeF}_2$ to $\text{XeF}_2^-$ as discussed on page 834.

b. Write balanced equations for all of these reactions.

17.18. The xenon fluorides are described in this chapter as both fluoridators and fluorinators. Is this a typographical error? Can these terms be differentiated? Discuss.

17.19. On page 827 the statement is made that "the electron affinity of positive helium, etc. is greater than that of any appropriate species $X$ . . . ." What is the electron affinity (numerical value) of He?  

17.20. A general rule of molecular structure derived from VSEPR theory and Bunn's rule is that lone pairs and substituents of low electronegativity prefer equatorial positions in a trigonal bipyramid, whereas substituents of high electronegativity prefer axial positions. The pentafluoroxoenate(IV) ion, $\text{XeOF}_5^-$, seems to reverse this rule by having the LPs preferentially occupying the axial positions. Discuss.

17.21. On page 832 the statement is made that in "most fluorides the reduction of steric factors allows the lone pair to emerge to the surface of the molecule, . . . ." and yet there are two hexafluoro species mentioned in this chapter that are perfectly octahedral. What are they? How can they be octahedral in light of the above statement?

17.22. Although the $\text{Xe-O}$ bond ($\sim 80$ kJ mol$^{-1}$) is not as strong as that in the xenon fluorides ($\sim 180$ kJ mol$^{-1}$), it is far from being the weakest bond known. How then is it possible for $\text{XeOF}_3$ to be so violently exothermic (explosive) when it decomposes?

17.23. If you did not do Problem 14.15 when you read Chapter 14, do so now.

17.24. On page 834, the statement is made: "Hydrogen xenato ions disproportionate in alkaline solution to yield peroxenates . . . ." Can you confirm this assertion based on the Latimer diagrams for xenon?

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Chapter 18

Periodicity

The most fascinating aspect of inorganic chemistry as well as its most difficult problem is the diversity of reactions and structures encountered in the chemistry of somewhat over one hundred elements. The challenge is to be able to treat adequately the chemistry of boranes and noble gas fluorides, transition metals and inner transition metals, cuprate superconductors and zeolites, all without developing a separate set of rules and theories for each element or system. Much of this book has been devoted to establishing relationships that connect various aspects of inorganic chemistry. The tool that the inorganic chemist uses to systematize elemental relationships is the periodic table, now somewhat over one hundred years old. It is considered so essential that no general chemistry textbook would be complete without a discussion of the trends summed up in Chapter 2. Unfortunately, the impression left by these textbooks is often simply that all periodic properties vary smoothly.

Fundamental Trends

The basic trends of the periodic chart have been discussed in Chapter 2. They may be summarized as follows. Within a given family there are increases in size and decreases in ionization energy, electron affinity, electronegativity, etc. Increasing the atomic number across a given period results in concomitant increases in ionization, electron affinity, and electronegativity, but a decrease in size. The change in effective nuclear charge within a period is reasonably smooth, but the various periods differ in length (8, 18, and 32 elements). The properties of an element will depend upon whether it follows an 8, 18, or 32 sequence. One of the best known examples is the very close similarity in properties of hafnium, tantalum, tungsten, and rhenium to those of zirconium, niobium, molybdenum, and technetium, respectively, as a result of the lanthanide contraction and associated effects. These anomalies continue through the elements gold, mercury, thallium, and lead. Similar but smaller effects follow the filling of the $3d$ orbitals (rarely referred to as the "scandide" contraction).

Another area of the periodic chart revealing pronounced differences between similar elements is between the first ten, H–Ne, and those immediately following.
### C<sub>10</sub> Groups

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</table>

#### C<sub>10</sub> Groups

<table>
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<th>i</th>
<th>σ&lt;sub&gt;b&lt;/sub&gt;</th>
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<td>1</td>
</tr>
<tr>
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<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
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#### D<sub>2d</sub> Groups

<table>
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<tr>
<th>D&lt;sub&gt;2d&lt;/sub&gt;</th>
<th>E</th>
<th>2S&lt;sub&gt;s&lt;/sub&gt;, 1C&lt;sub&gt;2&lt;/sub&gt;, 2C&lt;sub&gt;4&lt;/sub&gt;</th>
<th>2σ&lt;sub&gt;d&lt;/sub&gt;</th>
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</thead>
<tbody>
<tr>
<td>A&lt;sub&gt;v&lt;/sub&gt;</td>
<td>1</td>
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<td>1</td>
</tr>
<tr>
<td>B&lt;sub&gt;v&lt;/sub&gt;</td>
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<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>E&lt;sub&gt;1&lt;/sub&gt;</td>
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<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>E&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1</td>
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### D<sub>2d</sub> Groups

<table>
<thead>
<tr>
<th>D&lt;sub&gt;2d&lt;/sub&gt;</th>
<th>E</th>
<th>2S&lt;sub&gt;s&lt;/sub&gt;, 1C&lt;sub&gt;2&lt;/sub&gt;, 2C&lt;sub&gt;4&lt;/sub&gt;, 1C&lt;sub&gt;4&lt;/sub&gt;</th>
<th>2σ&lt;sub&gt;d&lt;/sub&gt;, 4σ&lt;sub&gt;d&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>A&lt;sub&gt;v&lt;/sub&gt;</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>B&lt;sub&gt;v&lt;/sub&gt;</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>E&lt;sub&gt;1&lt;/sub&gt;</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>E&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>
The inherent unreactivity of lithium is offset in aqueous solution by the exothermic hydration of the hydride ion. H\textsuperscript{-} has no chemical oxidation state in common with the alkali metals but the bare H\textsuperscript{+} has orbital approaches, and has been one of the most controversial topics in bonding theory. Before entering this theoretical discussion, a brief examination of chemical differences is appropriate.

First- and Second-Row Anomalies

In many ways the first ten elements differ considerably from the remaining 99. Hydrogen is a classic example—it belongs neither with the alkali metals nor with the halogens although it has some properties in common with both. Thus, it has a +1 oxidation state in common with the alkali metals but the bare H\textsuperscript{+} has no chemical existence\textsuperscript{2} and hydrogen tends to form covalent bonds that have properties more closely resembling those of carbon than those of the alkali metals. With the halogens it shares the tendency to form a −1 oxidation state, even to the extent of forming the hydride ion, H\textsuperscript{-}; however, the latter is a curious chemical species. In contrast to the proton which was anomalous because of its vanishingly small size, the hydride ion is unusually large. It is larger than any of the halide ions except iodide\textsuperscript{3}. The source of this apparent paradox lies in the lack of control of a single nuclear proton over two mutually repelling electrons. Since the hydride ion is large and very polarizable it certainly does not extend the trend of I\textsuperscript{-} through F\textsuperscript{-} of decreasing size and increasing basicity and hardness.

The elements of the second row also differ from their heavier congeners. Lithium is anomalous among the alkali metals and resembles magnesium more than its congeners. In turn, in Group IIA Be beryllium is more closely akin to aluminum than to the other alkaline earths. The source of this effect is discussed below. We have already seen that fluorine has been termed a superhalogen on the basis of its differences from the other halogens although it has some properties in common with both. Thus it has a +1 oxidation state, even to the extent of forming the hydroxy group, OH\textsuperscript{-}; however, the latter is a curious chemical species. In contrast to the proton which was anomalous because of its vanishingly small size, the hydride ion is unusually large. It is larger than any of the halide ions except iodide\textsuperscript{3}. The source of this apparent paradox lies in the lack of control of a single nuclear proton over two mutually repelling electrons. Since the hydride ion is large and very polarizable it certainly does not extend the trend of I\textsuperscript{-} through F\textsuperscript{-} of decreasing size and increasing basicity and hardness.

The great polarizing power of the Li\textsuperscript{+} cation was commented upon in Chapter 4. As a result of its small size and higher electronegativity this ion destabilizes salts that are stable for the remaining alkali metals.

\textsuperscript{2} Those who disparage of writing H\textsubscript{2}O often point out that the hydration number of the H\textsuperscript{+} is uncertain and "all cations are hydrated in solution." To treat H\textsuperscript{+} rather than H\textsubscript{2}O\textsuperscript{3} as a common similar to Na\textsuperscript{+}, for example, is to equate nuclear particles with atoms, a discrepancy for a factor of about 10\textsuperscript{7}.

\textsuperscript{3} Finding 'The Nature of the Chemical Bond,' 3rd ed.; Cornell: Ithaca. NY. 1960: p 514 has provided an estimate of 200 pm for the hydride ion compared to 124 pm for F\textsuperscript{-}. To be sure, the existence of an uncharged hydride ion is even less likely than a large anhydrated atom of some kind, but similar to both must have meaning this would be the key element of the size of a free hydride ion.

\textsuperscript{4} The inherent unreactivity of lithium is reflex in aqueous solution by the exothermic hydration of the very small Li\textsuperscript{+} ion. Nevertheless, in general, lithium is a less reactive metal than Na, K, Rb, or Cs.

Table 18.1

Maximum coordination numbers of the nonmetals as shown by the fluorides

<table>
<thead>
<tr>
<th>CF\textsubscript{4}</th>
<th>NF\textsubscript{3}</th>
<th>OF\textsubscript{2}</th>
<th>SF\textsubscript{6}</th>
<th>CIF\textsubscript{4}</th>
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</thead>
<tbody>
<tr>
<td>SF\textsubscript{6}</td>
<td>PF\textsubscript{6}</td>
<td>SF\textsubscript{6}</td>
<td>CIF\textsubscript{4}</td>
<td>IF\textsubscript{3}</td>
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</tbody>
</table>

\textsuperscript{5} N, O, and other elements can achieve higher coordination in oxides salts, e.g., NH\textsubscript{4}.

\textsuperscript{6} This advantage arises not only from the steric viewpoint but also from the fact that the rules behavior of fluorine is well suited to stabilize high oxidation states. To put it another, less equivalent, way: High oxidation state species are hard acids and the fluoride ion is the hardest possible base.
### $D_{4h}$ Groups (Continued)

<table>
<thead>
<tr>
<th>$D_{4h}$</th>
<th>$E$</th>
<th>$2C_4$</th>
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<th>$i$</th>
<th>$2S_4$</th>
<th>$C_2v$</th>
<th>$3C_{2h}$</th>
<th>$3C_{2v}$</th>
<th>$3σ_d$</th>
<th>$3σ_v$</th>
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<td>1</td>
<td>1</td>
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<td>1</td>
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<td>1</td>
<td>1</td>
<td>$i$</td>
</tr>
<tr>
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<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
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<td>1</td>
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<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
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<td>1</td>
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<td>1</td>
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<td>1</td>
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### Cubic Groups

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<td>1</td>
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<tr>
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<td>$(2z^2-x^2-y^2, 0)$</td>
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<tr>
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<td>$e^{120}$</td>
<td>1</td>
<td>$(x, y, z)$</td>
</tr>
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<td>0</td>
<td>$i$</td>
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<th>$4C_4'$</th>
<th>$3C_3$</th>
<th>$2S_4$</th>
<th>$4S_4'$</th>
<th>$3σ_v$</th>
<th>$e = \exp(2\pi i/3)$</th>
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<tbody>
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<td>1</td>
<td>1</td>
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<td>1</td>
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<td>1</td>
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<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
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</tr>
<tr>
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<td>1</td>
<td>$e$</td>
<td>$e^{120}$</td>
<td>1</td>
<td>$(x, y, z)$</td>
</tr>
<tr>
<td>$E_{2g}$</td>
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<td>$e$</td>
<td>$e^{120}$</td>
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</tr>
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<td>$T_{1g}$</td>
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<td>0</td>
<td>0</td>
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<td>-1</td>
<td>0</td>
<td>$(R_x, R_y, R_z)$</td>
</tr>
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<td>0</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
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<th>$6S_4$</th>
<th>$6S_4'$</th>
<th>$3σ_v$</th>
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<tbody>
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<td>1</td>
<td>1</td>
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<td>1</td>
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</tr>
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<td>$e$</td>
<td>$e^{120}$</td>
<td>1</td>
<td>$e$</td>
<td>$e^{120}$</td>
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<td>0</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
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</table>
number of four as in \( \text{H}_2\text{PO}_4 \), \( \text{HClO}_4 \), and \( \text{HBrO}_4 \), and the silicates (see Chapters 16 and 17).

The largest nonmetals show coordination numbers as high as eight in the octahedraneons, \( \text{IF}_6^2^- \) and \( \text{XeF}_6^2^- \) (see Chapter 17). The corresponding oxyacids and oxoanions show a maximum coordination number of six: \( \text{Si}^4+(\text{OH})_4^2-, \text{Te}^4+(\text{OH})_4^2-, \text{Sb}^5+(\text{OH})_4^2-, \text{Xe}^6+(\text{OH})_4^2- \). Of these, apparently only iodine shows a maximum oxidation state with a coordination number as low as four: Periodic acid can exist as either \( \text{IO}_4^- \) or \( \text{IO}_6^2- \). It was mentioned previously that a strong resemblance obtains between Li and Mg, Be and Al, C and P, and other "diagonal elements," and it was pointed out that this could be related to a size-charge phenomenon. Some examples of these resemblances are as follows:

**Lithium—Magnesium**

There is a large series of lithium alkyls and lithium aryls which are useful in organic chemistry in much the same way as the magnesium Grignard reagents. Unlike Na, K, Rb, or Cs, but like Mg, lithium reacts directly with nitrogen to form a nitride:

\[
\text{Li}_2 + \text{N}_2 \rightarrow 2\text{Li}_2\text{N}_2 \tag{18.7}
\]

\[
6\text{Li} + 2\text{N}_2 \rightarrow 2\text{Li}_3\text{N}_2 \tag{18.8}
\]

Finally, the solubilities of several lithium compounds more closely resemble those of the corresponding magnesium salts than of other alkali metal salts.

**Beryllium—Aluminum**

These two elements resemble each other in several ways. The oxidation emfs of the elements are similar (\( E^{0}_\text{Be}^+ = 1.85 \); \( E^{0}_\text{Al}^3+ = 1.66 \)), and although reaction with acid is thermodynamically favored, it is rather slow, especially if the surface is protected by the oxide. The similarity of the ionic potentials for the ions is remarkable (Be\(^{2+} = 48 \), Al\(^{3+} = 50 \)) and results in similar polarizing power and acidity of the cations. For example, the carbonates are unstable, the hydroxides dissolve readily in excess base, and the Lewis acids of the halides are comparable.

**Boron—Silicon**

Boron differs from aluminum in showing almost no metallic properties and its resemblance to silicon is greater. Both boron and silicon form volatile, very reactive hydrides; the hydride of aluminum is a polymeric solid. The halides (except BF\(_3\)) hydrolyze to form boron acid and silicic acid. The oxygen chemistry of the boranes and silicas also shows certain resemblances.

**Carbon—Phosphorous, Nitrogen—Sulfur, and Oxygen—Chlorine**

All metallic properties have been lost in these elements, and so charge-to-size ratios have little meaning. However, the same effects appear in the electronegativities of these elements, which show a strong diagonal effect.\(^8\)

\(^8\) These values are Pauling thermochemical electronegativities rather than those based on ionization energy—electron affinity. This choice of empirical values was made to obtain the necessary of choosing (arbitrarily) the proper valence state hybridization.

### S\(_5\) Groups

<table>
<thead>
<tr>
<th>S(_4)</th>
<th>E</th>
<th>S(_4)</th>
<th>C(_3)</th>
<th>C(_1)</th>
<th>x(^2) + y(^2), z(^2)</th>
<th>S(_5)</th>
<th>E</th>
<th>C(_3)</th>
<th>C(_1)</th>
<th>i</th>
<th>S(_5)</th>
<th>S(_6)</th>
<th>(\epsilon = \exp(2\pi i/3))</th>
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<td>1</td>
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<tr>
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<td>i</td>
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### C\(_{10}\) Groups

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</tr>
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<td>1</td>
</tr>
<tr>
<td>B(_1)</td>
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<td>i</td>
<td>i</td>
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<td>-i</td>
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<td>C(_2)</td>
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<tr>
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<td>-1</td>
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<tr>
<td>B(_2)</td>
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<td>-i</td>
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### D\(_{10b}\) Groups

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<th>i</th>
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<td>1</td>
<td>-1</td>
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### D\(_{10a}\) Groups

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<th>C(_1)</th>
<th>i</th>
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<th>y((x,y))</th>
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<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
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<tr>
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### D\(_{15}\) Groups

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<th>2C(_2)</th>
<th>3C(_1)</th>
<th>2x(_3)</th>
<th>2x(_2)</th>
<th>2x(_1)</th>
<th>3x(_1)</th>
<th>3x(_2)</th>
<th>3x(_3)</th>
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<td>1</td>
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<td>A(_2)</td>
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<td>1</td>
<td>-1</td>
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<td>-1</td>
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<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

### Notes

- The table represents the groups and their corresponding symmetries and transformations.
- Each entry in the table indicates a specific operation or transformation related to the group.
- The symbols used in the table are standard in group theory, where E represents the identity, C\(_n\) represents a cyclic group of order n, i is the identity, and \(\epsilon\) is the identity in the group of order 3.
Compounds that are formally analogous to carbon compounds are found to have quite different structures. Thus carbon dioxide is a gaseous monomer, but silicon dioxide is an infinite single-bonded polymer. In a similar manner, gem-diolks are unstable relative to ketones:

\[
(CH_3)_2C(OH)_2 \rightarrow CH_3C(O)CH_3 + H_2O \tag{18.13}
\]

and the analogous silicon compounds are also unstable, but the "dimethylsilicone" that forms is a linear polymer:

\[
(CH_3)_2SiCl_2 \rightarrow [(CH_3)_2Si(OH)_2] \rightarrow \quad O \quad Si \quad O \quad Si \quad O \quad Si \quad O
\tag{18.14}
\]

The term "silicone" was coined by analogy to ketone under the mistaken belief that monomeric R-Si-O compounds could be isolated. See Chapter 16.

The contrast between the strengths of 2p_π-2p_π bonds and their higher-n congeners is responsible for much of the stability of groups important in organic chemistry: alkenes, aldehydes, ketones, and nitriles. It also permits doubly bonded molecules such as carbonic and nitric acids, rather than their ortho analogues. A source of the greater stability of π bonds between the smaller atoms could be better overlap of the 2p orbitals. The overlap integral \( \langle p_a | p_b \rangle \) is only poorly depicted by a drawing such as Fig. 18.1. The overlap is strongly affected by the magnitude of the wave function in the overlap region and, especially for π bonds, is increased by small, "dense" orbitals. The first time a given type of orbital (2p, 3d, 4f) appears, it is nodeless and anomalously small. The small size results from the absence of inner shells having the same value of \( l \) against which this set of orbitals must be orthogonal.\(^{11}\) The 2p orbitals thus are as small as the 2s orbital, in contrast to the 3p orbitals which are larger and more diffuse than the 3s orbitals.\(^{12}\)

For the heavier congeners in Group IVA (14), the differences are even more striking. Thus, although carbon is generally tetravalent except as transient carbene or methylene intermediates, it is possible to prepare divalent germanium, tin, and lead compounds. For example, if bulky substituents \([R = CH_3(SiMe_3)]\) are present, the compounds \(RGe, R_2Sn, \text{ and } R_2Pb \) exist as diamagnetic monomers in solution, although there is a tendency for them to dimerize in the solid. The molecular structure of the tin dimer has been determined and found to be in the trans conformation:

![Fig. 18.1 Diagrammatic representation of the possibly poorer overlap of the p orbitals in Si-Si as compared with C-C.](image)

\(^{11}\) Pyysik, P. Chem. Rev. 1980, 80, 363-392.


### Terms of various electron configurations

<table>
<thead>
<tr>
<th>Equivalent electrons</th>
<th>Nonequivalent electrons</th>
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</thead>
<tbody>
<tr>
<td>s^2, p^6, and d^10</td>
<td>IS</td>
</tr>
<tr>
<td>p and p^1</td>
<td>1P</td>
</tr>
<tr>
<td>p^2 and p^1</td>
<td>3P, 1D, 1S</td>
</tr>
<tr>
<td>p^2</td>
<td>3S, 3D, 3P</td>
</tr>
<tr>
<td>d and d^1</td>
<td>4D</td>
</tr>
<tr>
<td>d^1 and d^1</td>
<td>3F, 3P, 1G, 1D, 1S</td>
</tr>
<tr>
<td>d^1 and d^3</td>
<td>4F, 3P, 4H, 3G, 1F, 1D, 1D, 1P</td>
</tr>
<tr>
<td>d^1 and d^3</td>
<td>5F, 4P, 5H, 4G, 1F, 1D, 1D, 1S</td>
</tr>
<tr>
<td>d^1</td>
<td>5S, 5G, 4F, 4P, 3P, 3H, 3G, 3F, 3P, 1D, 1D, 1D, 1P, 1S</td>
</tr>
</tbody>
</table>

### Hund's Rules

The ground state of an atom may be chosen by application of Hund's rules. Hund's first rule is that of maximum multiplicity. It states that the ground state will be that having the largest value of S, in the case of carbon the 3F. Such a system having a maximum number of parallel spins will be stabilized by the exchange energy resulting from their more favorable spatial distribution compared with that of paired electrons (see Pauli principle, Chapter 2).

The second rule states that if two states have the same multiplicity, the one with the higher value of L will lie lower in energy. Thus the 3D lies lower in energy than the 1S.3 The greater stability of states in which electrons are coupled to produce maximum angular momentum is also related to the spatial distribution and movement of the electrons.

---

*Hund's rules are inviolate in predicting the correct ground state of an atom. There are occasional exceptions when the rules are used to predict the ordering of excited states.*
The stable form of nitrogen at room temperature is N₂, which has an extraordinarily strong (946 kJ mol⁻¹) triple bond. In contrast, white phosphorus consists of P₄ molecules (see Chapter 16), and the thermodynamically stable form is black phosphorus, a polymer. At temperatures above 800 °C dissociation to P₄ molecules does take place, but these are considerably less stable than N₂ with a bond energy of 895 kJ mol⁻¹. In this case, too, in the heavier elements several single bonds are more effective than the multiple bond.

The phosphorus analogue of hydrogen cyanide can be prepared:

\[ \text{CH}_3 + \text{PH}_2 \xrightarrow{\text{HCl}} \text{HC} = \text{P} + 3\text{H}_2 \]  

(18.15)

In contrast to stable hydrogen cyanide, HCP is a highly pyrophoric gas which polymerizes above -130 °C. In this decade the number of molecules containing C=P bonds has increased to over a dozen. One method of obtaining them is by dehydrohalogenation:

\[ \text{CH}_3\text{PCl}_3 \xrightarrow{\text{heat}} \text{HCP} \]  

(18.16)

\[ \text{CF}_3\text{PH}_2 \xrightarrow{\text{heat}} \text{CF}_2 = \text{PH} \xrightarrow{\text{heat}} \text{FC} = \text{P} \]  

(18.17)

Kinetically stable phosphinylalkynes can be synthesized if a sufficiently bulky substituent (R) is present:

\[ \text{P}_4 + 12\text{Na/K} + 12\text{SiMe}_3 \xrightarrow{\text{heat}} 4\text{P(SiMe}_3\text{)}_3 + 12(\text{Na/K})\text{Cl} \]  

(18.18)

One of the first challenges facing chemists attempting to prepare phosphorus analogues of nitrogen compounds was phosphabenzene. First the phosphorus analogue of 1,5-pyridine was synthesized, and now all of the group VA (15) analogues of pyridine have been prepared.

However, these compounds must be considered the exception rather than the rule as far as the heavier elements are concerned.

---

Summary on the Occurrence of \( p_\pi-p_\pi \) Bonding in Heavier Nonmetals

The isolation of compounds containing simple C= P double bonds parallels the triple-bond work. The first stable acyclic phosphabenzene was synthesized over fifteen years ago. Again, base-induced dehydrohalogenation and stabilization by bulky groups is important:

\[ \text{H} - \text{C} = \text{P} \xrightarrow{\text{base}} \text{C} = \text{P} \]  

(18.20)

The steric biosphere is critical: if R = phenyl or 2-methylphenyl, the bulkiness is insufficient to stabilize the molecules, but the 2,6-dimethylphenyl and 2,4,6-trimethylphenyl derivatives are stable.

For many yeasts the occurrence of double and triple bonds such as discussed above for silicon and phosphorus was equally rare among other nonmetals, leading to the conclusion that only C=C, C≡N, C=O, N≡N, etc. were stable multiple bonds. This, of course, was taken as challenge and much synthetic work was directed at the problem. None of the multiple bonds between heavier nonmetals is as strong as those between the 2p elements. Some typical estimates of the strengths of the v bond (cf. to \( \text{H}_2\text{C} = \text{CH}_2 \) as a "standard" from organic chemistry) are (values in kJ mol⁻¹):

- C=C: 727
- C≡Si: 159
- C≡Ge: 130
- C≡Sn: 79

It now appears that any X= Y double bond can be prepared, given an energetic enough research attack. Hundreds of these compounds have now been synthesized. The general method has been to involve bulky substituents. In this way the multiple bond chemistry of the heavier nonmetals has resembled attempts to make low-coordinate complexes (Chapter 12).

The number of triple bonds of the heavier nonmetals that are known is considerably smaller—perhaps a dozen. It has already been noted above that protecting a multiple bond sterically is considerably more difficult than for the case of a corresponding double bond. One very interesting aspect of the C≡N bond is that, in contrast to the C≡C in acetylenes, the triple bond does not ensure linearity at the carbon atom (Fig. 18.18). The reasons are not completely clear but may be related to the nonplanarity of \( \text{R}_2\text{Ge} = \text{GeR}_2 \) and \( \text{R}_2\text{Sn} = \text{SnR}_2 \) (see page 863).

The successful isolation of all of these compounds is more a tribute to the persistence with which they were pursued than to any inherent stability of the bonds themselves. To invert George Leigh Mallory's remark about Mt. Everest, the extraordinary efforts expended on this class of compounds stemmed from the fact that they were not there. These efforts and their corresponding successes have caused one observer to comment: "Finding exceptions to the double-bond rule has become a..."
values are entered directly into the table, \(^3\), but if the electron configurations have been carefully worked out, there is no need of this. The fifteen microstates of \(p^2\) yield:

\[
\begin{array}{c|ccc}
M_L & M_s & +1 & 0 & -1 \\
\hline
-2 & x & -1 & x & x \\
0 & x & x & x & x \\
+1 & x & x & x & x \\
+2 & x & -1 & x & x \\
\end{array}
\]

\(3.\) To ensure that all microstates have been written, the total number \(N\), of microstates associated with an electronic configuration, \(I\), having \(x\) electrons in an orbital set with an azimuthal quantum number, \(l\), is

\[
N = \frac{2I(I+1)}{x(x-1)}
\]  
(C.10)

where \(I = 2(l+1)\), the number of \(m_l\) combinations for a single electron in the orbital set.


Fig. C.2 Term splitting in the ground-state \((1s^2\text{-}2s\text{-}2p)\) configuration of carbon. All energies are in cm\(^{-1}\). The \(3p\), \(1D\), and \(1S\) terms are split as a result of electron-electron repulsion. The \(3P\) term is further split with \(J = 0, 1, 2\) a result of spin-orbit coupling. The scale of the latter is exaggerated in this figure. [From DeKock, R. L.; Gray, H. B. Chemical Structure and Bonding: Benjamin/Commins: Menlo Park, CA, 1980. Reproduced with permission.]

The states of carbon are therefore \(1S, 1D, 3P\). The \(3P\) is further split by differing \(J\) values to the terms \(3P_0, 3P_1, 3P_2\). The relative magnitudes of these splittings can be seen in Fig. C.2.

Although the complexity of determining the appropriate terms increases with the number of electrons and with higher \(L\) values, the method outlined above (known as Russell-Saunders coupling) may be applied to atoms with more electrons than the carbon atom in the foregoing example. States for various electron configurations are shown in Table C.1. Russell-Saunders coupling (also called \(LS\) coupling because it assumes that the individual values of \(l\) and \(s\) couple to form \(L\) and \(S\), respectively) is normally adequate, especially for lighter atoms. For heavier atoms with higher nuclear charges, coupling occurs between the spin and orbit for each electron. \((J = l + s)\). The resultant coupling is known as \(Jj\) coupling. In general, \(LS\) coupling is usually assumed and deviations are discussed in terms of the effects of spin-orbital interactions (see Chapters 11 and 16).

\(4.\) For alternative approaches and discussions, see Kiremire, E. M. R. J. Chem. Educ. 1987, 64, 651-653; the inorganic textbooks listed on pp A-1 and A-2, and the references therein.
Arguments against the Use (or Not) of Orbitals by Nonmetals

The principal objection is to the large promotion energy required to effect
\[ s^p^{m+1} \rightarrow s^p^{m+1}d^{m+1} \]  
(18.21)

where \( m = 0, 1, 2, \text{or} 3 \), to achieve a maximum multiplicity and availability of electrons for bonding. A second factor which does not favor the utilization of \( d \) orbitals is the poor overlap that they make with the orbitals of neighboring atoms. The \( 3d \) orbitals of the free sulfur atoms, for example, are shielded completely by the lower-energy \( p \) and \( s \) electrons. As a result they are extremely diffuse, having radial distribution maxima at a distance which is approximately twice a typical bond distance (Fig. 18.3). This results in extremely poor overlap and weak bonding.²⁰

Two alternatives have been suggested to account for the higher oxidation states of the nonmetals; both reduce the importance of high-energy \( d \) orbitals. Pauling has suggested that resonance of the following type could take place:

\[ \begin{align*}
&\text{(I)} \\
&\text{(II)}
\end{align*} 

(18.22)

The second alternative is the three-center, four-electron bond developed by several workers have objected to the inclusion of \( d \) orbitals in bonding in nonmetals. The principal objection is to the large promotion energy required to effect

\[ s^p^{m+1} \rightarrow s^p^{m+1}d^{m+1} \]  
(18.21)

Several workers have objected to the inclusion of \( d \) orbitals in bonding in nonmetals. The principal objection is to the large promotion energy required to effect

\[ s^p^{m+1} \rightarrow s^p^{m+1}d^{m+1} \]  
(18.21)
A-8 C- Atomic States and Term Symbols

For a given value of \( S \), there will be \( 2S + 1 \) spin states characterized by \( M_S \):

\[
M_S = S, S - 1, S - 2, \ldots, -S
\]

(C.6)

or

\[
M_L = m_n + m_m + \cdots + m
\]

(C.7)

Now the total angular momentum of an electron is the resultant of the orbital angular momentum vector and the electron-spin angular momentum vector. Both of these are quantized, and we can define a new quantum number, \( J \):

\[
J = l + s
\]

(C.8)

Since \( \pm 1 \), it is obvious that every value of \( J \) will have two values of \( \pm J \), equal to \( l + 1 \) and \( l - 1 \). The only exception is \( l = 0 \), for which \( J = \pm \frac{1}{2} \); these values are identical since it is the absolute magnitude of \( J \) that determines the angular momentum.

We can now couple the resultant orbital angular momentum \( (L) \) with the spin angular momentum \( (S) \). The new quantum number \( J \) is obtained:

\[
J = L + S, L + S - 1, L + S - 2, \ldots, |L - S|
\]

(C.9)

The origin of the \( J \) values can be seen from a pictorial representation of the vectors involved.

The number of \( J \) values available when \( L > S \) will be equal to \( 2S + 1 \), and is termed the multiplicity of the state. In both of the examples pictured above, the multiplicity is three. The multiplicity is appended to the upper left of the symbol of \( S \) and \( J \) to the lower right. The above examples are thus \( 2P \) and \( 3D \) states (pronounced "triplet \( P \)" and "triplet \( D \)"). The individual terms are \( 2p_\perp \), \( 2p_\parallel \), and \( 2p \) (left), and \( 3d_\perp \), \( 3d_\parallel \), and \( 3d \) (right).

When \( L < S \), the series in Eq. C.9 is truncated (note the absolute magnitude of the spin symbol in the last term) and there are only \( 2L + 1 \) values. An example is the \( 6S \) configuration, where \( L = 0 \) and \( S = 4 \); \( J \) can have only the single value of \( + \frac{7}{2} \).

2. Despite the fact there is a single value of \( J \) for the ground state of hydrogen, spectroscopists write its term symbol as \( 1S_0 \). The reasons for this is that transitions between states of different spin multiplicities are spin forbidden; this transitions from a spin-paired singlet state \( (0) \) to a spin-uncoupled triplet \( (S) \) are allowed. However, with hydrogen and the alkali metals so well the ground state has an unpaired electron, and transitions to doublet states with a single unpaired electron are allowed. For one to be noting which transitions are allowed and which are spin forbidden, spectroscopists write \( 1S \), though admittedly it can lead to confusion.

To turn again momentarily from the abstractions of orbitals and quantum numbers back to the spectra that generated them, consider the transition from \( 1S \) orbital in hydrogen to a \( 2p \) orbital. The terms and transitions are:

\[
\begin{align*}
2S_\perp & \rightarrow 2P_\perp \\
2S_\parallel & \rightarrow 2P_\parallel
\end{align*}
\]

(C.10)

The \( 2P \) term lies slightly higher in energy than the \( 2S \), and therefore the spectral line is split into a "doublet"; hence the origin of the usage. It may be noted that in respect to these transitions the following selection rules operate: \( \Delta m = \pm 1 \); \( \Delta n = \pm 2 \), \( \pm 3 \), etc.

Assigning Term Symbols

We have seen that the term symbol for the ground state of the hydrogen atom is \( S_0 \). For a helium atom \( L = 0, S = 0, J = 0 \), and the term symbol for the ground state is \( 1S_0 \). For an atom such as boron, we can make use of the fact that all closed shells and subshells (such as the \( 1s^2 \) example just given) contribute nothing to the term symbol. Hence both the \( 1s^2 \) and \( 2s^2 \) electrons give \( L = S = J = 0 \). The \( 2s^2 \) electrons have \( L = 1 \), \( S = 1 \), and \( J = 1 \), yielding \( 2s^2 \) \( 2p_\perp \) and \( 2p_\parallel \). For carbon there are two \( p \) electrons. The spins may be paired or unpaired, so \( L = 2, 1, 0; S = 1, 0; \) and \( J = 3, 2, 1, 0 \). To work out the appropriate states for this atom requires a systematic approach. Note, however, that when neon is reached we have again a \( 1S_0 \), sodium repeats the \( 2S \), magnesium \( 3S \), etc.

A Systematic Approach to Term Symbols

In Chapter 2 it was shown how \( m_l \) and \( m_s \), values could be summed to give \( m_J \) and \( M_J \), values to yield terms for the spectroscopic states of an atom. If there are two or more electrons, it is usually necessary to proceed in a systematic fashion in generating these terms. The following is one method of doing so. The \( p^2 \) configuration of carbon is used.

1. Determine the possible values of \( m_S \) and \( M_S \). For the \( p^2 \) configuration, \( L \) can have a maximum value of \( 2 \) and \( M_L \) can have values of \( -2, -1, 0, +1, +2 \). The electrons can have paired values (\( M_L = 0 \) or parallel (\( M_L = \pm 1, -1 \).)

2. Determine the electron configurations that are allowed by the Pauli principle. The easiest way to do this is to draw up a number of sets of \( p \) orbitals as in Fig. C.1 (each vertical column represents a set of three \( p \) orbitals) and fill in electrons until all possible arrangements have been found. The \( M_L \) value for each arrangement can be found by summing \( m_p \) and \( M_L \) from the sum of \( m_p \) (spin-up electrons have arbitrarily been assigned \( m_p = + \)). Each microstate consists of one combination of \( M_L \) and \( M_S \).

3. Set up a chart of microstates. For example, the microstate corresponding to the first vertical column in Fig. C.1 has \( M_L = +2 \) and \( M_S = 0 \). It is then entered into the table below under those values. Sometimes the \( m_p \) and \( m_s \)
hexacordinate nitrogen do not occur. On the other hand, a theoretical case has been made for the possibility of pentacordinate nitrogen in a molecule such as $\text{NF}_5$.

In the case of $d_{x^2-y^2}$ bonding we again find the old problem of detecting the existence of a bond. We can infer the presence of a $\sigma$ bond when we find two atoms at distances considerably shorter than the sum of their van der Waals radii. The detection of a $\sigma$ bond depends on more subtle criteria: shortening or strengthening of a bond, stabilization of a charge distribution, etc., experimental data which may be equivocal.

One example of the apparent existence of $\sigma$ bonding is in phosphine oxides. Most tertiary phosphines are unstable relative to oxidation to the phosphine oxide. However, the tertiary phosphines are unstable relative to oxidation to the phosphine oxide:

$$2\text{PR}_3 + \text{O}_2 \rightarrow 2\text{RPO} \quad (18.26)$$

This reaction takes place so readily that aliphatic phosphines must be protected from atmospheric oxygen. The triarylphosphines are more stable in this regard but still can be oxidized readily:

$$\text{Ph}_3\text{P} \rightarrow \text{Ph}_3\text{PO} \quad (18.27)$$

In contrast, aliphatic amines do not have to be protected from the atmosphere although they can be oxidized:

$$\text{R}_3\text{N} + \text{HOH} \rightarrow [\text{R}_3\text{NOH}]^+ \cdot \text{OH}^- + \text{R}_2\text{NO} \quad (18.28)$$

However, the amine oxides decompose upon heating:

$$\text{Et}_2\text{NO} \rightarrow \text{Et}_2\text{NOH} + \text{CH}_2=\text{CH}_2 \quad (18.29)$$

This reaction is completely unknown for the phosphine oxides, which are thermally stable. In fact, the tertiary phosphine oxides form the most stable class of organophosphorus compounds. Those oxides with no $\beta$ hydrogen atom are particularly stable: Triarylphosphine oxide and triphenylphosphine oxide do not decompose below 700°C. They are not reduced even by heating with metallic sodium. The tendency of phosphorus to form $\text{P=O}$ or $\text{P=O}$ linkages is one of the driving forces of phosphorus chemistry and may be used to rationalize and predict reactions and structures.

For example, the lower phosphorus acids exist in the four-coordinate structures even though they can be oxidized:

$$\text{ROH} + \text{P} \rightarrow \text{RO} \cdot \text{P} + \text{OH}^{-} \quad (18.29)$$

The difference between the behavior of the amine oxides and phosphine oxides lies in the polarity of the molecules. The dipole moment of trimethylamine oxide is $16.6 \times 10^{-30}$ C m compared with $14.8 \times 10^{-30}$ C m (4.37 D) for triethylphosphine oxide. A consequence of this polarity is the tendency of the amine oxides to form hydrates, $\text{R}_3\text{NOH} \cdot \text{H}_2\text{O}$, and their greater basicity relative to the phosphine oxides.

The difference between the behavior of the amine oxides and phosphine oxides can be rationalized in terms of the possibility of back bonding in the latter. Whereas amine oxides are restricted to a single structure containing a dative $\eta^1\text{N-O}$ bond, the phosphine oxides can have contributions from $d_{x^2-y^2}$ bonding between the phosphorus and oxygen atoms:

$$\text{R}_3\text{P}=\text{O}^* \rightarrow \text{R}_3\text{P}=\text{O} \quad (18.36)$$

The double bond character introduced by the latter strengthens the bond and accounts for the extraordinary stability of the phosphorus oxygen linkage. Note that this extra stability cannot be attributed to ionic resonance energy (a priori a reasonable suggestion since the difference in electronegativity is greater in $\text{P=O}$ than $\text{N=O}$) because the dipole moment of the nitrogen compound is greater than that of the phosphorus compound, a result completely unexpected on the basis of electronegativities, unless consideration is taken of canonical form 18.36(H), which would be expected to lead to a reduced moment.

A comparison of the bond energies also supports the above interpretation. The dissociation energies of $\text{P=O}$ bonds in a variety of compounds lie in the range of 500-600 kJ mol$^{-1}$ compared with values for $\text{N=O}$ of about 200-300 kJ mol$^{-1}$. The value for the latter is typical of what we might expect for a single bond, but 600 kJ mol$^{-1}$
SI units in their education—they may wonder what all of the fuss is about. They will know as soon as they stop reading textbooks and start reading the original literature!

Length, molecular dimensions. As mentioned above, this surely is the easiest conversion to make. Bond lengths in picometers are exactly 100 times greater than when expressed in angstroms.

Energies. Ionization energies expressed in kJ mol⁻¹ are approximately (31% error) 100 times greater than when expressed in electron volts. Bond energies in kJ mol⁻¹ are approximately (45% error) four times their values in kcal mol⁻¹.

The calculation of lattice energies (and other Coulomb’s law energies) is complicated somewhat by the fact that in SI the permittivity (dielectric constant) of a vacuum is no longer defined as one but has an experimentally determined value. Furthermore, for reasons we need not explore at present, Coulomb’s law is stated in the form:

\[ E = \frac{q_1 q_2}{4\pi\varepsilon_0 r} \]  
(B.1)

The calculation may be simplified if the values for \( \varepsilon_0 \) and \( \pi \) are included in the conversion factor, 1.389 \times 10⁶ kJ mol⁻¹ pm (the reader should confirm this value), which allows direct calculation of the lattice energy using ionic charges and distances in picometers.

Dipole moments. The differences between the two systems are such that there appears to be no simple correlation. Nevertheless, since most SI tables will probably list values as coefficients of 10⁻³⁰ the following mnemonic and rule of thumb should help: To get SI values from Debyes, divide by 0.3.

Pressure. Fortunately, an atmosphere is almost (1% error) 10⁴ Pa. So a standard atmosphere is about 100 kPa, and when high pressure experiments are presented in terms of GPa, each gigapascal represents about 10⁴ atmospheres.

Atomic States and Term Symbols

The energy of a spectral transition for the hydrogen atom is given by the Rydberg formula:

\[ v = \frac{109,737 \text{ cm}^{-1} \left( \frac{1}{n_2^2} - \frac{1}{n_1^2} \right)}{h} \]  
(C.1)

which consists of two terms. It is common for spectroscopists to apply the word term to the energies associated with the states of an atom involved in a transition. Term symbols are an abbreviated description of the energy, angular momentum, and spin multiplicity of an atom in a particular state. Although the inorganic chemist generates the term symbols used from knowledge of atomic orbitals, the historical process was the reverse: S, P, D, and F states were observed spectroscopically, and named after sharp (S —> P), principal (P —> S), diffuse (D —> P), and fundamental (F —> D) characteristics of the spectra. Later the symbols s, p, d, f, and j were applied to orbitals.

Atoms in S, P, D, F states have the same orbital angular momentum as a hydrogen atom with its single electron in an s, p, d, f, . . . orbital. Thus we can define a quantum number \( L \) which has the same relationship to the atomic state as \( l \) has to an atomic orbital (e.g., \( L = 2 \) describes a D state). \( L \) is given by:

\[ L = l_1 + l_2, l_1 + l_2 - 1, l_1 + l_2 - 2, \ldots, \lvert l_1 - l_2 \rvert \]  
(C.2)

We can also define the component of the total angular momentum along a given axis:

\[ M_L = L, L - 1, L - 2, \ldots, 0, \ldots, -L \]  
(C.3)

The number of possible values of \( M_L \) is given by 2L + 1. \( M_L \) is also given by:

\[ M_L = m_{l_1} + m_{l_2} + \cdots + m_{l_n} \]  
(C.4)

Likewise we can define an atomic spin quantum number representing the total spin:

\[ S = \sum \frac{m}{2} \]  
(C.5)

For an extensive discussion of terms, symbols, and states, see Gerloch, M. Orbitals, Terms, and States; Wiley: New York, 1986.

A-7
The stretching frequencies are plotted as a function of the sum of the electronegativities of the substituents, a straight line is obtained:

$$v_{PO} = 930 + 402\chi$$

where $\chi$ is the Pauling electronegativity of a substituent atom or group on phosphorus.

The correlation between the electronegativity of substituent groups and the strength of the $P=O$ bond provides support for a $\pi$-bonding model but not for the alternative dative $\sigma-\pi$ model. A $\sigma$ bond might be expected to be destabilized as atoms external to the cage. It is interesting to note that the ratio or these two bond proper and four shorter ones (141 pm) between the phosphorus atoms and the oxygen double-bond character. In the simplest case, that of $P\equiv O$, there are two $P=O$ bond lengths. There are twelve relatively long ones (158 pm) within the cage framework and four shorter ones (141 pm) between the phosphorus atoms and the oxygen atoms external to the cage. It is interesting to note that the ratio of these two bond lengths (0.89) is about the same as C=C to C—C or C—O.

Isoelectronic with the phosphine oxides are the phosphorus ylids, $R,PCH_3$. As for the oxides, two resonance forms $R,P=CH_3 \rightarrow R,P=CH_3$.

### Table 18.2

<table>
<thead>
<tr>
<th>Compound</th>
<th>$v_{PO}$ (cm$^{-1}$)</th>
<th>$\chi$</th>
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<tbody>
<tr>
<td>F$_3$PO</td>
<td>1404</td>
<td>11.70</td>
</tr>
<tr>
<td>Cl$_3$PO</td>
<td>1328</td>
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<tr>
<td>ClBrPO</td>
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<td>Br$_2$PO</td>
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</tr>
<tr>
<td>BrFPO</td>
<td>1261</td>
<td>7.86</td>
</tr>
<tr>
<td>PfPO</td>
<td>1190</td>
<td>7.23</td>
</tr>
<tr>
<td>Me$_2$PO</td>
<td>1176</td>
<td>6.60</td>
</tr>
</tbody>
</table>

$\chi$ = substituent electronegativity

Note that the dissociation energy, $R,P=O \rightarrow R,P+O$ is not a sensitive measure of the $P=O$ bond energy because the remaining three bonds may be strengthened or weakened in the dissociation process. The $R,P$ stretching frequency is a function of the force constant, $k$, and the reduced mass, $\mu$, of the vibrating group. If the molecule is assumed to be a light oxygen atom vibrating on a "fixed" larger mass of the $R,P$ group, the reduced mass is constant, and so changes in frequency will reflect corresponding changes in the force constant. For similar molecules the force constant will be related to the bond energy.

The controversy over the nature of the $P=O$ bond is reminiscent of that over the nature of phosphorus-metal bonds in coordination compounds. In both, interpretations have long ranged from a $\sigma$-only to a highly synergistic $\pi-\sigma$ model. As we have seen in Chapters 11 and 15, $\sigma$ orbital have also been invoked in more recent phosphorus $\pi$ bonding arguments, especially as $d-\pi$ hybrids may be involved. So the question turns out not to be simply $\sigma$ or $\pi$ but the relative contributions of $d$ and $\sigma$ orbitals to the latter. As with so many questions in inorganic chemistry, the answer is neither black nor white, but gray. If the symmetries and energies of orbitals are compatible, bonding will occur. The appropriate question is one of relative importance.

The trimethylenemethane molecule has a pyramidal structure much like that of ammonia with a $\mathrm{CH}_2—N—\mathrm{CH}_3$ bond angle of $107.8\pm 1^\circ$. In contrast, the trisilylamine molecule is planar. Although steric effects of the larger silyl groups might be expected to open up the bond angles, it seems hardly possible that they could force the lone pair out of a fourth "tetrahedral" orbital and make the molecule perfectly planar (even $\mathrm{PH}_3\,\mathrm{N}$ has bond angles of $116^\circ$). It seems more likely that the lone pair adopts a pure $\pi$ orbital on the nitrogen atom because orbitals on the three silicon atoms can overlap with it and delocalize the lone pair over the entire system (Fig. 18.4).
B- Units and Conversion Factors

Physical and chemical constants*  
Bi-Units and Conversion Factors  

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<th>Prefix</th>
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<tr>
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<td>f</td>
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<tr>
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<tr>
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Notes  
SI units are obviously going to displace older systems and units. We must all familiarize ourselves with them. Just as obvious is the fact that this displacement is going to take time, and the contemporary literature is going to exhibit a variety of units. Therefore, this book has tried to take a middle course: To report all values in SI or SI-derived units but also to include frequently that same value expressed in "traditional" units. We realize that by so doing, we run the risk of being "neither fish nor fowl," and of alienating both the progressive, who would like to see 100% SI, and the conservative, who would like to stick to the cgs system. Nevertheless, the decision must be based on consideration of the students as future chemists who will encounter kilojoules, kilocalories, electron volts, picometers, nanometers, angstroms, coulomb meters, and Debyes; they had better have some familiarity with each of these units. The irony of it all is that the easiest change to make and the one that causes no confusion whatsoever is that of angstroms to picometers: 1 Å = 10 pm. No one is apt to confuse a bond length of Au—Au = 300 Å (in the unusual gold compounds of Chapter 18) with Au—Au = 300 pm. No one is apt to confuse a bond length of Au—Au = 300 Å (in the unusual gold compounds of Chapter 18) with Au—Au = 300 pm. No one is apt to confuse a bond length of Au—Au = 300 Å (in the unusual gold compounds of Chapter 18) with Au—Au = 300 pm.

Rather similar results are obtained by comparing the bond angles in the silyl and methyl ethers (Fig. 18.5) and isothiocyanates (Fig. 18.6). In the dimethyl ether the oxygen is hybridized approximately sp³ with two lone pairs on the oxygen atom as compared to an approximate sp³ hybrid in disiloxane with π bonding. In the same way the methyl isothiocyanate molecule, CH₃N=C=S, has a lone pair localized on the nitrogen atom, hence is bent (N ≈ 90°), but the delocalization of this lone pair into a π bond on the silicon atom of H₂Si=N=C=S leads to a linear structure for this molecule.

The hypothesized delocalization of lone pair electrons in the above silicon compounds is supported by the lowered basicity of the silyl compounds as compared to the corresponding carbon compounds. This reduced basicity is contrary to that expected on the basis of electronegativity effects operating through the σ system since silicon is less electronegative than carbon. It is consistent with an "induced Lewis acid-base interaction" between the nitrogen and oxygen lone pairs and empty acceptor orbitals.

Bonding is known in the very well studied phosphorus and sulfur systems. In view of the uncertainty with which π bonding is known in the very well studied phosphorus and sulfur systems, it is not surprising that little can be said concerning the possibility of similar effects in arsenic, antimony, selenium, tellurium, etc. In general it is thought that the problems faced in phosphorus and sulfur chemistry concerning promotion energies and diffuse character may be even larger in the heavier congeners. In the latter regard it is interesting to note the apparent effectiveness of π bonding in metal complexes. To the extent that softness in a ligand can be equated with the ability to accept electrons from soft metal ions in dπ-dπ "back bonds," information can be obtained from the tendency to complex with (d) metal ions (see Chapter 9). P > As > Sb. This order would indicate that the smaller phosphorus atom can more effectively π bond with the metal atom.

In contrast to the arguments presented against participation of d orbitals in the bonding of nonmetals, several workers have pointed out that the large promotion energies and diffuse character described above are properties of an isolated sulfur or phosphorus atom. What we need to know are the properties of a sulfur or phosphorus atom. This is an exceedingly difficult problem and cannot be dealt with in detail here. However, we have seen how it is possible to calculate some properties as electronegativity on isolated atoms as charge is added or withdrawn (see Chapter 5) and how this might approximate such properties in a molecular environment.

It is apparent from the preceding discussions that participation of d orbitals, if it occurs at all, is found only in the nonmetals when in high oxidation states with electronegative substituents. The partial charge induced on the central P or S atom will be large merely from the electronegativity of the fluorine (as in PF₃, SF₃) or oxygen (as in OPX₂, O₃SₓLₓ) irrespective of any bonding model (such as Pauling's or the three-center bond) invoked.

We have seen in Chapter 2 that increasing effective nuclear charge makes the energy levels of an atom approach more closely the degenerate levels of the hydrogen atom. We might expect, in general, that increasing the effective nuclear charge on the central atom as a result of induction effects would result in the lowering of the d orbitals more than the corresponding s and p orbitals since the former are initially shielded more and hence will be more sensitive to changes in electron density. The promotion energy would thus be lowered. A second effect of large partial charges on the central atom will be a shrinking of the large, diffuse orbitals into smaller, more compact orbitals that will be more effective in overlapping neighboring atoms. For example, sample calculations indicate that in SF₄, the d orbitals have been contracted to an extent that the radius of maximum probability is only 120 pm compared with the values of 200-400 pm in the free sulfur atom (Fig. 18.3).

One of the most remarkable molecules is thiazyl trifluoride, NSF₃ (Fig. 18.7). This compound is very stable. It does not react with ammonia at room temperature, with hydrogen chloride even when heated, or with metallic sodium at temperatures below 400°C. The S=N bond, 141.6 pm, is the shortest known between these two elements. The SF₃ bond angles of 94° are compatible with approximate sp³ hybrid π bond and the presence of an sp³ hybrid π bond and two p-π bonds between the sulfur and the nitrogen. The contraction of the d orbitals by the inductive effect of the fluorine atoms presumably permits effective overlap and π bond formation. The alternative explanation would require a double dative bond from the sulfur atom, extremely unlikely in view of the positive character of the sulfur atom.

The bond length is consistent with a triple bond. Bond lengths of 174 pm for single S=N bonds (in NH₂SO₃H) and 154 pm for double S=N bonds (in N₂S₄F₄) are consistent with a bond order of 2.7 in thiazyl trifluoride. This value is also in agreement with an estimate based upon the force constant. The relative bond lengths of S=N, S≡N, and S=N≡N bonds are thus 1.00:0.87:0.78 compared with similar shortening of 1.00:0.87:0.78 for corresponding C=N, C≡N, and C≡N bonds.

In view of the uncertainty with which π bonding is known in the very well studied phosphorus and sulfur systems, it is not surprising that little can be said concerning the possibility of similar effects in arsenic, antimony, selenium, tellurium, etc. In general it is thought that the problems faced in phosphorus and sulfur chemistry concerning promotion energies and diffuse character may be even larger in the heavier congeners. In the latter regard it is interesting to note the apparent effectiveness of π bonding in metal complexes. To the extent that softness in a ligand can be equated with the ability to accept electrons from soft metal ions in dπ-dπ "back bonds," information can be obtained from the tendency to complex with (d) metal ions (see Chapter 9). P > As > Sb. This order would indicate that the smaller phosphorus atom can more effectively π bond with the metal atom.

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Units and Conversion Factors

The International System of Units (SI)

SI base units

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<tr>
<td>Time</td>
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<tr>
<td>Electric current</td>
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<tr>
<td>Thermodynamic temperature</td>
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<td>K</td>
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<tr>
<td>Amount of substance</td>
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<tr>
<td>Luminous intensity</td>
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Common derived units

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The three nitrogen atoms and the fluoro-substituted phosphorus atoms are coplanar (within 2.5 pm), but the phenyl-substituted phosphorus atom lies 20.5 pm above this plane. The explanation offered is that the more electropositive phenyl groups cause an expansion of the phosphorus \(d\) orbitals, less efficient overlap with the \(p\) orbitals of the nitrogen atom, and a weakening of the \(\pi\) system at that point. This allows the ring to deform and the \(\text{Ph}_4\text{P}^+\) monomer to bond out of the plane.

Further examples of the jeopardy involved in casually dismissing \(d\) orbitals participation are the findings of Haddon and coworkers\(^{28}\) that \(d\) orbital participation is especially important in \(\text{SF}_4\), which is nonplanar, and also that it accounts for about one-half of the delocalization energy in the one-dimensional conductor (SNN). In the latter case, the low electronegativity of the \(d\) orbitals (see Chapter 5) increases the ionicity of the \(S\)--\(N\) bond and stabilizes the structure.

Finally, it will be recalled that the existence of strong \(P=O\) bonds in \(\text{OPF}_4\) (see page 870) is consistent with enhanced back donation of electron density from the oxygen atom to the phosphorus atom bearing a positive partial charge from the four \(\sigma\) bonds to electronegative atoms. In light of the above discussion of the contraction of phosphorus and sulfur \(d\) orbitals when bearing a positive charge, better overlap may be added to the previous discussion as a second factor stabilizing this molecule.

The question of \(d\) orbital participation in nonmetals is still an open controversy. In the case of \(\sigma\)-bonded species such as \(\text{SF}_4\), the question is not of too much importance since all of the models predict an octahedral molecule with very polar bonds. Participation in \(\pi\) bonding is of considerably more interest, however, inorganic chemists of a more theoretical bent tend to be somewhat skeptical, feeling that the arguments regarding promotion energies and poor overlap have not been adequately solved. On the other hand, chemists interested in synthesis and characterization tend to favor the use of \(d\) orbitals in describing these compounds, pointing to the great heuristic value that has been provided by such descriptions in the past and arguing that until rigorous and complete calculations on these molecules show the absence of significant \(d\) orbital participation it is too soon to abandon a useful model.

Reactivity and \(d\) Orbital Participation

It has been pointed out that the elements of the second row (Li to F) not only resemble their heavier congeners in a certain extent (in their formal oxidation state, at least) but also the lower right diagonal element (as far as charge, size, and electronegativity are concerned). For example, both silicon and phosphorus form hydrides that have some properties in common with alkanes, although they are much less stable. As a result of the electronegativity relationship the \(P=\text{H}\) bond more closely approaches the polarity of the \(C=\text{H}\) bond than does the \(\text{Si}=\text{H}\) bond. The resemblance of phosphorus to carbon has even been extended to the suggestion that a discipline be built around it in the same manner as organic chemistry is built on carbon.

There is one important aspect of the chemistry of both silicon and phosphorus which differs markedly from that of carbon. Consider the following reactions:

- \(\text{CCl}_4 + \text{H}_2\text{O} \rightarrow \text{No reaction} \quad (18.42)\)
- \(\text{SiCl}_4 + 4\text{H}_2\text{O} \rightarrow 8\text{H}_2\text{O} + 4\text{HCl} \quad \text{rapid} \quad (18.43)\)

\(^{27}\) Note that this explanation does not state that the presence of the weakening of the \(\pi\) bonding causes the ring bending but allows it, perhaps resulting from crystal packing forces.

19.30 For each of the above for which you predicted an adverse effect, speculate as to the likelihood that there actually will be an effect, i.e., whether there will be acid rain at that particular geographic site or not.

19.31 Page 916 refers to "the rust-red soils of Oahu." What is the chemical origin of the "rust-red" color? What is the physical source of the color?

19.32 Niebohr and Richardson have written an extremely interesting article entitled, "The replacement of the nondescript term 'heavy metals' by a biologically and chemically significant classification of metal ions." Their abstract states, in part:

"It is proposed that the term "heavy metals" be abandoned in favor of a classification which separates metals... according to their binding preferences... related to atomic properties... A review of the roles of metal ions in biological systems demonstrates the potential of the proposed classification for interpreting the biochemical basis for metal-ion toxicity..."

Discuss in terms of the suggestions provided by the abstract. Propose a theme for the Niebohr/Richardson article (as though it were your own) and give some illustrative examples.

19.33 Review your knowledge of coordination chemistry with respect to nomenclature: Why is the molecule shown in Fig. 19.27 the "A" isomer?

19.34 The parallelism of sunlight driven photosynthesis/respiration and the chemolithotrophic oxidation of sulfide and sulfur by bacteria (page 950), as well as the possibility of metal toxicity near hydrothermal vents (page 952), has been noted. Suggest other problems and possible solutions to be expected from hydrothermal vent organisms.

19.35 If you did not work Problem 12.34 when you read Chapter 12, do so now.

19.36 Bioinorganic compounds tend to change structure (bond lengths and bond angles), more or less, upon changes in oxidation state or coordination number. The spectrum runs from blue copper proteins (almost no changes) to hemoglobin (considerable rearrangement). Discuss the chemical reasons for these differences in behavior and how they affect the biological function of these molecules.

19.37 If CoO and CuO n° are isoelectronic, why does hemoglobin (Fe 3+) have the stronger interaction with CoO, but methemoglobin (Fe 2+) breaks CoO n° more tightly? (Hint: Compare Fe 3°−CO, Fe 3°−CO, Fe 2°−CN, and Fe 2°−CN.)

19.38 At pH 7.8, the structure of reduced (Cu 1°) plastocyanin has a structure very similar to that of Cu 1°plastocyanin (Fig. 19.15) except for small differences in bond lengths. At pH 3.8, the copper is trigonally coordinated with the fourth interaction (Cu-imidazole) broken. Predict and discuss the redox activity of plastocyanin as a function of pH.

Texts and General Reference Books


Appendix

The Literature of Inorganic Chemistry

The following is not meant to be an exhaustive list of all of the books of interest to an inorganic chemist, but it is a short list of useful titles.
Periodic Anomalies

The best known exceptions to the general reluctance of bromine to accept a +7 oxidation state are perbromic acid and the perbromate ion, which were unknown prior to 1968 (see Chapter 17). Their subsequent synthesis has made their "nonexistence" somewhat less crucial as a topic of immediate concern to inorganic chemists, but bromine certainly continues the trend started by arsenic and selenium. Thus the perbromate ion is a stronger oxidizing agent than either perchlorate or periodate.

Before seeking an explanation of the reluctance of As, Se, and Br to exhibit maximum oxidation states, a related phenomenon will be explored. This involves a tendency for germanium to resemble carbon more than silicon. Some examples are:

1. Reduction of halides (X) with zinc and hydrochloric acid. Germanium resembles carbon and tin resembles silicon:

   \[
   \begin{align*}
   & C + \frac{1}{2} \text{XCl}_2 \rightarrow C\text{Cl} \quad (18.47) \\
   & \text{Si} + \frac{1}{2} \text{XCl}_2 \rightarrow \text{SiCl} \quad (18.48) \\
   & \text{Ge} + \frac{1}{2} \text{XCl}_2 \rightarrow \text{GeCl} \quad (18.49) \\
   & \text{Sn} + \frac{1}{2} \text{XCl}_2 \rightarrow \text{SnCl} \quad (18.50)
   \end{align*}
   \]

2. Hydrolysis of the tetrahalides. Silane hydrolyzes in the presence of catalytic amounts of hydroxide. In contrast, methane, germane, and stannane do not hydrolyze even in the presence of large amounts of hydroxide ion.

3. Reaction of organolithium compounds with (C/H)₃/MH. Triphenylmethyl and triphenylgermane differ in their reaction with organolithium compounds from triphenylaluminum and triphenylstannane:

   \[
   \begin{align*}
   & \text{Ph}_3\text{CH} + \text{LiR} \rightarrow \text{LiCl} + \text{Ph}_3\text{H} \quad (18.51) \\
   & \text{Ph}_3\text{SiH} + \text{LiR} \rightarrow \text{LiH} + \text{Ph}_3\text{SiR} \quad (18.52) \\
   & \text{Ph}_3\text{GeH} + \text{LiR} \rightarrow \text{LiH} + \text{Ph}_3\text{GeH} \quad (18.53) \\
   & \text{Ph}_3\text{SnH} + \text{LiR} \rightarrow \text{LiH} + \text{Ph}_3\text{SnR} \quad (18.54)
   \end{align*}
   \]

4. Alternation in enthalpies of formation. There is a tendency for the enthalpies of formation of compounds of the Group IVA (14) elements to alternate from C-Si-Ge-Sn-Pb. Although closely related to the previous phenomena, this variation is also related to the "inert pair effect" and will be discussed further below.

The elements of Group IIIA (13) show similar properties, although, in general, the differences are not so striking as for Group IVA (14). It may be noted that the covalent radius of gallium appears to be slightly smaller than that of aluminium in contrast to what might have been expected. The first ionization energies of the two elements are surprisingly close (578 and 579 kJ mol⁻¹), and if the sum of the first three ionization energies is taken, there is an alternation in the series: B = 6887, Al = 5139, Ga = 5521, In = 5884, TI = 5488 kJ mol⁻¹.
19.16 Predict which way the following equilibrium will lie:

\[
\text{Hb} + \text{Hb(O}_2\text{)} \rightleftharpoons 2\text{Hb(O}_2\text{)}
\]

Explain.

19.17 Although sickle cell anemia causes problems in many organ systems, the chief cause of death of children with SCA is bacterial infection. Discuss.

19.18 Using the reduction emfs given in Appendix F, construct a Latimer diagram, complete with skip-step emfs for one-, two-, and four-electron reduction of oxygen to superoxide, peroxide, and hydroxide. Discuss the biological significance of these emfs. Recall that a living cell is basically a reduced system threatened by oxidizing agents. 157

19.19 Biochemists tend to speak of "dismutation reactions" such as:

\[
\text{H}^+ + 2\text{O}_2 \rightleftharpoons \text{H}_2\text{O}_2 + \text{O}_2
\]

that are catalyzed by superoxide dismutase. What term do inorganic chemists use for this phenomenon? What type of metal do you suppose is in superoxide dismutase?

19.20 Gray and coworkers158 have prepared copper(II) carboxypeptidase A, Cu\textsuperscript{II}CPA, and compared its spectrum, that of the enzyme with inhibitor present, and that of several other copper(II) complexes with nitrogen and oxygen ligating atoms. Some of these data together with the geometry about the copper ion are:

<table>
<thead>
<tr>
<th>Set of ligating atoms</th>
<th>Structure</th>
<th>(r_{max}) (\text{cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>N, N, N, N</td>
<td>Planar</td>
<td>19,200 - 19,600</td>
</tr>
<tr>
<td>N, N, O, O</td>
<td>Planar</td>
<td>14,100 - 17,500</td>
</tr>
<tr>
<td>N, N, O, O</td>
<td>Peptidic peptide</td>
<td>12,900 - 14,700</td>
</tr>
<tr>
<td>O, O, O, O</td>
<td>Planar</td>
<td>13,500 - 15,000</td>
</tr>
<tr>
<td>Cu\textsuperscript{II}CPA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N, N, O, O</td>
<td>?</td>
<td>12,340</td>
</tr>
<tr>
<td>Cu\textsuperscript{II}CPA\textsuperscript{0PP\textsuperscript{is}}</td>
<td>?</td>
<td>7</td>
</tr>
</tbody>
</table>

These are the four atoms in the coordination sphere of the copper(II) ion.

19.21 For simplicity the iron-oxygen interaction in myoglobin and hemoglobin (but not hemerythrin) was discussed in terms of neutral oxygen molecules binding to Fe\textsuperscript{II}. However, much of the current literature discusses these phenomena in terms of superoxo and peroxo complexes and one sees Fe\textsuperscript{II+}O\textsuperscript{-2}. Discuss what these formulations and terms mean, and describe the related consequences in terms of charges, electron spins, etc. 159

19.22 Using your knowledge of periodic relationships, predict which element might come closest to reproducing the behavior of molybdenum in nitrogenase. Recall that nitrogen fixation involves both complexation and redox reactions. 160

19.23 In order to study the function of oxygen binding by myoglobin and its effect on muscle function, Cole (Footnote 16) perfused an isolated muscle with hydrogen peroxide. Why did he do this?

19.24 Discuss each of the following situations:

a. One protein encountered in the manufacture and preservation of H\textsubscript{2}O\textsubscript{2} is its spontaneous decomposition:

\[
2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2
\]

which is exothermic (\(\Delta H = -196 \text{ kJ mol}^{-1}\)). To reduce this decomposition, copper ions are carefully excluded or chelated. 157

b. Nature’s protection against the destructive oxidative powers of H\textsubscript{2}O\textsubscript{2} are the enzyme catalase and peroxidase, both of which contain iron.

c. Superoxide, O\textsubscript{2}\textsuperscript{-}, is perhaps even more dangerous than hydrogen peroxide as an oxidant and free radical, though otherwise somewhat similar.

d. Superoxo dismutase contains both zinc and copper. Zinc may be replaced by Cu\textsuperscript{II} and Hg\textsuperscript{II} and the enzyme retains its activity; no substitution of copper with retention of activity has yet been found. Discuss. (Hint: You can displace this on several levels, from the most astute conjectures to a quantitative demonstration with numbers. Choose an appropriate level for your professor and attack the problem accordingly.)

e. Procaryotes have a primitive superoxo dismutase with a metal other than copper. Suggest possible metals. 157

19.25 If you did not work Problem 12.16 when you read Chapter 12, do so now.

19.26 PotOHs (\(K_w = 1.8 \times 10^{-15}\)) and PotOhs (\(K_w = 2.64 \times 10^{-18}\)) have sorbabilities unusual for water. If one can remember the exponents, one can “instantly” estimate the pH necessary to make a 1 M solution of Fe\textsuperscript{II} or Fe\textsuperscript{III}.

a. Explain. What are the approximate pHs of these solutions?

b. Calculate the exact pHs assuming local behavior.

19.27 Bezadorov cites several studies indicating reduced iron absorption during febrile illnesses. Frame a hypothesis for the unresponsiveness of such an effect. 157

19.28 Acid rain has been defined as any precipitation with a pH lower than 5.6. Why 5.6 instead of 7.0? Can you perform a calculation to reproduce this value?

19.29 Explain what effect acid rain would have on the condition of each of the following, and why:

a. The Taj Mahal, Agra, India

b. A limestone barn near Antietam Battlefield, Maryland, dating from the Civil War

c. The Karyatides, the Acropolis, Athens, Greece

156 Fridovich, I. Am. Sec. 1971, 63, 54.


The "Inert Pair Effect"

Among the heavier posttransition metals there is a definite reluctance to exhibit the highest possible oxidation state. Thus in Group IVA (14), Ti has a stable +2 oxidation state in addition to +4, and for lead the +2 oxidation state is far more important. Other examples are stable Ti (Group IVA, 13) and Br (Group VA, 15). These oxidation states correspond to the loss of the np electrons and the retention of the ns electrons as an "inert pair". It can readily be shown that there is no exceptional stability (in an absolute sense) of the ns electrons in the heavier elements. Table 18.3 lists the ionization energies of the valence shell ns electrons of the elements of Groups IVA (14) and IVA (15). Although the ns electrons are stabilized to the extent of ~300 kJ mol⁻¹ (3 eV) relative to the ns electrons, this cannot be the only source of the inert pair effect since the ns electrons of Ca and Ge have even greater ionization energies and these elements do not show the effect—the lower valence Ge(II) and Ge(III) compounds are obtained only with difficulty.

The pragmatic criterion of the presence or absence of an inert pair effect can be taken as the tendency (or lack thereof) for the following reaction to proceed to the right:

\[ Mn_2 → Mn_{n-2} + X_2 \]  

(18.55)

We might then inquire as to the systematic variation in thermodynamic stability of the higher and lower halves of these elements. There seem to be two general effects operating. The combination of the two effects gives irregular changes in covalent bond energies (see Table 18.4). The simplest is the tendency for weaker covalent bond formation by larger atoms (see Chapter 9). The second is the "anomalous" properties of those elements that follow the first filling of a given type of orbital (s, p, d, f, ...). Among the heavier posttransition metals there is a definite reluctance to exhibit the higher oxidation states. For example, the +4 oxidation state is far more important in lead than in tin (Group IIIA, 13) and Bi (Group IVA, 14). The combination of the two effects gives irregular changes in covalent bond energies. There seem to be two general effects operating. The combination of the two effects gives irregular changes in covalent bond energies (see Table 18.4). The simplest is the tendency for weaker covalent bond formation by larger atoms (see Chapter 9). The second is the "anomalous" properties of those elements that follow the first filling of a given type of orbital (s, p, d, f, ...). Among the heavier posttransition metals there is a definite reluctance to exhibit the higher oxidation states. For example, the +4 oxidation state is far more important in lead than in tin (Group IIIA, 13) and Bi (Group IVA, 14).

Periodic Anomalies of the Nonmetals and Posttransition Metals

Relativistic Effects

Normally the theoretical basis of chemistry is the nonrelativistic Schrödinger equation. To this are added the postulates of electron spin and ideas related to it such as the Pauli exclusion principle. Although the latter are thus seemingly ad hoc "add-ons" to make the work theory, most of the theoretical chemistry has been done on this basis. The corresponding relativistic approach yields the Dirac equation. This gives four quantum numbers directly, although only the principal quantum number n is the same in both treatments. The relativistic treatment results in a number of novel effects, both descriptive and theoretical, some of which can usually be neglected with little loss of accuracy and a great gain in convenience. There are two exceptions to this generalization however. One is spin-orbit coupling (see Chapter 11 and Appendix C). The second is that neglect of relativistic effects becomes increasingly serious as the atomic number increases. The first and to a slightly lesser extent, p electrons will accelerate greatly as they approach the nucleus, and their speed relative to the fixed speed of light cannot be ignored. It has been estimated that for mercury (Z = 80) the speed of a 1s electron is over half that of light. This results in an approximately 20% increase in electron mass and an approximately 20% decrease in orbital size. In the simplest case we can say that s and p orbitals will contract, and that d and f orbitals will expand somewhat. The seeming paradox that the d and f orbitals expand instead of contract in an "inert pair effect" is largely a postdictive effect. Direct relativistic effects on d and f orbitals are small because these orbitals do not have electron density near the nucleus. However, the

<table>
<thead>
<tr>
<th>Element</th>
<th>p&lt;sub&gt;5&lt;/sub&gt; + p&lt;sub&gt;6&lt;/sub&gt;</th>
<th>p&lt;sub&gt;5&lt;/sub&gt; + p&lt;sub&gt;5&lt;/sub&gt;</th>
<th>p&lt;sub&gt;5&lt;/sub&gt; + p&lt;sub&gt;6&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>6.687 (65.1)</td>
<td>C</td>
<td>10.803 (124)</td>
</tr>
<tr>
<td>Al</td>
<td>4.561 (67.2)</td>
<td>Si</td>
<td>7.387 (78.5)</td>
</tr>
<tr>
<td>Ca</td>
<td>4.542 (67.2)</td>
<td>Ge</td>
<td>7.712 (79.9)</td>
</tr>
<tr>
<td>In</td>
<td>4.726 (69.5)</td>
<td>Sn</td>
<td>8.673 (77.2)</td>
</tr>
<tr>
<td>TI</td>
<td>4.869 (70.4)</td>
<td>Pb</td>
<td>9.165 (64.9)</td>
</tr>
</tbody>
</table>

Table 18.4

| Bond energies of some group IVA (14) halides in kJ mol⁻¹ (kcal mol⁻¹) |
|----------------|----------------|----------------|----------------|
| Element | M^2⁺ | M⁺ | M²⁻ | | |
| Sn       | 665 (152) | 381 (91) | 316 (79) | 221 (53.9) |
| Ge       | 481 (115) | 432 (108) | 383 (92.0) | 349 (83.4) | 326 (77.8) | 276 (66.0) | 264 (63.2) | 213 (50.6) |
| Sn       | 481 (115) | 414 (98.9) | 386 (92.2) | 323 (77.2) | 329 (78.7) | 273 (65.2) | 262 (62.5) | 201 (48.0) | 195 (49.0) | 142 (33.9) |

For the lighter elements these effects can readily be formulated in terms of ordinary shielding effects as discussed in Chapter 2. For heavier elements, however, the theory of relativity must be invoked.

2 Some of these, such as the fact that gold metal has its familiar color and that mercury metal is a liquid, fall outside the scope of this text. See Pytkovitch, F.; Desclaux, J.-P.; Adv. Chem. Res. 1979, 12, 276-281. Others will be discussed below.
3 Some of these are: Although the quantum number n still determines orbital type, p, d, f, . . ., it no longer determines orbital shape. All orbitals of given value of n and l no longer have the same energy. Orbital shape is determined by the angular momentum quantum number j; and the magnetic quantum number m. The shapes of orbitals are not the familiar ones given by the Schrödinger equation, but scientifically "redefined" molecular analogs. See McKee, D. R.; J. Chem. Educ. 1983, 60, 113-116; Powell, R. E.; Ibid. 1968, 45, 558.
4 This is most readily seen from the inverse relationship between Bohr radius and mass (m = $4\pi\varepsilon_0\varepsilon_n^2$).
We may thus end this chapter on bioinorganic chemistry and this book on modern inorganic chemistry by noting that a complex that Werner could have synthesized a century ago (and resolved a short time later) is being used to answer questions that neither he nor his contemporary biologists could have conceived.

Summary

It is true that many of the facts in this chapter were gathered by biologists, biochemists, and X-ray crystallographers, not only by inorganic chemists. But the interpretation of these facts and their further exploration falls within the realm of inorganic chemistry. Such factors as (1) attention of ends by complexation; (2) stabilization of complexes by ligand field effects; (3) hardness and softness of acids and bases; (4) the thermodynamics and kinetics of both "natural" and "unnatural" (i.e., polynuclear) species; (5) catalysis by metal ions; (6) preferred geometry of metal complexes; and (7) energetics of (a) complex formation, (b) redox reactions, and (c) polymerization formation come within the ken of inorganic chemists, and they should be able to contribute fully to the future study of these systems. The effect is already being felt. One need only compare a recent biochemistry text with one of a decade ago to note the emphasis on high spin vs. low spin metal ions, coordination geometry and configurational, and redox reactions and thermodynamics.

The present convergence of physical and analytical techniques combined with inorganic theory makes this one of the most exciting times to be involved in this area of chemistry. One can combine the hard facts and principles of our discipline with the ever elusive yet fascinating mystery of life.

Postscript

"I say that it touches a man that his blood is sea water and his tears are salt; that the seed of his loins is scarcely different from the same cells in a seaweed, and that of the stuff like his bones are coral made. I say that physical and biologic law lies down with his mental conclusions, and that a man who goes in no consciousness of them is a drifter and a dreamer, without a home or any contact with reality."'142

Donald Culross Peattie

Problems

19.1 Why was the covalent radius of the metal used on page 891 instead of that of the +2 ion?

19.2 Why are transition metals such as Mn, Fe, Co, and Cu needed in photosynthesis and respiration rather than metals such as Zn, Ga, or Ca?

19.3 Calculate the energy available from one photon of light at wavelength 700 nm. If it generates a potential difference of 1.0 V, what is the conversion efficiency?

19.4 Discuss how the use of simple model systems can aid our understanding of biochemical systems. Is there any way they might detract?144

19.5 There are two ways in which photosynthesis increases the energy available: (1) by using two light capturing mechanisms, PS I and PS II; (2) by stacking the chlorophyll in the grana which are in turn stacked in the chloroplast (see Lehninger, A. L. Sci. Am., September, 1961, for the structures). Which corresponds to hooking batteries in parallel and which to hooking them in series?

19.6 Common ions in enzyme systems that have low site preference energies (from LPSQ) such as Co$^{2+}$, Zn$^{2+}$, and Mn$^{2+}$ rather than Fe$^{2+}$, Ni$^{2+}$, or Cu$^{2+}$ Discount this phenomenon in terms of the entatic hypothesis.145

19.7 Discuss the probable difference in the pockets present in carbamoylase and carbamoyl hydrolase.

19.8 The toxicity of metals has been variously correlated with their (1) electronegativity; (2) insolubility of the sulfides; (3) stability of chelates. Discuss.

19.9 Show how coordination of an O$_2$ molecule to a heme group can result in pairing of the electron on the oxygen molecule when the bonding is a. through a μ bond

b. through a lone pair of our oxygen atom

19.10 Directions for the use of the antibiotic tetracycline advise against drinking milk or taking antacids with the medication. In addition, warnings are given concerning its use (teeth may be stained in certain cases). Discuss the chemical property of tetracycline that may be involved in these effects.

19.11 High mercury levels in terminal food chain predators like tuna fish have caused considerable worry. It has been found that tuna contain larger than average amounts of selenium.146 Discuss the possible role of selenium with respect to the presence of mercury.147

19.12 Although the hypothesis of Eganii may be an oversimplification, it is certainly true that Fe$^{3+}$/Fe$^{2+}$ is widely used in redox systems, Zn$^{2+}$ in hydrolysis, esenicolin, and similar reactions, and molybdenum in nitrogenase, xanthine oxidase, nitrate reductase, etc. Pairing abundance aside, discuss the specific chemical properties of these metals that make them well suited for their tasks.

19.13 Carbamoylase (AcO$^{2-}$) not only retains the activity of carbamoylase (AcO$^{2-}$). It is actually a more active enzyme. This being the case, why do you suppose that Co$^{2+}$ is not used in the natural systems?

19.14 If you did not answer Problem 14.59 when you read Chapter 14, do so now.

19.15 When patients are treated with D-penicillamine for scleroderma, cystinuria, rheumatoid arthritis, and idiopathic pulmonary fibrosis, 30% show decreased taste acuity (hypogeusia). In contrast, only 4% of the patients being treated with D-penicillamine for Wilson's disease exhibit hypogeusia. Discuss a possible mechanism. Might the hypogeusia be treated?148

19.16 Common ions in enzyme systems are those that have low site preference energies (from LPSQ) such as Co$^{2+}$, Zn$^{2+}$, and Mn$^{2+}$ rather than Fe$^{2+}$, Ni$^{2+}$, or Cu$^{2+}$ Discount this phenomenon in terms of the entatic hypothesis.145

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142 Peattie, D. C. An Almanac for Moderns; Nonpareil: Boston, 1909; p 14.


144 Peattie, D. C. An Almanac for Moderns; Nonpareil: Boston, 1909; p 14.


146 Peattie, D. C. An Almanac for Moderns; Nonpareil: Boston, 1909; p 14.


increased shielding of d and f orbitals by relativistically contracted z and p orbitals tends to cancel the effect of increased Z. Therefore, the s and p electrons are moved closer to the nucleus, their energy is lowered (made more negative), and they are stabilized. The d and f orbitals are raised in energy (detranslated) and expand. Since the outermost orbitals are the ns and np rather than the (n − 1)d or (n − 2)f, each atom as a whole contracts. 33

The relativistic effect goes approximately as Z 2, and this is the reason for its importance in the heavier elements. In terms of energy and size, it starts to become important in the vicinity of Z = 60−70, contributing perhaps an additional 10% to the nonrelativistic first-row contraction (see Chapter 13). 34 As we have seen, this results in an almost exact cancellation of the expected increase in size with increase in Z from zirconium to hafnium.

While the contraction resulting from the poor shielding of 4f electrons ceases at hafnium, the relativistic effect continues across the sixth row of the periodic table. It is largely responsible for the stabilization of the 5f orbital and the more z 2 electron effect shown by the elements Hg–Bi. It also stabilizes one of the 6p orbitals of bismuth, allowing the unusual +1 oxidation state in addition to +3 and +5. 35

Many introductory chemistry books give simple rules for remembering the periodic changes of ionization energies and electron affinities. The rules usually follow some modification of the “ionization energies and electron affinities increase as one moves to the right in the periodic chart; they decrease as one moves from the top to the bottom.” 36 These generalizations, as well as the shielding rules that account for the atomic behavior, were discussed in Chapter 2, along with some of the exceptions. Unfortunately for simplicity, the exceptions are somewhat more numerous than is generally realized. Many of the problems discussed in the preceding sections result from these exceptions.

The horizontal behavior of atoms follows the general rule with good regularity as might be expected from adding a single proton at a time with expected monotonic changes in properties. We have already seen the exception of the inversion of ionization potentials of the VA (15) and VIA (16) groups related to the stability changes in properties. We have already seen the exception of the inversion of the “exceptions.”

The vertical exceptions to the generalizations are much more widespread: If we count every time that a heavier element has a higher ionization potential or higher electron affinity than its next lighter congeners, we find that about one-third of the elements show “ionization energy anomalies.” 37 With such a high fraction of exceptions, one wonders why the rules were formulated as they were originally. The answer seems to lie in the lack of data available until recently: most of the good data were for familiar elements, such as the alkaline metals and the halogens. For these main-group elements, with the exception of the lower electron affinity of fluorine resulting from electron-electron repulsion (and paralleled by oxygen and nitrogen), the rules work fairly well; however, the poorer shielding of d and f electrons upset the simple picture. For the transition metals, higher ionization energies with increasing atomic number in a group are the rule, not the exception. As we have seen, in the preceding discussion, this carries over somewhat into the p-block elements, causing some of the problems associated with families IIA (13) and IVA (14).

The increased ionization energies of the heavier transition metals should not be unexpected by anyone who has had a modicum of laboratory experience with any of these elements. Although none of the coinage metals is very reactive, gold has a well-deserved reputation for being less reactive than copper or silver; 38 iron, cobalt, and nickel rust and corrode, but osmium, iridium, and platinum are noble and unreactive and therefore are used in jewelry: platinum wires are the material of choice for flame tests without contamination; and one generates hydrogen with zinc and simple acids, not with mercury.

Although the increased electron affinity associated with the heavier elements usually manifests itself only indirectly (via electronegativity, etc.), it is directly responsible for the fact that cesium iodide, CsI, an ionic salt rather than an alloy, both the increased ionization energy and increased electron affinity in these elements result from relativistic effects.

We have seen the use of macrocyclic ligands to aid in the isolation of auride salts (Chapter 12). The characterization of this unusual oxidation state, both [Cs(C222)Au] and Cs2Au, was accomplished by the use of photodetector spectroscopy (Chapter 5). When the binding energy of gold d electrons is plotted as a function of the formal oxidation state of gold (0, +1, +2, +3), a straight line is obtained (Fig. 18.8). The fact that Cs2Au lies on this line at a point corresponding to an oxidation state of −1 is good evidence for the formation of the auride, Au−. 39

In the same way, the 195Au Mossbauer spectrum of Cs2Au is very similar to that of [Cs(C222)Au] (Chapter 12), indicating that the Au− anion is present in both (Fig. 18.9). Since the Mossbauer effect is a nuclear one, it is very sensitive to electron density at the nucleus and therefore to both atomic charge and electron density.

Gold exhibits other interesting anomalies. For example, some AuII compounds with an unexpected coordination number of two (Chapter 12) or a filled core of 5d10
Metal Complexes as Probes of Nucleic Acids

The coordination of cis-diammineplatinum(II) to guanine bases in DNA is only one example of a large number of possibilities. The Mg$^{2+}$ ion has several important functions with respect to DNA and RNA structure and action. Nature has also anticipated the chemist through the use of "zinc finger" proteins, which coordinate tetrahedrally to a zinc atom by two cysteines and two histidines and provide specific structural information for site recognition on DNA.

Transition metal complexes may be used to probe specific sites on DNA and RNA chains. Such interactions may yield information concerning the structure at those sites or may induce specific reactions at them. Only one example will be given here. DNA helices are chiral. They would thus be expected to interact with chiral metal complexes in an enantioselective manner. This is illustrated in Fig. 19.32. The intercalation of the A enantiomer of tris(o-phenanthroline)ruthenium(II) into the right-handed helix of B-DNA is more favorable than that of A-(Ru(phen))$_3^2+$. This is a necessary result of the interaction of the "right-handed" ligands with the right-handed helical groove of the DNA. Obviously the chirality of the metal complex is predominant in its interaction with the DNA. We can expect further progress in the use of such enantioselective probes.

\[ \text{Fig. 19.31 (a) Structure of the cis-[P(t)(d(pGpG)) = guanine} \]

Chloride ion concentration of only 4 mM: Hydrolysis and subsequent reactions with the appropriate biological targets can then readily take place. An interesting aspect of the chemotherapeutic use of cis-diamminechloplat-nium(II) and related drugs consists of some negative side effects including nephrotoxicity. They are thought to be the result of the inactivation of enzymes by coordination of Pt(II), like Hg(II), to thiol groups. Application of the ideas of HSAB theory would suggest the protection of these thiols by the use of competitive "rescue agents" that have soft sulfur atoms. These include the diethyldithiocarbamate, $\text{Et}_2\text{NCS}_2^-$, and thiosulfate, $\text{Si}_2\text{O}_2^-$, ions.

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\[ \text{Fig. 19.32 Illustration of } \text{[Ru(phen)}_3^2+ \text{] enantiomers bound by intercalation to B-DNA. The } A \text{-enantiomer (right) fits easily into the right-handed helix, since the auxiliary ligands are oriented along the right-handed groove. For the } A \text{-enantiomer (left), in contrast, steric interference is evident between the auxiliary phenanthroline ligands and the phosphate backbone, since these left-handed enantiomers the auxiliary ligands are disposed contrary to the right-handed groove. [From Barton, J. K.; Danishefsky, A. T.; Goldberg, I. M. J. Am. Chem. Soc. 1994, 106, 2172-2176. Reproduced with permission.]} \]
Fig. 18.8 Binding energies of the Au (4f7/2) levels of gold atoms in various oxidation states. Note that the value for RbAu and CsAu corresponds to that expected for an -1 oxidation state. [From Knecht, J.; Fischer, R.; Overhof, H.; Honsel, F. J. Chem. Soc., Chem. Commun. 1978, 906. Reproduced with permission.]

Fig. 18.9 A comparison of the chemical shifts in the 197Au Mössbauer spectra of CsAu and [Cu(C22H3)2]Au⁺.

Fig. 18.10 Two examples of Au(I)-Au(III) interactions, (a) Intramolecular, Au–Au = 300 pm; (b) Intermolecular, Au–Au = 344 pm. See Table 18.5 for identification of compounds. [From Schmidbaur, H.; Graf, W.; Müller, G. Angew. Chem. Int. Ed. Engl. 1988, 27, 117-149; Schmidbaur, H.; Weidenhiller, G.; Steigelmann, O.; Müller, G. Chem. Ber. 1990, 123, 285-287. Reproduced with permission.]

Table 18.5

<table>
<thead>
<tr>
<th>Some examples of Au(I)-Au(III) interactions at less than the expected distance of van der Waals contacts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
</tr>
<tr>
<td>[Cu(C22H3)2]Au⁺</td>
</tr>
<tr>
<td>M₃[PP₃(CH₂)₃AuCl]₃ (Fig. 18.10a)</td>
</tr>
<tr>
<td>[P₆S₆]⁺[Au₁(C₂H₄)Cl]₄</td>
</tr>
<tr>
<td>[2.4-6-(Bu)₂C₆H₄]₂AuCl₄ (Fig. 18.10b)</td>
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</tbody>
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<table>
<thead>
<tr>
<th>Au–Au [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intra-</td>
</tr>
<tr>
<td>Inter-</td>
</tr>
</tbody>
</table>

| 279.6 Å |
| 300.6 Å |
| 316.6 Å |
| 361.6 Å |

* See Footnote 47(a).
* See Footnote 47(b).
* See Footnote 47(c).
* See Footnote 47(d).


Chelate Therapy

We have seen previously that chelating agents can be used therapeutically to treat problems caused by the presence of toxic elements. We have also seen that an essential element can be toxic if present in too great a quantity. This is the case in Wilson's disease (hepatocutaneous degeneration), a genetic disease involving the builiding of excessive quantities of copper in the body. Many chelating agents have been used to remove the excess copper, but one of the best is 8-penicillamine, HSO(CH₂)₂CHNHNH₃COOH. This chelating agent forms a complex with copper ions that is colored an intense purple and, surprisingly, has a molecular weight of 2600. Another surprising finding is that the complex will not form unless chloride or bromide ions are present and the isolated complex always contains a small amount of halide. These puzzling facts were explained when the X-ray crystal structure was done. The structure (Fig. 19.30) consists of a central halide ion surrounded by eight copper(I) atoms bridged by sulfur ligands. These are in turn coordinated to six copper(II) atoms. Finally, the chelating amino groups of the penicillamine complete the coordination sphere of the copper(II) atoms.

As we have seen, the body has essentially no means of eliminating iron, so an excessive intake of iron causes various problems known as siderosis. Chelating agents are used to treat the excessive buildup of iron. In many cases the chelates resemble or are identical to the analogous compounds used by bacteria to chelate iron. Thus desferroxamine B is the drug of choice for African siderosis. The ideal chelating agent will be specific for the metal to be detoxified since a more general chelating agent is apt to cause problems by altering the balance of other essential metals. The concept of hard and soft metal ions and ligands can be used to aid in this process of designing therapeutic chelators. A slightly different mode of therapy involves the use of cis-diaminedichloroplatinum(II), Pt(NH₃)₂Cl₂, and related binuclear complexes in the treatment of cancer. The exact action of the drug is not known, but only the cis isomer is active at low concentrations, not the trans isomer. It is thought that the platinum binds to DNA, with the chloride ligands first being replaced by water molecules and then by a DNA base such as guanine. Studies in vitro with nucleotide bases as well as in vivo studies on DNA support the hypothesis that the most important interaction is intrastand base pairing of two adjacent guanine bases on the DNA chain by the platinum atom (see Fig. 19.31). The trans isomer can bond to groups about 400 pm apart that approach the platinum atom from opposite directions, and it is chemotherapeutically inactive. The binding of cisplatin to DNA would seriously interfere with the ability of the guanine bases to undergo Watson-Crick base pairing. Thus when a self-complementary oligomer (a portion of a DNA chain) reacts with the cis isomer, two adjacent guanines are bound and Watson-Crick base pairing is disrupted.

For cis-diaminedichloroplatinum(II) to work according to the proposed mechanism, it must hydrolyze in the right place: if it hydrolyzes in the blood before it gets to the chromosomes within the cell, it will be more likely to react with a non-target species. Fortunately for the stability of the complex, the blood is approximately 0.1 M in chloride ion, forcing the hydrolysis equilibrium (Eq. 19.40) back to the chloro complex. Once the drug crosses the cell membrane into the cytoplasm, it finds a...
Alternation of Interactions

Some further examples of Table 18.6, Nonmetals

Electronegativities

Group IB (11) metal-metal interactions may not be stated in terms of an increased electronegativity in group IB (11) metal-metal interactions. In the same way, it has been suggested that the heavier member of each family, thallium, lead, perhaps bismuth, has a greater electronegativity than its lighter congeners.

According to the periodic chart, the inorganic chemist's single most powerful weapon when faced with the problem of relating the physical and chemical properties of over 100 elements. In addition to knowing the general trends painted in broad brush strokes by the simple rules, the adept chemist should know something of the "fine structure" that is not act as "good" core electrons but mix with low lying excited states. To rationalize, if not truly explain, one can consider promotion of electrons from the 5d° configuration and their involvement in the bonding.

Schmiderbacher's group 57 has synthesized some gold(I) compounds with unusual coordination numbers for small nonmetals. For example, the "hedgehog cation," [CuAu(PR)₃]⁺, has carbon with the unusual covalency of six (Fig. 18.11). While carbon has no low energy orbitals, there is nothing to prevent it from forming s₅p(2s) and s₅p(2p) MOs and forming three-center bonds. So why should it do so in this compound and never in "organic chemistry"? Ordinarily the better overlap of hybridized sp³ carbon orbitals ensures carbon's tetracovalency. Perhaps the possibility of a dozen Au(I)—Au(I) aurophilic bonds could provide another 300—400 kJ mol⁻¹, commensurate with the energy of a C—C bond, compensating for weaker C—Au bonding.

We have seen above the unusual properties of the nonmetals following the first row of transition metals. This is usually described as "a reluctance to exhibit maximum oxidation state," but it may also be stated in terms of an increased electronegativity in these elements. Indeed, gallium, germanium, arsenic and perhaps selenium seem to have higher electronegativities than their lighter congeners.

In the same way, it has been suggested that the heavier member of each family, thallium, lead, perhaps bismuth, has a greater electronegativity than its lighter congeners.

c) isoelectronic plus an inert pair with [e.g., THI], Pb(II)⁹ the gold(I) atom. Some examples are listed in Table 18.6. The number of these bonds is limited, but the subject is still a very new one.

The general tendency for atoms (including other gold atoms) to exhibit greater than expected valences toward gold atoms is often termed aurophilicity. This is a useful descriptive name for a bonding behavior that is not completely understood. It appears to result from relativistic effects and the fact that the gold 5d⁹ electrons do not act as "good" core electrons but mix with low lying excited states. To rationalize, if not truly explain, one can consider promotion of electrons from the 5d⁹ configuration and their involvement in the bonding.

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Conclusion

The periodic chart is the inorganic chemist's single most powerful weapon when faced with the problem of relating the physical and chemical properties of over 100 elements. In addition to knowing the general trends painted in broad brush strokes by the simple rules, the adept chemist should know something of the "fine structure" that is at the heart of making inorganic chemistry diverse and fascinating.

Problems

18.1 Compare Figs. 16.16 and 16.17. The difference in P—O bond lengths in P₂O₅ is 139 — 144.1 = 17 pm (1%), but the difference in the P—S bonds in P₂S₅ is only 309 — 306 = 13 pm (0.4%). Explain.

18.2 With regard to nuclear engineering, the separation of zirconium and hafnium has been of considerable interest because of the low neutron cross section of zirconium and the high neutron cross section of hafnium. Unfortunately, the separation of these two elements is perhaps the most difficult of any pair of elements. Explain why.
name "scouring rushes." Some Protozoa (radiolarians), Gastropoda (limpets), and Porifera (glass sponges) employ silica as a structural component. Silicon is an essential trace element in chicks and rats\(^{131}\) and is probably necessary for proper bone growth in all higher animals.

The third type of compound used extensively as a structural component is apatite, \(\text{Ca}_3(\text{PO}_4)_2X\). Hydroxyapatite \((X = \text{OH})\) is the major component of bone tissue in the vertebrate skeleton. It is also the principal strengthening material in teeth. Partial formation of fluorapatite \((X = \text{F})\) from application of fluorides strengthens the structure and causes it to be less soluble in the acid formed from fermenting organic material, hence a reduction of caries. Fluorapatite is also used structurally in certain Brachiopod shells.

### Medicinal Chemistry

#### Antibiotics and Related Compounds

The suggested antibiotic action of transferrin is typical of the possible action of several antibiotics in tying up essential metal ions. Streptomycin, aspergillic acid, usnic acid, the tetracyclines, and other antibiotics are known to have chelating properties. Presumably some antibiotics are delicately balanced so as to be able to compete successfully with the metal-binding agents of the bacteria while not disturbing the metal processing by the host. There is evidence that at least some bacteria have developed resistance to antibiotics through the development of altered enzyme systems that can compete successfully with the antibiotic.\(^{132}\) The action of the antibiotic need not be a simple competitive one. The chelating properties of the antibiotic may be used in metal transport across membranes or to attach the antibiotic to a specific site from which it can interfere with the growth of bacteria.

The behavior of valinomycin is typical of a group known as "ionophore antibiotics."\(^{133}\) These compounds resemble the crown ethers and cryptates (Chapter 12) by having several oxygen or nitrogen atoms spaced along a chain or ring that can wrap around a metal ion (Fig. 19.29a). These antibiotics are useless in humans because they are toxic to mammalian cells, but some of them find use in treating coccidiosis in chickens. The toxicity arises from the low-transporting ability. Cells become "leaky" with respect to potassium, which is transported across the cell membrane by valinomycin. In the absence of a metal ion, valinomycin has a quite different conformation (Fig. 19.29b), one stabilized by hydrogen bonds between amide and carbonyl groups. It has been postulated\(^{134}\) that the potassium ion can initially coordinate to the four free carbonyl groups (A) and that this can provide sufficient stabilization to break two of the weaker hydrogen bonds (B). This provides two additional carbonyl groups to coordinate and complete the change in conformation to that shown in Fig. 19.29a. Such a stepwise mechanism would indicate that the whole system is a balanced one and that the reverse process can be readily triggered by a change in environment such as at a membrane surface or if there is a change in hydrogen binding competition.


The tetracyclines form an important group of antibiotics. The activity appears to result from their ability to chelate metal ions since the extent of antibacterial activity parallels the ability to form stable chelates. The metal in question appears to be magnesium or calcium since the addition of large amounts of magnesium can inhibit the antibiotic effects. In addition, it is known that in blood plasma the tetracyclines exist as calcium and magnesium complexes.\(^{133}\)

18.3 Carbon tetrachloride is inert towards water, but when trichloride is hydrolyzed in moist air, 
suggest a reason.
18.4 Below are some conclusions that an average general chemistry student might have after reading about the periodic table in a general chemistry textbook. Write each statement to clarify possible 
mechanisms (if any).
  a. Electron affinities increase toward the upper right of the periodic table.
  b. Ionization energies decrease toward the bottom of the table.
  c. Atomic radii increase toward the bottom of the table.
  d. Atomic radii decrease toward the right of the table.
  e. Electronegativity decreases toward the left and toward the bottom of the table.

18.5 Gallium dichloride, GaCl₂, is a diamagnetic compound that conducts electricity when 
fused. Suggest a structure.

18.6 If a major break through in nuclear synthesis were achieved, two elements that are hoped 
for are those with atomic numbers 114 and 164, both congeners of lead. Look at the extended periodic table in Chapter 14 and suggest properties (such as stable oxidation states) for these two elements. How do you suppose their electronegativities will compare with those of the other Group 1VA (14) elements?²⁴

18.7 The small F—S—F bond angles in P₄S₄N can be rationalized by 
  a. Born’s rule
  b. Gillespie-type VSEPR rules
  c. Bent bonds
Discuss each and explain their usefulness (or lack thereof) in the present case.

18.8 Either look up the article by Chen and Wentworth;²⁵ or plot the electron affinities from 
Table 2.5 onto a periodic chart. Discuss the reasons for the “exceptions” that you observe.

18.9 Write the first ionization energies from Table 2.3 on a periodic chart. Discuss the reasons 
for the “exceptions” that you observe.

18.10 On page 860 the statement is rather casually made that “R₂Ge, R₂Sn, and R₂Pb exist as 
diamagnetic monomers in solution.” What experiments must an inorganic chemist per¬
	form to substantiate these statements?

18.11 The compound R₂Ge, shown on page 860 is diamagnetic. Draw out the most reasonable 
electronic structure for it, and compare it with the geometric structure. Discuss.

18.12 Lithium carbonate is often administered orally in the treatment of mania or depression or 
Sn shown on page 863 is diamagnetic. Draw out the most reasonable 
electronic structure for it, and compare it with the geometric structure. Discuss.

18.13 Zinc is a much more reactive metal than cadmium, as expected from the discussion on 
page 877. Yet both are used to protect iron from rusting. How is this possible?

18.14 Of the five data points in Fig. 18.8, that of AuCH₂⁻ is the most poorly. Suggest a possible reason.

18.15 The simplest relationship between electronegativity and dipole moments is a linear one: 
The greater the difference in electronegativity, the greater the dipole. How can you 
reconcile this with the N—O and F—O dipoles cited in this chapter (page 889)?

18.16 The P₄O₆ molecule in white phosphorus has extremely strained bonds. The bond angles in 
the T₂ molecule are only 90°. Therefore the bonds are weaker, only 20.1 kJ/mol for each 
one. The total bond energy of two moles of P₄O₆ is 244 kJ less than that 
of one mole of P₄O₆ (159 kJ). Appendix E in contrast, the total bond energy of two moles of 
N₂ has been calculated²⁶ to be 777 kJ greater than that of one mole of N₂ (a hypothetical 
tetrahedral molecule isomeric with P₄O₆).
  a. Explain the disparity of bond energies of these isoelectronic and isomorphic 
molecules.
  b. If you could manufacture N₂ and keep it as a metastable material, could you think of any 
uses for it?

18.17 Footnote 33 suggests that a reluctance to exhibit maximum oxidation state may be 
equivalent to an increased electronegativity in the post-transition elements. Discuss.

18.18 Either look up the data points in Fig. 18.8, that of AuCH₂⁻PCH₂⁻AuCH₂⁻PCH₂⁻. It’s most 
poorly. Suggest a possible reason.

18.19 Assuming that C₅A₅ is ionic, what is its most probable structure? Estimate an enthalpy of 
formation for it.

18.20 Two variables affecting the isomer shift in Mössbauer spectroscopy are the character 
of the orbitals involved and the partial charges on the atom being studied. Explain this 
phenomenon chemically, i.e., in terms of how these two quantities affect the electron 
density at the nucleus.

18.21 Despite the half-century history of Scaborg’s hypothesis with respect to the placement of 
the lanthanides and actinides in the periodic table, many bench chemists proceed success¬
fully with the working hypothesis that uranium is a congener of molybdenum and tung¬
sten. Does this indicate that Seaborg is wrong? That the bench chemists are wrong? 
Discuss.

18.22 How many parallels can you find between [Fe(CO)₅]⁻ and [Au(CH₂)₅Cl]⁻?²⁷ (Figs. 15.21c and 18.11) that contribute to the unusual hexacoordinate 
carbon atom?

18.23 Explain the electronic and structural changes involved in the following reaction:

Chemistry of the Actinide Elements; Katz, J. J.; Mana, L. R.; Seaborg, G. T., Eds.; Chapman and 
Hall: New York, 1986. See also Footnote 31.
²⁵ See Footnote 42.
²⁶ See Footnote 13.
Adaptations to Natural Abundances

When the abundance of an element is unusually high or unusually low, organisms develop mechanisms to handle the stress. The first documented examples were the presence of “indicator species” (plants) that grow where soils contain an unusually high concentration of a metal. For example, the sea pink, *Armeria maritima*, has been used in North Wales as an indicator of copper deposits. In one extreme case, the drainage from the copper deposits has concentrated in a bog to an extent of 20,000–20,000 ppm, and the sea pink thrives. Closely related is the adaptation of various plants to exceptionally high concentrations of various heavy metals in mine dumps and tailings. Not only have some species adapted to extremely high concentrations of normally toxic metals, but they have also evolved a high level of self-fermentation to prevent pollination and gene exchange with nearby populations that are not metal tolerant.

Some of the chemolithotrophic bacteria discussed earlier in this chapter illustrate these ideas. In undisturbed habitats their habitat is extremely restricted. During the process of mining, however, large surfaces of the appropriate metal sulfide are created and oxidized both in the mine and in the tailings with resultant leaching. This creates a favorable habitat for exploitation by the bacteria. One unfavorable result is the lowering of the pH and the solubilization of metals, usually toxic, into the drainage system. On the other hand, the isolation and selection of productive strains from such sites, and their controlled application, may lead to useful biometallurgical methods of extraction of metals from low-grade ores (see Chapter 10).

The hydrothermal vents discussed previously provide a parallel, natural environment with unusually large amounts of various metals—iron, copper, zinc—dissolved from the crustal rocks by the superheated water. It will be of interest to learn how the animals in the hydrothermal ecosystem have developed mechanisms to avoid toxicity from these metals. Another source of possible toxicity, hydrogen sulfide, is of somewhat better understood. Hydrogen sulfide is comparable to the cyanide ion in its toxicity towards respiration. The vent organisms have evolved a variety of mechanisms to prevent sulfide toxicity. One of the more interesting is that of the tube worm, *Riftia pachyptila*. Its hemoglobin has a molecular weight of about two million, with an extremely high affinity for dioxygen (recall that the vent waters are anoxic) and a second, high-affinity site to bind sulfide. This second site serves the dual purpose of protecting the tube worm’s cytochrome c oxidase from sulfide poisoning and protecting the sulfide from premature oxidation. Instead, both the dioxygen and sulfide are transported to symbiotic bacteria that metabolize them to drive the synthesis of ATP, protecting the tube worm’s cytochrome c oxidase from sulfide poisoning and preventing the sulfide from premature oxidation. Instead, both the dioxygen and sulfide are transported to symbiotic bacteria that metabolize them to drive the synthesis of ATP and carbohydrates.

At the other extreme are adaptations to very low concentrations of a particular element. We have already seen mechanisms directed towards the sequestration of iron when it is present in small amounts. The ability to detect extremely small amounts of an element can be a useful adaptation for an animal if that element is important to it. For example, hermit crabs recognize shells suitable for occupation not only by tactile stimuli but apparently also by the minute amount of calcium carbonate that is dissolved in the water around a shell. They can readily distinguish natural shells (CaCO₃, calcium-bearing replicas (Ca₂SiO₅), and naturally containing calcium minerals (calcite, aragonite, and gypsum) from non-calcium minerals (einsteinite, SrSO₄, rhodochoerite, MnCO₃, siderite, FeCO₃, and quartz, SiO₂). Inasmuch as the solubility product of calcium carbonate is only 10⁻¹₀, the concentration of calcium detected by the hermit crab is of the order of 4 ppm or less. Almost nothing is known about the chemical mechanisms used by organisms in detecting various elements.

Biochemistry of the Nonmetals

Many of the nonmetals such as hydrogen, carbon, nitrogen, oxygen, phosphorus, sulfur, chlorine, and iodine are essential elements, and most are used in quantities far beyond the trace levels. Nevertheless, most of the chemistry of these elements in biological systems is more closely associated with organic chemistry than with inorganic chemistry.

There are three important minerals used by organisms to form hard tissues such as bones and shells. The most widespread of these is calcium carbonate, an important structural component in animals ranging from Protozoa to molluscs and echinoderms. It is also a minor component of vertebrate bones. Its widespread use is probably related to the generally uniform distribution of dissolved calcium bicarbonate. Animals employing calcium carbonate are most abundant in fresh waters containing large amounts of calcium and magnesium (“hard water”) and in warm, shallow seas where the partial pressure of carbon dioxide is low (e.g., the formation of coral reefs by coelenterates). The successful precipitation of calcium carbonate depends upon the equilibrium:

\[
Ca^{2+} + 2HC\text{O}_3^- \rightleftharpoons CaCO_3 + CO_2 + H_2O
\]

and is favored by high [Ca²⁺] and low [CO₃²⁻]. Nevertheless, organisms exhibit a remarkable ability to deposit calcium carbonate from hostile environments. A few freshwater clams and snails are able to build reasonably large and thick shells in lakes with a pH of 5.7-6.0 and as little as 1.1 ppm dissolved calcium carbonate. It is of interest that two thermodynamically unstable forms of calcium carbonate, aragonite and vaterite, are found in living organisms as well as the more stable calcite. These minerals seem to be the simple explanation for the distribution of the different forms in the various species. Tissues containing silica are found in the primitive algal phyla Pyrophyta (diatoms and chrysophytes) and Chrysophyta (diatoms and silicoflagellates). One family of higher plants, the Equisetaceae, or horsetails, contains gritty deposits of silica—hence their tree-like form in the marine environment and their presence in the land plant.[128]

18.24 Discuss any similarities and differences between Eq. 18.56 above and the behavior of "Pittop" catalysts in Chapter 15.

18.25 From the discussions in this chapter and those in Chapter 14, plus any further data you find in standard reference works, write a Journal of Chemical Education-type article entitled: "Alchemy reversed: The remarkable chemistry of turning gold into even more interesting substances!"  

The Inorganic Chemistry of Biological Systems

The chemistry of life can ultimately be referred to two chemical processes: (1) the use of radiant solar energy to drive chemical reactions that produce oxygen and reduced organic compounds from carbon dioxide and water; and (2) the oxidation of the products of (1) with the production of carbon dioxide, water, and energy. Alternatively, living organisms have been defined as systems capable of reducing their own entropy at the expense of their surroundings (which must gain in entropy). An important feature of living systems is thus their unique dependence upon kinetic stability for their existence. All are thermodynamically unstable—they would burn up immediately to carbon dioxide and water if the system came to thermodynamic equilibrium. Life processes depend upon the ability to restrict these thermodynamic tendencies by controlled kinetics to produce energy as needed. Two important aspects of life will be of interest to us: (1) the ability to capture solar energy; (2) the ability to employ catalysts for the controlled release of that energy. Examples of such catalysts are the enzymes which control the synthesis and degradation of biologically important molecules. Many enzymes depend upon a metal ion for their activity. Metal-containing compounds are also important in the process of chemical and energy transfer, reactions which involve the transport of oxygen to the site of oxidation and various redox reactions resulting from its use.

Energy Sources for Life

Nonphotosynthetic Processes

It may be somewhat surprising that most of the reactions for obtaining energy for living systems are basically inorganic. Of course, the reactions are mediated and made possible by complex biochemical systems.

Even though almost all living organisms depend either directly (green plants) or indirectly (saprophytes and animals) upon photosynthesis to capture the energy of the sun, there are a few reactions, relatively unimportant in terms of scale but extremely

---

24 Lest we get carried away by the rhetoric, this would simply be a review article of gold chemistry with the provocative thesis that it has a more varied and interesting chemistry than any other element.

1 These reductionist definitions of life are not meant to imply that life processes or living organisms are simplistic or any less interesting. A similar definition of physics and chemistry might be: "the study of the interactions of matter and energy." None of these definitions hints at the fascination of some of the problems presented by these branches of science.
### Table 19.4 (Continued)

<table>
<thead>
<tr>
<th>Element</th>
<th>Earth's crust g kg⁻¹</th>
<th>cmass/10⁵ atoms Si</th>
<th>River water mg L⁻¹</th>
<th>Ocean water mg L⁻¹</th>
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<tr>
<td>Tin</td>
<td>0.0002</td>
<td>0.02</td>
<td>3.00</td>
<td>6.90</td>
</tr>
<tr>
<td>Antimony</td>
<td>0.0001</td>
<td>0.001</td>
<td>0.003</td>
<td>0.0002</td>
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<tr>
<td>Tellurium</td>
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<td>0.01</td>
<td>0.003</td>
</tr>
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<td>0.004</td>
<td>0.005</td>
<td>0.006</td>
</tr>
<tr>
<td>Xenon</td>
<td>0.0001</td>
<td>0.02</td>
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<td>5.0 × 10⁻⁴</td>
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<td>3.00</td>
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<td>0.04</td>
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<td>5.0 × 10⁻⁷</td>
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<td>Samarium</td>
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<td>4.5 × 10⁻⁷</td>
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<td>Europium</td>
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<td>0.08</td>
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<td>2 × 10⁻⁷</td>
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<td>2 × 10⁻⁷</td>
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<td>Ytterbium</td>
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<td>3 × 10⁻⁷</td>
</tr>
<tr>
<td>Tantalum</td>
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<td>0.01</td>
<td>2 × 10⁻⁷</td>
<td>2 × 10⁻⁷</td>
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<tr>
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<td>0.001</td>
<td>5.0 × 10⁻⁷</td>
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</tr>
<tr>
<td>Rhodium</td>
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<td>1 × 10⁻⁴</td>
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<td>Osmium</td>
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<td>5 × 10⁻⁴</td>
<td>6 × 10⁻⁴</td>
<td>6 × 10⁻⁴</td>
</tr>
<tr>
<td>Iridium</td>
<td>1 × 10⁻⁴</td>
<td>5 × 10⁻⁴</td>
<td>6 × 10⁻⁴</td>
<td>6 × 10⁻⁴</td>
</tr>
<tr>
<td>Gold</td>
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<td>2 × 10⁻⁴</td>
<td>2 × 10⁻⁴</td>
<td>2 × 10⁻⁴</td>
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<tr>
<td>Mercury</td>
<td>8 × 10⁻⁵</td>
<td>4 × 10⁻⁵</td>
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<td>7 × 10⁻⁵</td>
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<td>Thallium</td>
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<td>Bismuth</td>
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<tr>
<td>Polonium</td>
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<td>4 × 10⁻⁴</td>
<td>6 × 10⁻⁴</td>
<td>6 × 10⁻⁴</td>
</tr>
<tr>
<td>Antimony</td>
<td>2.0 × 10⁻⁴</td>
<td>4 × 10⁻⁴</td>
<td>6 × 10⁻⁴</td>
<td>6 × 10⁻⁴</td>
</tr>
<tr>
<td>Francium</td>
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<td>6 × 10⁻⁴</td>
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<tr>
<td>Radon</td>
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<td>4 × 10⁻⁴</td>
<td>6 × 10⁻⁴</td>
<td>6 × 10⁻⁴</td>
</tr>
<tr>
<td>Rhenium</td>
<td>1.0 × 10⁻⁴</td>
<td>4 × 10⁻⁴</td>
<td>6 × 10⁻⁴</td>
<td>6 × 10⁻⁴</td>
</tr>
<tr>
<td>Radium</td>
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<td>4 × 10⁻⁴</td>
<td>6 × 10⁻⁴</td>
<td>6 × 10⁻⁴</td>
</tr>
<tr>
<td>Astatine</td>
<td>1.0 × 10⁻⁴</td>
<td>4 × 10⁻⁴</td>
<td>6 × 10⁻⁴</td>
<td>6 × 10⁻⁴</td>
</tr>
</tbody>
</table>

* Inorganic carbon.
* Combined nitrogen; about 15 mg L⁻¹, dissolved NO₃⁻.
* Considered by some to be ultratrace.

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124 See Broda, E., J. J. Mol. Biol. 1974, 77, 1163; for a discussion of this and related questions concerning the primitive biosphere.
interesting in terms of chemistry, utilizing inorganic sources of energy. Even these may be indirectly dependent upon photosynthesis, since it is believed that all free oxygen on earth has been formed by photosynthesis.

Chemolithotrophic4 bacteria obtain energy from various sources. For example, iron bacteria produce energy by the oxidation of iron(II) compounds:

\[
2\text{Fe}^++\text{O}_2\rightarrow\text{Fe}_2\text{O}_3+\text{energy} \quad (19.1)
\]

Nitrofying bacteria are of two types, utilizing ammonia and nitrite ions as nutrients:

\[
2\text{NH}_4^++2\text{NO}_2^-+3\text{H}_2\text{O}\rightarrow2\text{NH}_3+2\text{H}_2\text{O}+\text{O}_2+\text{energy} \quad (19.2)
\]

\[
\text{NO}_2^-+\text{H}_2\text{O}\rightarrow\text{NO}_3^-+2\text{H}^+ + \text{energy} \quad (19.3)
\]

Though they are photosynthethic (Gr. photos, "light") and thus more closely related to the chemistry of normal photosynthesis (see page 916), the green sulfur bacteria and the purple sulfur bacteria are included here to demonstrate the diverse bacterial chemistry based on sulfur paralleling the common biochemistry involving water and oxygen. Light energy is used to split hydrogen sulfide into sulfur, which is stored in the cells, and hydrogen which forms carbohydrates, etc., from carbon dioxide.

To return to the chemolithothrophs, there are species of sulfur bacteria that obtain energy from the oxidation of various states of sulfur:

\[
8\text{H}_2\text{S} \rightarrow 8\text{S}^0 + 8\text{H}^+ + \text{energy} \quad (19.4)
\]

\[
\text{S}^0 + 8\text{H}_2\text{O} \rightarrow 8\text{SO}_4^{2-} + 16\text{H}^+ + \text{energy} \quad (19.5)
\]

These latter reactions are the source of energy for a unique form, one completely isolated from the sun on the floor of the oceans. These ecosystems have been discovered at certain rifts in the earth’s crust on the ocean’s floor, where large amounts of sulfide minerals are spewed forth from hydrothermal vents.3 The sulfide concentration, principally in the form of hydrogen sulfide, ranges routinely up to 100 μM depending upon the dilution of vent water by surrounding sea water. The H2S has been shown to be depleted, along with O2, in the midst of the aggregated organisms, and it is the energetic basis of these communities.4 The sulfide is oxidized by bacteria as shown above. It is of considerable interest that the enzymes, mechanisms, and products of this chemically driven synthesis are essentially identical to those of photosynthesis (page 916), except that the source of electrons for the reduction of water to carbohydrates is sulfur (11) rather than photosynthesized chlorophyll.

In addition to free-living bacteria, many of the vent animals contain endosymbiotic bacteria that serve as primary energy sources as well as the source of reduced carbon compounds. The parallel between these endosymbioses in rift animals, such as tube worms, clams, and mussels, and the chloroplasts of plants is striking.5 Whether this parallelism results from an adaptation of the cycle from photosynthetic bacteria, or whether these chemolithotrophic bacteria are possibly ancestral to photosynthetic organisms presents the age-old phylogenetic problem—which came first, the chicken or the egg? The entire community, including predator species such as crabs, is entirely independent of photosynthesis except for the use of by-product oxygen. There is even evidence that some of the animals such as gutless clams can exobiologically hydrogen sulfide independently, simultaneously detoxifying it and using it as an energy source.6

---


Table 19.4

<table>
<thead>
<tr>
<th>Essential and Trace Elements in Biological Systems</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Element</strong></td>
<td><strong>G kg⁻¹</strong></td>
</tr>
<tr>
<td><strong>Hydrogen</strong></td>
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<tr>
<td><strong>Lithium</strong></td>
<td>0.021</td>
</tr>
<tr>
<td><strong>Beryllium</strong></td>
<td>0.0025</td>
</tr>
<tr>
<td><strong>Magnesium</strong></td>
<td>0.12</td>
</tr>
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<td><strong>Aluminum</strong></td>
<td>200</td>
</tr>
<tr>
<td><strong>Silicon</strong></td>
<td>28</td>
</tr>
<tr>
<td><strong>Phosphorus</strong></td>
<td>1</td>
</tr>
<tr>
<td><strong>Sulfur</strong></td>
<td>0.26</td>
</tr>
<tr>
<td><strong>Chlorine</strong></td>
<td>0.12</td>
</tr>
<tr>
<td><strong>Argon</strong></td>
<td>0.045</td>
</tr>
<tr>
<td><strong>Potassium</strong></td>
<td>24</td>
</tr>
<tr>
<td><strong>Calcium</strong></td>
<td>100</td>
</tr>
<tr>
<td><strong>Scandium</strong></td>
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<td><strong>Titanium</strong></td>
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<td><strong>Vanadium</strong></td>
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</tr>
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<td><strong>Chromium</strong></td>
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<td><strong>Manganese</strong></td>
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</tr>
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<td><strong>Iron</strong></td>
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<tr>
<td><strong>Cobalt</strong></td>
<td>0.032</td>
</tr>
<tr>
<td><strong>Nickel</strong></td>
<td>0.075</td>
</tr>
<tr>
<td><strong>Copper</strong></td>
<td>0.035</td>
</tr>
<tr>
<td><strong>Zinc</strong></td>
<td>0.019</td>
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<tr>
<td><strong>Lead</strong></td>
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<td><strong>Antimony</strong></td>
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<td><strong>Bismuth</strong></td>
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</tr>
<tr>
<td><strong>Radium</strong></td>
<td>0.0015</td>
</tr>
<tr>
<td><strong>Technetium</strong></td>
<td>0.00012</td>
</tr>
<tr>
<td><strong>Rubidium</strong></td>
<td>0.009</td>
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<tr>
<td><strong>Strontium</strong></td>
<td>0.037</td>
</tr>
<tr>
<td><strong>Yttrium</strong></td>
<td>0.035</td>
</tr>
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<td><strong>Zirconium</strong></td>
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<td><strong>Niobium</strong></td>
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<tr>
<td><strong>Molybdenum</strong></td>
<td>0.0015</td>
</tr>
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<td><strong>Technetium</strong></td>
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</tr>
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<td><strong>Rhenium</strong></td>
<td>1 x 10⁻⁸</td>
</tr>
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<td><strong>Rhodium</strong></td>
<td>2 x 10⁻⁸</td>
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<tr>
<td><strong>Paladium</strong></td>
<td>8 x 10⁻⁹</td>
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<tr>
<td><strong>Silver</strong></td>
<td>7 x 10⁻⁹</td>
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<td><strong>Cadmium</strong></td>
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</tr>
<tr>
<td><strong>Indium</strong></td>
<td>0.00023</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
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</table>
and the metal-nitrogen bond distance does not vary greatly from 193-196 pm in nickel porphyrins to 210 pm in high spin iron(II) porphyrins. The rigidity of the ring derives from the delocalization of the π electrons in the pyrrole rings. Nevertheless, if the metal atom is too small, as in nickel porphyrinates, the ring becomes ruffled to allow closer approach of the nitrogen atoms to the metal. At the other extreme, if the metal atom is too large, it cannot fit into the hole and sits above the ring which also becomes domed (see page 903).

The order of stability of complexes of porphyrins with +2 metal ions is that expected on the basis of the Irving-Williams series (see Chapter 9), except that the square planar ligand favors the d^5 configuration of Ni^{2+}. The order is Ni^{2+} > Cu^{2+} > Co^{2+} > Fe^{2+} > Zn^{2+}. The kinetics of formation of these metalloporphyrins has also been measured and found to be in the order Cu^{+} > Co^{2+} > Fe^{2+} > Ni^{2+}. If this order holds in biological systems, it poses interesting questions related to the much greater abundance of iron porphyrins (see below). What might have been the implications for the origin and evolution of biological systems if the natural abundance of iron were not over a thousandfold greater than those of cobalt and copper?

The porphyrin ring or modifications of it are important in several quite different biological processes. The reason for the importance of porphyrin complexes in a variety of biological systems is probably twofold: (1) They are biologically accessible compounds whose functions can be varied by changing the metal, its oxidation state, or the nature of the organic substituents on the porphyrin structure; (2) it is a general principle that evolution tends to proceed by modifying structures and functions that are already present in an organism rather than producing new ones de novo.

The heme group is a porphyrin ring with an iron atom at the center (Fig. 19.2). The oxidation state of the iron may be either +2 or +3, and the importance of the

![Fig. 19.2 The heme group: Type A hemes are found in cytochrome c; Type B hemes are found in hemoglobin, myoglobin, peroxidase, and cytochrome b. Type C hemes are found in cytochrome c; chloroheme is found in chlorophyllin.](image)

---

9 For the complete structures of ferrocyanide ions FeCN^3−, see Takano, T.; Tomin, B. L.; Mandel, N.; Mandell, G.; Kant, O. B.; Swanson, R.; Dickerson, R. E. J. Biol. Chem. 1972, 247, 776-785.


11 The prefix met is used to signify that the iron atom, normally in the +2 oxidation state, has been oxidized to +3.

cytoclines lies in their ability to act as reduct intermediates in electron transfer. They are present not only in the chloroplasts for photosynthesis but also in mitochondria to take part in the reverse process of respiration.

The heme group in cytochrome c has a polypeptide chain attached and wrapped around it (Fig. 19.3). This chain contains a polypeptide chain with amino acids ranging from 103 in some fish and 104 in other fish and terrestrial vertebrates to 112 in some green plants. A nitrogen atom from a histidine segment and a sulfur atom from a methionine segment of this chain are coordinated to the fifth and sixth coordination sites of the iron atom. Thus, unlike the iron in hemoglobin and myoglobin (see below), there is no position for further coordination. Cytochrome c therefore cannot react by simple coordination but must react indirectly by an electron transfer mechanism. It can reduce the oxygen and transmit its oxidizing power towards the burning of food and release of energy in respiration (the reverse process to complement photosynthesis). The importance of cytochrome c in photosynthesis and respiration indicates that it is probably one of the oldest (in terms of evolutionary history) of the chemicals involved in biological processes. An interesting "family tree" of the evolution of living organisms can be constructed from the differences in amino acid sequences in the peptide chains between the various types of cytochrome c found, for example, in yeasts, higher plants, insects, and humans. Despite these differences, however, it should be noted that cytochrome c is evolutionarily conservative. Cytochrome c from any eucaryotic species will react with the cytochrome oxidase of any other eucaryotic species, plant or animal, though not at reduced rates.

There is quite a variety of cytochromes, most of which have not been as well characterized as cytochrome c. Depending upon the ligands present, the redox potential of a given cytochrome can be tailored to meet the specific need in the electron transfer scheme, whether in photosynthesis or in respiration. The potentials are such that the electrons flow in h → c → a → O₂. At least some of the a type (cytochrome a-oxidase) are capable of binding dioxygen molecules and reducing them. They are thus the last link in the respiratory chain of electrons flowing from reduced foodstuffs to oxygen. Therefore, they must be two electron carriers (in the absence of O₂) in contrast to cytochrome c. They are responsible for the unusually severe and rapid toxicity of the cyanide ion, CN^-. The cyanide binds strongly to the sixth position and stabilizes the cytochrome oxidase form usually present only in small quantities. Cyanide poisoning is thus not the result of lack of hemoglobin function (as is CO poisoning). In fact, the standard treatment for cyanide poisoning is administration of amyl nitrite or injection of sodium nitrite to oxidize some of the hemoglobin to methemoglobin (see page 997). The latter,
<table>
<thead>
<tr>
<th>Atomic number</th>
<th>Element</th>
<th>Biological functions</th>
<th>Toxicity*</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>Iron</td>
<td>Essential to all organisms. See text.</td>
<td>Normally only slight toxicity, but excessive intake can cause idiosyncrasy and damage to organs through excessive iron storage (hemochromatosis).</td>
<td>A very abundant element (1% of earth's crust); may not be available at high pHs.</td>
</tr>
<tr>
<td>27</td>
<td>Cobalt</td>
<td>Essential for many organisms including minerals; activates a number of enzymes; vitamin B12.</td>
<td>Very toxic to plants and moderately so when injected intravenously in mammals.</td>
<td>Essential trace element.</td>
</tr>
<tr>
<td>28</td>
<td>Nickel</td>
<td>Essential trace element. Chicks and rats raised on deficient diet show impaired liver function and morphology; stabilizes coiled ribosomes. Active metal in several hydrogenases and plant umeeners.</td>
<td>Very toxic to most plants; moderately so to mammals; cardiacogenic.</td>
<td>Essential trace element.</td>
</tr>
<tr>
<td>29</td>
<td>Copper</td>
<td>Essential to all organisms; constituent of redox enzymes and hemocyanin.</td>
<td>Very toxic to most plants; highly toxic to invertebrates, moderately so to mammals.</td>
<td>Essential trace element.</td>
</tr>
<tr>
<td>30</td>
<td>Zinc</td>
<td>Essential to all organisms; used in &gt;70 enzymes; stabilizes coiled ribosomes. Plays a role in sexual maturation and reproduction. U.S. population marginally deficient.</td>
<td>Moderately to slightly toxic; orally causes vomiting and diarrheal.</td>
<td>Essential trace element.</td>
</tr>
<tr>
<td>33</td>
<td>Arsenic</td>
<td>Essential ultratrace element in red algae, chick, rat, pig, goat, and probably humans. Deficiency results in depressed growth and increased mortality.</td>
<td>Moderately toxic to plants, highly toxic to mammals.</td>
<td>Most of the heavier elements are comparatively unimportant biologically. Some of the exceptions are:</td>
</tr>
<tr>
<td>34</td>
<td>Selenium</td>
<td>Essential to mammals and some higher plants. Component of glutathione peroxidase, protects against free-radical oxidant stressors; protects against &quot;heavy&quot; (&quot;soft&quot;) metal ions.</td>
<td>Moderately toxic to plants, highly toxic to mammals.</td>
<td>Selenium is involved in Keyshian disease in China.</td>
</tr>
<tr>
<td>35</td>
<td>Bromine</td>
<td>May be essential in red algae and mammals.</td>
<td>Nonotoxic except in oxidizing forms, e.g., Br2.</td>
<td>Function unknown, but found in the molasses pigmen, purple.</td>
</tr>
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</table>

### Table 19.3 (Continued)

<table>
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<tr>
<th>Atomic number</th>
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<th>Toxicity*</th>
<th>Comments</th>
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<tr>
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<td>Rubidium</td>
<td>None known.</td>
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<tr>
<td>42</td>
<td>Molybdenum</td>
<td>Essential to all organisms with the possible exception of green algae; used in enzymes connected with nitrogen fixation and nitric oxide reduction.</td>
<td>Moderately toxic and antagonistic to copper—molybdenum excesses in pasture can cause copper deficiency. Excessive exposure in parts of U.S.S.R., associated with a goat-like syndrome.</td>
<td>Has caused serious disease (&quot;milk cal&quot;) in Japan from pollution. May also pose pollution problem associated with industrial use of zinc, e.g., galvanization.</td>
</tr>
<tr>
<td>48</td>
<td>Cadmium</td>
<td>Weak evidence for ultratrace essentiality in rats.</td>
<td>Moderately toxic to all organisms; a cumulative poison in mammals, causing renal failure; possibly linked with hypertension in man.</td>
<td>U.S. population marginally deficient.</td>
</tr>
<tr>
<td>50</td>
<td>Tin</td>
<td>Weak evidence for ultratrace essentiality in rats.</td>
<td>Organotin compounds used as bactericides and fungicides; its use in anti-fouling boat paints now discouraged because of danger to estuaries and marine life.</td>
<td>Organotin compounds used as bactericides and fungicides; its use in anti-fouling boat paints now discouraged because of danger to estuaries and marine life.</td>
</tr>
<tr>
<td>53</td>
<td>Iodine</td>
<td>Essential in many organisms; thyroxine important in metabolism and growth regulation, amphibian metamorphosis.</td>
<td>Sarcoid toxicity as the iodide; low iodide availability in certain areas increases the incidence of goiter, largely eliminated by the use of iodized salt. Elemental iodine is toxic like Cl2 and Br2.</td>
<td>Concentrated up to 2.5 ppt by some marine algae.</td>
</tr>
<tr>
<td>74</td>
<td>Tungsten</td>
<td>Rare.</td>
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<td>Platinum</td>
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<td>Gold</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>Mercury</td>
<td>None known.</td>
<td>Very toxic to fungi and green plants, and to mammals if in soluble form; a cumulative poison in mammals.</td>
<td>Serious pollution problems from use of organometallics as fungicides and from industrial uses of mercury.</td>
</tr>
</tbody>
</table>

### Essential and Trace Elements in Biological Systems

Serious pollution problems in some areas: sources include mining, burning coal, impure sulfuric acid, and others. Insecticides, herbicides, and pesticides. Livestock grown on soils high in selenium are poisoned by eating Astredea ("buckwheat"), which concentrates it; sheep grown on land deficient in selenium develop "white muscle disease." Deficiency of selenium involves in Keyshian disease in China. Function unknown, but found in the molasses pigmen, purple.
The Interaction between Heme and Dioxygen

While all of the biochemical uses of the heme group are obviously important, the one that has perhaps attracted the most attention because of its central biological role and its intricate chemistry is the binding of the dioxygen molecule, O₂. This has been mentioned briefly above with regard to the binding and reduction of dioxygen by cytochrome oxidase. Before this step occurs, vertebrates have already utilized two other heme-containing proteins: Hemoglobin picks up the dioxygen from the lungs or gills and transports it to the tissues where it is stored by myoglobin. The function of hemoglobin in the red blood cells is obvious, that of myoglobin is more subtle. Besides being a simple repository for dioxygen, it also serves as a dioxygen reserve against which the organism can draw during increased metabolism or oxygen deprivation.

Dioxygen is far from a typical ligand. It probably resembles the carbon monoxide, nitrosyl, and dinitrogen ligands more than any others. None of these has a significant dipole moment contributing to the bond, but the electronegativity difference between the atoms in CO and NO enhances π* interactions (see Chapter 11). Dinitrogen and dioxygen lack this advantage, but may be considered soft ligands with some π-bonding capacity. Iron(II, III) is not a particularly soft metal cation, but the "soften-
The binding of dioxygen to myoglobin

Dioxygen Binding, Transport, and Utilization

Obviously, living systems have found a way to frustrate reactions 19.7-19.10: otherwise all of the heme would be precipitated as hematin rather than shuttling electrons in the cytochromes or carrying dioxygen molecules in oxyhemoglobin (and storing them in oxymyoglobin). There may be more than one mechanism in effect here, but certainly the primary one is steric hindrance: The globin part of the molecule prevents one oxoheme from attacking another heme. This was first illustrated over thirty years ago by embedding the heme group in a polymer matrix that allowed only restricted access to the iron atom: The embedded heme will reversibly bind dioxygen. More recently this same result has been achieved by “picket-fence” hemes and related compounds (Fig. 19.4) but reversibly bind dioxygen, and not only confirm the steric hypothesis with regard to the stability of hemoglobin, but allow detailed structural measurements to be made of a heme model compound. Thus the angular or bent coordination of dioxygen to heme (in hemoglobin and myoglobin) was first indicated by the structure shown in Fig. 19.4. It has since been confirmed in myoglobin and hemoglobin (see below).

Myoglobin is a protein of molecular weight of about 17,000 with the protein chain containing 153 amino acid residues folded about the single heme group (Fig. 19.5). This restricts access to the iron atom (by a second heme) and reduces the likelihood of formation of a hematin-like Fe(III) dimer. The microenvironment is similar to that in cytochrome c, but there is no sixth ligand (methionine) to complete the coordination.

The oxidation states may occasionally be ambiguous—the adduct in Eq. 19.7 may be formulated as hemi-Fe(III)-dioxygen or as hemi-Fe(II)-superoxide. See Problem 19.21.

\[
\begin{align*}
F_{(II)} + O_2 & \rightarrow F_{(II)}O_2^- \\
F_{(III)} - O & \rightarrow F_{(III)}O - F_{(III)} \\
F_{(IV)}O & \rightarrow 2 F_{(III)}O \\
F_{(IV)}O & \rightarrow F_{(II)} + F_{(III)}
\end{align*}
\]

13 Carbon monoxide poisoning may be treated by flooding the system with oxygen. Nevertheless, the binding of CO is about 500 times stronger than the binding of O₂. It could be worse. Carbon monoxide binds even more strongly (by about two orders of magnitude) to free hem. The steric hindrance about the heme in hemoglobin and myoglobin may favor the bent O₂ over the (optimally) linear carbon monoxide. (Seyfer, L. Biochemistry, 2nd ed.; Freeman: New York, 1981, p 54.)


15 The oxidation states may occasionally be ambiguous—the adduct in Eq. 19.7 may be formulated as hemi-Fe(III)-dioxygen or as hemi-Fe(II)-superoxide. See Problem 19.21.


Fig. 19.4 Perspective view of picket-fence dioxygen adduct. The apparent presence of four different O₂ atoms results from a four-way statistical disorder of the oxygen atoms on different molecules responding to the X-ray diffraction. [From Collman, J. P.; Gagne, R. R.; Reed, C. A.; Robinson, W. T.; Rodeney, G. A. Proc. Natl. Acad. Sci. U. S. A. 1974, 71, 1326-1329. Reproduced with permission.]
<table>
<thead>
<tr>
<th>Name</th>
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<th>Atomic weight</th>
<th>Name</th>
<th>Symbol</th>
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Indeed, hemoglobin has been dubbed a "frustrated oxidase" [Wintemberg, C. C.; French, K. E.; Strangburg, B. E.; Hutt, R. G.; Davies, D. R.; Phillips, D. C.; Shore, V. C. Nature 1960, 185, 422-427. Reproduced with permission.]

sphere of the iron atom. Thus there is a site to which a dioxygen molecule may reversibly bind.

Note how the differences in structure between the dioxygen-binding molecules (myoglobin, hemoglobin, and cytochrome oxidase) and the electron carriers (various cytochromes, including cytochrome oxidase which performs both functions) correlate with their specific functions. In myoglobin and hemoglobin the redox behavior is retarded, and there is room for the dioxygen molecule to coordinate without electron transfer taking place.22

Myoglobin contains iron(II) in the high spin state. Iron(II) is d⁶ and, when high spin, has a radius of approximately 92 pm in a pseudo-octahedral environment (the square pyramidal arrangement of heme in myoglobin and hemoglobin may be considered an octahedron with the sixth ligand removed), and the iron atom will not fit into the hole of the porphyrin ring. The iron(II) atom thus lies some 42 pm above the plane of the nitrogen atoms in the porphyrin ring (see Fig. 19.6). When a dioxygen molecule binds to the iron(II) atom, the latter becomes low spin d⁶ (cf. the extremely stable Co⁷ complexes with 2.4A LFSE). The ionic radius of low spin iron(II) with coordination number six is only 75 pm, in contrast with the 92 pm of high spin iron. Why the difference? Recall that in octahedral complexes the e₂ orbitals are those aimed at the ligands. If they contain electrons, which they do in the high spin case, they will repel the ligands as opposed to the low spin case (t₁₂, t₂₃), where unoccupied access of the ligands along the coordinate axes thus the effective radius of the iron atom is greater (along the z, x, y, axes) in the high spin state than in the low spin state. The result is that the iron atom shrinks upon spin pairing and drops into the hole in the porphyrin ring. All of the ligands (including the proximal histidine) are able to approach the iron atom more closely. The net effect in myoglobin is minimal, because of the high molecular weight of the molecules and the low resolution of the X-ray-determined structures. The structure that has been determined to the greatest resolution is that of oxyerythrocruciorin, which has been refined to a resolution of 1:10 pm.23 The dioxygen is bonded to the iron with an angle of about 150° and an Fe—O bond length of about 1:80 pm. Oxymyoglobin trimers which24 contain hemoglobin (human) have not been resolved as high as (1:10 pm), but the Fe—O bond lengths are similar. All of these are compatible with the more accurate value of 1:90 pm in the picket-fence compound.25 The source of the differences is not clear, but calculations26 indicate that the bond energy changes little with bond angle, and so other factors such as steric effects or hydrogen bonding with a neighboring group could be important (Fig. 19.7).

A knowledge of the exact molecular arrangement of dioxygen in oxymyoglobin and oxyhemoglobin has been desirable in order to understand the chemistry of dioxygen transport and storage. Unfortunately, this has been difficult to achieve because of the high molecular weight of the molecules and the low resolution of the X-ray-determined structures. The structure that has been determined to the greatest resolution is that of oxyerythrocruciorin, which has been refined to a resolution of 1:10 pm.23 The dioxygen is bonded to the iron with an angle of about 150° and an Fe—O bond length of about 1:80 pm. Oxymyoglobin trimers which24 contain hemoglobin (human) have not been resolved as high as (1:10 pm), but the Fe—O bond lengths are similar. All of these are compatible with the more accurate value of 1:90 pm in the picket-fence compound.25 The source of the differences is not clear, but calculations26 indicate that the bond energy changes little with bond angle, and so other factors such as steric effects or hydrogen bonding with a neighboring group could be important (Fig. 19.7).

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25 The structure that has been determined to the greatest resolution is that of oxyerythrocruciorin, which has been refined to a resolution of 1:10 pm. The dioxygen is bonded to the iron with an angle of about 150° and an Fe—O bond length of about 1:80 pm. Oxymyoglobin trimers which24 contain hemoglobin (human) have not been resolved as high as (1:10 pm), but the Fe—O bond lengths are similar. All of these are compatible with the more accurate value of 1:90 pm in the picket-fence compound.25 The source of the differences is not clear, but calculations26 indicate that the bond energy changes little with bond angle, and so other factors such as steric effects or hydrogen bonding with a neighboring group could be important (Fig. 19.7).

26 The structure that has been determined to the greatest resolution is that of oxyerythrocruciorin, which has been refined to a resolution of 1:10 pm. The dioxygen is bonded to the iron with an angle of about 150° and an Fe—O bond length of about 1:80 pm. Oxymyoglobin trimers which24 contain hemoglobin (human) have not been resolved as high as (1:10 pm), but the Fe—O bond lengths are similar. All of these are compatible with the more accurate value of 1:90 pm in the picket-fence compound.25 The source of the differences is not clear, but calculations26 indicate that the bond energy changes little with bond angle, and so other factors such as steric effects or hydrogen bonding with a neighboring group could be important (Fig. 19.7).

27 The structure that has been determined to the greatest resolution is that of oxyerythrocruciorin, which has been refined to a resolution of 1:10 pm. The dioxygen is bonded to the iron with an angle of about 150° and an Fe—O bond length of about 1:80 pm. Oxymyoglobin trimers which24 contain hemoglobin (human) have not been resolved as high as (1:10 pm), but the Fe—O bond lengths are similar. All of these are compatible with the more accurate value of 1:90 pm in the picket-fence compound.25 The source of the differences is not clear, but calculations26 indicate that the bond energy changes little with bond angle, and so other factors such as steric effects or hydrogen bonding with a neighboring group could be important (Fig. 19.7).
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<tr>
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<th>Element</th>
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<th>Toxicity*</th>
<th>Comments</th>
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<td>Important in nerve functioning in animals; major causation of extracellular fluid in animals.</td>
<td>Relatively harmless except in excessive amounts (lethal dose ca. 3 g kg(^{-1}))</td>
<td>Associated with some forms of hypertension.</td>
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<td>11</td>
<td>Sodium</td>
<td>Important in nerve functioning in animals; major causation of extracellular fluid in animals.</td>
<td>Relatively harmless except in excessive amounts (lethal dose ca. 3 g kg(^{-1}))</td>
<td>Associated with some forms of hypertension.</td>
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<td>Essential to all eukaryotes. Present in all chlorophylls. Has other electrochemical and enzyme activating functions. Us. S. population may be marginally deficient.</td>
<td>Moderately toxic to most plants; slightly toxic to mammals.</td>
<td>Suggested as involved in the etiology of Alzheimer’s disease and other neurologic diseases.</td>
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<td>Aluminium</td>
<td>May activate tisue dehydrogenase and -oxygenate dehydrogenase. The latter is involved in porphyrin synthesis.</td>
<td>Relatively inaccessible except in acidic media as a result of insolubility of Al(OH)(_3) and low in Mg(^{2+}) and Ca(^{2+})</td>
<td>Implicated in neurologic diseases.</td>
</tr>
<tr>
<td>14</td>
<td>Silicon</td>
<td>Essential element for growth and skeletal development in chicks and rats; probably essential in higher plants. Used in the form of silicon dioxide for structural purposes in clastics, some porozites, some sponges, jars and one family of plants.</td>
<td>Not chemically toxic, but large amounts of finely divided silicates or silica are injurious to the mammalian lung.</td>
<td>Long-term exposure to finely divided asbestos from construction work poses a health problem. Some evidence for a negative correlation between silicon content of drinking water and heart disease.</td>
</tr>
<tr>
<td>15</td>
<td>Phosphorus</td>
<td>Important constituents of DNA, RNA, bones, teeth, some shells, membrane phospholipids, ADP and ATP, and metabolic intermediates.</td>
<td>Inorganic phosphates are relatively harmless; P, and PO(_4)(^{3-}) are very toxic to mammals and fish. Phosphate esters are used as insecticides (nerve poisons). Elemental sulfur is highly toxic to most bacteria and fungi, relatively harmless to higher organisms. H(_2)S is highly toxic to mammals; SO(_2) is highly toxic.</td>
<td>Leached from fertilizers applied to agricultural land; present in detergents and other sewage sources.</td>
</tr>
<tr>
<td>16</td>
<td>Sulfur</td>
<td>Essential element in most proteins; important in intermediary structure (through S-S link) of proteins; involved in vitamins, fat metabolism, and detoxification processes. H(_2)SO(_4) in digestive fluid in animals (“sweat sweat”). H(_2)S reduces H(_2)O in photosynthesis of some bacteria. H(_2)S and S(_2) are oxidized by other bacteria.</td>
<td>Sulfur dioxide is a serious atmospheric pollutant, especially serious when it settles in unattended pockets oxidized to H(_2)SO(_4). Widespread cause of acid rain. Sulfide minerals cause acid mine drainage.</td>
<td>Sulfur dioxide is a serious atmospheric pollutant, especially serious when it settles in unattended pockets oxidized to H(_2)SO(_4). Widespread cause of acid rain. Sulfide minerals cause acid mine drainage.</td>
</tr>
</tbody>
</table>
The Inorganic Chemistry of Biological Systems

Fig. 19.7 Stereoview of superimposed heme environments in oxyhemoglobin and oxymyoglobin. Solid lines denote HbO₂ and dashed lines MbO₂. Note the difference in the Fe—O₁—O₂ bond angles and the presumed hydrogen bond (dotted line) to the histidine (His E7). [From Shaanan, B. Nature (London) 1982, 296, 683. Reproduced with permission.]

The Physiology of Myoglobin and Hemoglobin

In vertebrates dioxygen enters the blood in the lungs or gills where the partial pressure of dioxygen is relatively high [21% oxygen = 0.21 x 1.01 x 10⁵ Pa (750 mm Hg) = 2.1 x 10⁵ Pa (160 mm Hg)] under ideal conditions; in the lungs with mixing of inhaled and nonexhaled gases, the value is closer to 1.3 x 10⁵ Pa (100 mm Hg). It is then carried by red blood cells (Fig. 19.8a) to the tissues where the partial pressure is considerably lower [of the order of 2.5 x 10⁴ to 6.5 x 10⁴ Pa (20–50 mm Hg)]. The reactions are as follows:

Lungs (gills) Hb + 4O₂ $\rightarrow$ Hb(O₂)₄ (19.11)

Tissues Hb(O₂)₄ + 4Mb $\rightarrow$ 4MbO₂ + Hb (19.12)

Note that hemoglobin has an ambivalent function: It should bind dioxygen tightly and carry as much as possible to the tissues, but once there it should, chameleon-like, relinquish it readily to myoglobin which can store it for oxidation of foodstuffs. Hemoglobin serves this function admirably as shown by Fig. 19.9: (1) Myoglobin must have a greater affinity for dioxygen than hemoglobin in order to effect the transfer of dioxygen at the cell. (2) The equilibrium constant for the myoglobin-dioxygen complexation is given by the simple equilibrium expression:

$$K_{\text{Mb}} = \frac{[\text{Mb}(\text{O}_2)]}{[\text{Mb}][\text{O}_2]}$$  (19.13)

If the total amount of myoglobin ([Mb] + [MbO₂]) is held constant (as it must be in the cell) while the concentration of oxygen is varied (in terms of partial pressure), the

Fig. 19.8 Relative scale of (a) red blood cells, the biological unit of dioxygen transport; (b) the hemoglobin molecule, the biochemical unit of dioxygen transport; and (c) the dioxygen-heme group, the inorganic unit of dioxygen transport. The relative sizes are given by the factors over the arrows. [Scanning electron micrograph courtesy of M. Barnhart, Wayne State University of Medicine. Hemoglobin molecule modified from Perutz, M.; Rossman, M. G.; Cullis, A. P.; Muirhead, H.; Will, G.; North, A. C. T. Nature (London) 1960, 185, 416. Reproduced with permission.]

28 Small organisms require no oxygen transport system beyond simple diffusion. There is a family of lungless salamanders, the Plethodontidae, which have neither gills nor lungs (as adults) and rely upon oxygen exchange through the skin and through buccopharyngeal ("mouth and throat") exchange. Some worms and mollusks have proteins related to hemoglobin for oxygen transport and storage. Some polychaete worms employ chlorocruorin which turns green upon oxygenation. Sipunculid worms and some other species utilize nonheme iron proteins, the hemerythrins. For these functions (see page 909), lobsters, crabs, snails, cephalopods, and some seals use a copper-containing protein (hemocyanin, see page 909) for oxygen transport.

Fig. 19.9 Dioxygen binding curves for (1) myoglobin and for hemoglobin at various partial pressures of carbon dioxide: (2) 20 mm Hg; (3) 40 mm Hg; (4) 80 mm Hg. Note that myoglobin has a stronger affinity for dioxygen than hemoglobin and that this effect is more pronounced in the presence of large amounts of carbon dioxide. (Modified from Bock, A. V.; Field, H., Jr.; Adair, G. S. J. Biol. Chem. 1924, 59, 333-336. Reproduced with permission.)
The biochemistry of iron has just been discussed in some detail including the biochemical species involved, bioaccumulation, transport, storage, and toxicity. Space does not permit an extensive discussion of other elements of importance. However, a brief discussion will be presented here with a table summarizing what is currently known.

The number of elements that are known to be biologically important comprises a relatively small fraction of the 109 known elements. Natural abundance limits the availability of the elements for such use. Molybdenum (Z = 42) is the heaviest metal, and iodine (Z = 53) is the heaviest nonmetal of known biological importance. The metals of importance in enzymes are principally those of the first transition series, and the other elements of importance are relatively light: sodium, potassium, magnesium, calcium, carbon, nitrogen, phosphorus, oxygen, chlorine, and, of course, hydrogen.

Table 19.3 lists elements that have been found to be essential or poisonous, together with notes on biological functions and leading references that may be followed by the interested reader. It is certain that the information in this list will be expanded as the present techniques and theory are improved.

There are at least two ways, maybe more, of looking at the fitness of particular elements to serve particular biological functions. The more "chemical" approach is to suggest that iron functions well in cytochromes and ferredoxins because the Fe^{2+}/Fe^{3+} couple has a reduction potential in the appropriate range for life processes. Conversely, that mercury is poisonous because it binds irreversibly with enzymes, destroying their activity. Basically, a given element cannot function in a biological role unless it has specific properties. Yet chemical properties are fixed, biological systems are not, and there is the "biological" perspective of deciding how those biological systems adapted to the working materials available to them: the "fitness of the organism" to exploit fixed chemical starting materials. From this position of view, one is immediately attracted to the question: "What are the starting materials?" It is then useful to attempt to correlate biological activity with the crustal abundance of a given element. If we look at some typical essential transition elements, we find in addition to Fe, Co, Zn, Cu, and Mo mentioned previously, V, Cr, Mn, and Ni. Representative essential metals are Na, K, Mg, and Ca, and essential nonmetals are C, N, O, P, S, and Cl (see page 953). All of these elements except Mo are relatively abundant in the earth's crust (Table 9.4).

When we look for abundant elements that are not essential elements, we find only three—Al, Ti, and Zr—all of which form extremely insoluble oxides at biologically reasonable pH values. No common element is toxic at levels normally encountered, though almost anything can be harmful at too high levels (e.g., toxicity of the sodium chloride in sea water to freshwater plants and animals). When we consider the elements that are currently causing problems in the environment, we find that they are all extremely rare in their natural state.

### Table 19.3

<table>
<thead>
<tr>
<th>Atomic number</th>
<th>Element</th>
<th>Biological functions</th>
<th>Toxicity</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hydrogen</td>
<td>Molecular hydrogen metabolized by some bacteria.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Helium</td>
<td>None known.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Lithium</td>
<td>None known.</td>
<td>Slightly toxic.</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Beryllium</td>
<td>None known.</td>
<td>Very toxic.</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Boron</td>
<td>Unknown, but essential for green algae and higher plants; probably essential ultrarare element in animals.</td>
<td>Moderately toxic to plants: slightly toxic to mammals.</td>
<td>Carbon dioxide and CO are global pollutants from burning fossil fuels; CN(^-) is a local pollutant of rivers near mines.</td>
</tr>
<tr>
<td>6</td>
<td>Carbon</td>
<td>Synthesis of all organic molecules and of biogenic carbonates.</td>
<td>Carbon monoxide is slightly toxic to plants and very toxic to mammals; CN(^-) is very toxic to all organisms.</td>
<td>Leaching of nitrogenous fertilizers from agricultural land and nitrogenous materials in sewage cause serious water pollution. Nitrogen oxides are widespread source of acid rain.</td>
</tr>
<tr>
<td>7</td>
<td>Nitrogen</td>
<td>Synthesis of proteins, nucleic acids, etc. Steps in the nitrogen cycle (organic N → NH(_3) → NO(_2) → NO(_3) → N(_2) → organic N) are important activities of certain microorganisms.</td>
<td>Ammonia is toxic at high concentrations.</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Oxygen</td>
<td>Structural atom of water and most organic molecules in biological systems; required for respiration by most organisms.</td>
<td>Induces convulsions at high Pb(_{2+}) very toxic to ozone, superoxide, peroxide, and hydroxyl radicals.</td>
<td>Pollution by fluoride present in superflophosphate fertilizers. Ca. 1 ppm in water provides curative action; beneficial in the treatment of osteoporosis.</td>
</tr>
<tr>
<td>9</td>
<td>Fluorine</td>
<td>Probably essential element: used as CaF(_2) by some mollusks.</td>
<td>Moderately toxic, may cause mottled teeth.</td>
<td></td>
</tr>
</tbody>
</table>
The Structure and Action of Proteins: 1959

The quaternary structure of the hemoglobin and are responsible for the cooperative effects. These movements are the result of a change in the environment of the heme groups that produces the curves shown in Fig. 19.9. The presence of several bound dioxygen molecules favors the addition of more dioxygen molecules; conversely, if only one dioxygen molecule is present, it dissociates more readily than from a more highly oxygenated species. The net result is that at low dioxygen concentrations hemoglobin is less oxygenated (tends to release O\(_2\)) than with high concentrations.

Myoglobin does not exhibit the sigmoid shape shown in Fig. 19.8, perhaps because each protein chain is smaller and does not exhibit cooperativity. Myoglobin is largely converted to oxymyoglobin upon oxygenation of hemoglobin, and it is considered an approximate tetramer of myoglobin. It has a molecular weight of 64,500 and contains four heme groups bound to four protein chains (Fig. 19.8a). Two of the chains, labeled beta, have 146 amino acids and are somewhat similar to the chain in myoglobin; the other two, labeled alpha, have 141 amino acids and are somewhat less like the myoglobin chain. The differences between hemoglobin and myoglobin in their behavior towards dioxygen (particularly 3 and 4) are related to the structure and movement of the four chains. If the tetrameric hemoglobin is broken down into dimers or monomers, these effects are lost, and the smaller units do not exhibit cooperativity. Myoglobin does not exhibit the sigmoid shape nor a Bohr effect.

Upon oxygenation of hemoglobin, two of the heme groups move about 100 pm towards each other while two others separate by about 700 pm. Perhaps a better way of describing the movement is to say that one a/b half of the molecule rotates 15° relative to the other half. These movements are the result of a change in the quaternary structure of the hemoglobin and are responsible for the cooperative effects observed. The quaternary structure exhibited by the dioxy form is called the T state.

The 2.8 exponent for dioxygen results from the fact that a single hemoglobin molecule can accept four dioxygen molecules and the binding of the fourth is not independent. It is not the presence of four heme groups to bind four dioxygen molecules per se that is important. If they acted independently, they would give a curve identical to that of myoglobin. It is the cooperativity of the four heme groups that produces the curves shown in Fig. 19.9. The presence of several bound dioxygen molecules favors the addition of more dioxygen molecules; conversely, if only one dioxygen molecule is present, it dissociates more readily than from a more highly oxygenated species. The net result is that at low dioxygen concentrations hemoglobin is less oxygenated (tends to release O\(_2\)) than high dioxygen concentrations.

Hemoglobin binds one H\(^+\) for every two dioxygen molecules released. This favors oxygen transport since it helps the hemoglobin become saturated in the lungs and deoxygenated in the capillaries. There is a pH dependence shown by hemoglobin. This is known as the Bohr effect.

A simplified illustration of the Perutz mechanism is shown in Fig. 19.10. The key or trigger in the Perutz mechanism is a high spin Fe(II) atom in a dioxygen-free hemoglobin. As we have seen, the radius of high spin Fe(II) is too large to fit within the plane of the four porphyrin nitrogen atoms. The iron ion is thus forced to sit above the center of the heme group (Fig. 19.6; Fig. 19.11a) with an Fe—N distance of about 7.6 pm. Furthermore, the heme group is tilted towards the proximal histidine.

Hemoglobin may be considered an approximately tetramer of myoglobin. It has a molecular weight of 64,500 and contains four heme groups bound to four protein chains (Fig. 19.8a). Two of the chains, labeled beta, have 146 amino acids and are somewhat similar to the chain in myoglobin; the other two, labeled alpha, have 141 amino acids and are somewhat less like the myoglobin chain. The differences between hemoglobin and myoglobin in their behavior towards dioxygen (particularly 3 and 4) are related to the structure and movement of the four chains. If the tetrameric hemoglobin is broken down into dimers or monomers, these effects are lost, and the smaller units do not exhibit cooperativity. Myoglobin does not exhibit the sigmoid shape nor a Bohr effect.

Upon oxygenation of hemoglobin, two of the heme groups move about 100 pm towards each other while two others separate by about 700 pm. Perhaps a better way of describing the movement is to say that one a/b half of the molecule rotates 15° relative to the other half. These movements are the result of a change in the quaternary structure of the hemoglobin and are responsible for the cooperative effects observed. The quaternary structure exhibited by the dioxy form is called the T state.
The excess dietary iron is derived from a traditional fermented maize beverage that is home-brewed in steel drums. It should be noted that this connection between the body and iron, and except for women in the child-bearing years, the dietary requirement for iron is extremely low.

The absorption of iron in the gut, preferentially in the +2 oxidation state, was once thought to be a result of special physiological mechanisms, but now is generally agreed to be merely another aspect of the differential solubility of Fe(OH) and Fe(OH)₃. However, there is a significant differential in the absorption of heme versus nonheme iron: Heme iron is absorbed 5-10 times more readily than nonheme iron. Since meat contains large quantities of hemoglobin, myoglobin, and cytochromes, this difference could be nutritionally significant.

It is conceivable that iron could be stored in the form of a complex such as transferrin or even hemoglobin, and in lower organisms ferrichrome apparently serves this purpose. Such storage is wasteful, however, and higher animals have evolved a simpler method of storing iron as ferritin. If iron(III) nitrate is allowed to hydrolyze in a solution made slightly basic by the hydrogen carbonate ion (HCO₃⁻), it spontaneously forms spheres of Fe(OH)₃ of about 7000 pm in diameter. The core of a ferritin particle is similar and contains up to 4500 iron atoms and apparently some phosphate as well as oxo and hydroxo ligands. This core is surrounded by a protein covering (called apoferritin) that allows controlled access to the core through eight hydrophilic channels (along threefold axes) and six hydrophobic channels (along fourfold axes) (see Fig. 19.28). It is thought that the iron(II) enters via the hydrophilic channels and leaves via the hydrophobic channels, but the mechanism of iron transfer is obscure. In any event, ferritin provides high-density storage of inorganic iron combined with ready availability.

Fig. 19.28 Structural features of apoferritin. The gross quaternary structure of the assembled molecule is shown in the center and more details on the fourfold channels (left), the threefold channels (upper right) and the subunits (lower right) are also illustrated. [From Harrison, P. M.; Treffry, A.; Lilley, T. H. J. Inorg. Biochem. 1986, 27, 287-293. Reproduced with permission.]
The coordination of the dioxygen molecule as a sixth ligand causes spin pairing to take place on the iron atom. Since the radius of low spin Fe(II) is about 17 pm smaller than high spin Fe(II), it should fit in the porphyrin hole; we expect the smaller iron atom to drop into the hole. As a matter of fact, it does move about 20 pm towards the porphyrin ring (Fig. 19.11b) and the Fe—N_porph distance shortens to 198 pm. However, it stops short of moving all the way into the plane of the ring. Data for the heme in myoglobin, hemoglobin, and related species are given in Table 19.1.

Table 19.1

Distances (pm) and angles (°) in various heme adducts

<table>
<thead>
<tr>
<th>Compound</th>
<th>Fe—N_porph</th>
<th>Fe—P_porph</th>
<th>Fe—P_porph</th>
<th>Movement</th>
<th>Fe—O</th>
<th>Fe—O—O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whale Mb</td>
<td>203</td>
<td>222</td>
<td>42</td>
<td>267</td>
<td>39</td>
<td>183</td>
</tr>
<tr>
<td>MbO_2</td>
<td>205</td>
<td>207</td>
<td>18</td>
<td>228</td>
<td>39</td>
<td>183</td>
</tr>
<tr>
<td>Human Hb</td>
<td>206</td>
<td>215</td>
<td>38</td>
<td>268</td>
<td>2</td>
<td>182</td>
</tr>
<tr>
<td>HbO_2</td>
<td>204</td>
<td>220</td>
<td>18</td>
<td>266</td>
<td>2</td>
<td>182</td>
</tr>
<tr>
<td>Picket fence</td>
<td>198</td>
<td>200</td>
<td>0 ± 5</td>
<td>210</td>
<td>58</td>
<td>176 ± 10</td>
</tr>
</tbody>
</table>


** Average value of several methods of determination. See references in Footnote a for details.

† Bond lengths.

‡ Distance between the iron atom and the plane of the nitrogen atoms in porphyrin ring.

§ Distance between the nitrogen atom in the proximal histidine (or imidazole in the ‘picket-fence’ compounds) and the plane of the porphyrin ring.

# Movement of the proximal histidine (or imidazole) towards the porphyrin ring upon oxygenation.

"Picket fence" = tertrastabilized tetrapyrrolic porphyrinoid (Fig. 19.4); 1-Melm = 1-methylimidazole (4-methylimidazole); 2-Melm = 2-methylimidazole.

Fig. 19.11 The "trigger action" of the Perutz mechanism in hemoglobin. (a) Deoxy-T accepts a dioxygen molecule, O_2, to form oxy-T (b) with partial movement of the iron atom into the ring, which is strained and unstable. Addition of more dioxygen molecules at other sites results in a rearrangement of oxy-T to oxy-R (c) with the iron atom moving completely into the ring. (d) The configuration about the heme group with respect to Leu FG3 in the T and R forms. Note that the flattening of the porphyrin on going from deoxy to oxy exerts a leverage onLeu FG3 and Val FG5 which lie at the switching contact between the two structures. The vertical bars indicate the distance of N_porph of the proximal histidine from the mean plane of the porphyrin nitrogens. The horizontal bar gives the Fe—N_porph distance, and the value to the right of the iron atom gives the displacement of the iron from the plane of the porphyrin nitrogens. Note that the porphyrin is flat only in oxy-R and that the proximal histidine sits relative to the heme normal in the T structures. Note also the water molecule attached to the distal histidine in deoxy-R. The differences in heme geometry between the deoxyhemes in the T and R structures shown here are closely similar to those found between peripherally hindered 2-methyl- and unhindered 1-methylimidazole adducts with picket-fence porphyrin. [From Perutz, M. F.; Fermi, G.; Luisi, B.; Shanan, B.; Liddington, R. C. Acc. Chem. Res. 1987, 20, 309-321. Reproduced with permission.]
Competition for Iron

In addition to the transport of iron, the transferrins of higher animals and the siderophores of bacteria show another interesting parallel. It can most readily be shown by ovotransferrin (called conalbumin in the older literature) of egg white, though we shall see other examples. There is a large amount, up to 16%, in the protein of egg white, although it has been impossible to find an iron-transporting function for it there. In fact, in some 200 species for which ovotransferrin has been studied, 99% were completely devoid of iron binding to the protein! Ovotransferrin and other transferrins, in general, have larger stability constants towards iron(III) than do the various siderophores. It is thus quite likely that they act as antibacterial agents. In the presence of excess ovotransferrin, bacteria would be iron deficient since the siderophore cannot compete successfully for the iron.

Lactoferrin, found in mother’s milk, appears to be the most potent antibacterial transferrin and seems to play a role in the protection of breast-fed infants from certain infectious diseases. It has been claimed that milk proteins remain intact in the infant’s stomach for up to 90 minutes and then pass into the small intestine uncharged, thus retaining their iron-binding capacity. In guinea pigs, addition of hematin to the diet abolishes the protective effects of the mother’s milk.

The question of iron chelation as an antibacterial defense is receiving increasing attention. It appears to be far more general than had previously been supposed. An interesting sidelight is that the fever that often accompanies infection enhances the bacteriostatic action of the body’s transferrins.

Another interesting example of this sort is the competition between bacteria and the roots of higher plants. Both use chelators to win iron from the soil. However, higher plants have one more mechanism with which to compete: The Fe(III) is reduced and absorbed by the roots in the uncomplexed Fe(II) form. When edta and other chelating agents are used to correct chlorosis in plants due to iron deficiency, the action is merely one of solubilizing the Fe(III) and making it physically accessible to the roots—the chelates are not absorbed intact. Indeed, chelates that strongly bind Fe(III) may actually inhibit iron uptake from the root medium.

Exactly the opposite problem may occur for plants whose roots are growing in anaerobic media. In flooded soils the roots may be exposed to high levels of iron(II), posing potential problems of iron toxicity. Rice plants and water lilies with roots in anaerobic soils transport dioxygen (from the air or photosynthesis, or both) to the periphery of the roots where it oxidizes the iron(II) to iron(III). In this case, the insolubility of iron(III) hydroxide is utilized to protect the plant from iron poisoning.

A similar problem from too much iron occurs in parts of sub-Saharan Africa.
The inhibition of free movement of the iron atom into the porphyrin ring has been attributed to steric interactions between the histidine ligand (which must follow the iron), the associated globin chain, and the heme group. This apparently results in considerable strain on the oxyheme and associated tertiary structure of the globin within the T form. This discourages the addition of the first molecule of dioxygen, or more important, it "pushes" the last dioxygen molecule off in the tissues, where it is needed. Addition of a second dioxygen molecule takes place with similar results and, for the most part, the hemoglobin molecule becomes "spring-loaded". The structure of the bis(dioxygen)-T state has been determined and shows little movement of the iron atom and negligible movement of the histidine. The addition of a third dioxygen molecule results in interconversion to the R state. This removes the tension of the intermediate species and allows the iron atom to move freely into the center of the porphyrin ring (Fig. 19.11c). The porphyrin ring also flattens, and the histidine is free to follow the iron atom, some 50-60 pm. This change allows the fourth hemoglobin molecule to accept the iron atom without paying the price of the protein constraint and accounts for the avidity of Hb(O_{2})-4 for the last dioxygen molecule. The relaxation of the globin-heme interaction in the R state versus the crowding in the oxy-T state is shown in Fig. 19.11d.

Support for the view that the globin portion of the molecule produces a constraint upon the iron atom (which would otherwise move into the heme pocket) comes from the behavior of myoglobin and model compounds (such as the picket-fence compounds with 1- or 2-methylimidazole mimicking the porphyrin and histidine), which are easier to study than the more complex hemoglobin.

In myoglobin and the sterically hindered 2-methylimidazole complex (as in hemoglobin), the iron atom does not move into the plane of the porphyrin nitrogen atoms (remaining 9 pm displaced in the complex), although it does so in unhindered imidazole models, indicating that the iron atom does indeed shrink enough to fit were it not constrained. The data on the Fe—O bond length fit this picture: It is longer (and presumably weaker) in myoglobin and the 2-methylimidazole/picket-fence adduct (as it is in T hemoglobin) and shorter (and presumably stronger) in the unhindered 1-methylimidazole/picket-fence adduct (a R hemoglobin).

It was mentioned above that the T = R equilibrium was affected by pH (Lehr effect) as well as the partial pressure of dioxygen. Other species such as a single chloride ion and 2,3-diphosphoglycerate also influence the equilibrium. Of perhaps the greatest interest is the fact that the T — R transition involves the addition of about 60 molecules of water to the hemoglobin. This hydration of newly exposed protein surfaces stabilizes the R form which might not even be capable of existence without this hydration energy.

The above discussion has been somewhat simplified (inasmuch as the number of possible interactions in a molecule as large as hemoglobin is great). On the other hand, even as presented in abbreviated form, it is quite complicated. Various workers have placed varying degrees of weight upon different factors. Nevertheless, one should not lose sight of the fact that the iron atom does undergo a change in spin state that causes it to move, and the result is a change in the quaternary structure from T to R. And lest we get too involved in the biomechanical "trees" and forget to look at the biological "forest," it is to be noted that it is the reduced affinity of the T form that is nature's device that makes it possible for hemoglobin to push the dioxygen molecule off in the tissues and transfer it to myoglobin. We can thus look at dioxygen transport at several levels (go back to Fig. 19.8 and review).

Before leaving the subject of the binding of dioxygen to hemoglobin, two molecular (genetic) diseases should be mentioned. One is sickle cell anemia (SCA): Upon stressful deoxygenation of the blood, the hemoglobin (Hb) polymerizes and precipitates, resulting in severe deformation of the red blood cells. The genetic defect responsible is the replacement of hydrophilic glutamic acid at B-6 with the hydrophobic valine. The exposure of the latter upon R — T conversion reduces the solubility of hemoglobin S compared to normal adult hemoglobin. A.

It was mentioned above that heme(Fe^{2+}) will not bind dioxygen. Home is always susceptible to oxidation when in the presence of dioxygen. This reaction results from the nucleophilic displacement of superoxide by water, and it is acid catalyzed: 39

\[
\text{[Fe(H)}_{2}\text{O}_{4}]^{2-} + \text{H}^+ \rightarrow \text{[Fe(H)}_{2}\text{O}_{3}]^{3+} + \text{H}_2\text{O}
\]

The globin chain gives some protection by providing a hydrophobic environment, but still about 3% of the hemoglobin is oxidized to methemoglobin daily. The enzyme methemoglobin reductase reduces the oxidized hemoglobin back to the R state at a rapid rate.

However, some individuals have an inherited metabolic defect that prevents the reduc-
Availability of Iron

Although iron is the fourth most abundant element in the earth's crust, it is not always available to the plant for the manufacture of amino acids. From Skinner, K. J. Chem. Eng. News 1976, 54(14), 22-35. Reproduced with permission.

Abundant transitional element and serves more biological roles than any other metal. It can therefore serve to illustrate the possibilities available for the absorption, storage, handling, and use of an essential metal. Iron has received much study, and similar results can be expected for other metals as studies of the chemistry of trace elements in biological systems advance.

The presence of organic chelates of iron in surface waters has been related to the "red tide," an explosive "bloom" of algae (Gymnodium breve) that results in mass mortality of fish. It is possible to correlate the occurrence of these outbreaks with the volume of stream flow and the concentrations of iron and humic acid. At least one of the dinoflagellates in the red tide possesses an iron-biding siderophore (see below).

Within the organism a variety of complexing agents are used to transport the iron. In higher animals it is carried in the bloodstream by the transferrins. These iron-binding proteins are responsible for the transport of iron to the site of synthesis of other iron-containing compounds (such as hemoglobin and the cytochromes) and its insertion via enzymes into the porphyrin ring. The iron is present in the +3 oxidation state (FeIII does not bind) and is coordinated to two or three tyrosyl residues, a couple of histidyl residues, and perhaps a tryptophanyl residue in a protein chain of molecular weight about 80,000. There are two iron-binding sites per molecule.

Most aerobic microorganisms have analogous compounds, called siderophores, which solubilize and transport iron(III). They have relatively low molecular weights (500-1000) and, depending upon their molecular structure and means of chelating iron, are classified into several groups such as the ferrichromes, ferrioxamines, and enterobactins. Some examples are shown in Fig. 19.26. It is obvious that these molecules are polydentate ligands with many potential ligating atoms to form chelates. They readily form extremely stable octahedral complexes with high spin Fe(II). Although the complexes are very stable, which is extremely important to their biological function (see below), they are labile, which allows the iron to be transported and transferred within the bacteria. The ferrichromes and ferrioxamines are trihydroxy acids which form neutral bischelates from three bidentate hydroxamates. Enterobactin contains a different chelating functional group, o-dihydroxybenzene ("catechol"). Each catechol group in enterobactin behaves as a dianion for a total charge of -6 for the ligand. A characteristic of all of these is that, in addition to the natural tendency of trischelates to form globular complexes, the remainder of the siderophore molecule consists of a symmetric, hydrophilic portion that presumably aids in transport across the cell membrane (Fig. 19.27).

It is interesting that biologically functioning iron compounds such as hemoglobin, myoglobin, and cytochromes, and ferrioxamines employ iron(II) compounds, but the siderophores and transferrins coordinate iron(III). The reduced iron compounds within biological systems may reflect an evolutionary history from a primitive reducing atmosphere on earth (see page 551), whereas the siderophores are the response to the need to deal currently with iron(III) in an oxidized external environment.

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Dioxygen Carriers invertebrates. Its chief interest to the chemist lies in certain similarities to and differences from hemoglobin and myoglobin. Like both of the latter, hemerythrin contains iron(II) which binds oxygen reversibly, but when oxidized to methemerythrin (Fe^{3+}) it does not bind dioxygen. There is an octameric form with a molecular weight of about 108,000 that transports dioxygen in the blood. In the tissues are lower molecular weight monomers, dimers, trimers, or tetramers. And just as hemoglobin consists of four chains each of which is very similar to the single chain of myoglobin, octameric hemerythrin consists of eight subunits very similar in quaternary structure to myohemerythrin. A major difference between the hemoglobins and hemerythrins is in the binding of dioxygen. Each dioxygen-binding site (whether monomer or octamer) contains two iron(II) atoms, and the reaction takes place via a redox reaction to form iron(III) and peroxide (O_2^-). Oxyhemerythrin is diamagnetic, indicating spin coupling of the odd electrons on the two iron(III) atoms. Mössbauer data indicate that the two iron(III) atoms are in different environments in oxyhemerythrin. This could result from the peroxide ion coordinating one iron atom and not the other, or from each of the iron atoms having different ligands in its coordination sphere. The first evidence concerning the nature of the ligands came from an X-ray study of methemerythrin. It indicated that the two iron atoms have approximately octahedral coordination and are bridged by an oxygen atom (from water, hydroxide, or oxo), aspartate, and glutamate. The remaining ligands are three histidine residues on one iron atom and two histidines on the other. This is a rather small difference, but it can be reconciled with the other data, and so until recently the consensus has tended to favor a simple peroxo bridge between the two iron atoms:

$$\text{Fe}^{III} + \text{O}_2 \rightarrow \text{Fe}^{III} + \text{O}_2^-$$

where the continuous line connecting the two iron atoms is a simplified representation of the coordination spheres and the protein chain holding the iron atoms in place. Malignant against this simple structure is the fact that the Mössbauer spectrum does not distinguish the iron atoms in deoxyhemerythrin. If the difference in amino acid environment is sufficient to distinguish the iron atoms in the Mössbauer spectrum of oxyhemerythrin, why not in deoxyhemerythrin?

Further data on this matter came from the Raman spectrum of oxy[^1O] hemerythrin, which shows the two oxygen atoms to be in nonequivalent positions. Of the various alternative structures that have been proposed, the Raman data are compatible with only two:

$$\text{Fe}^{III} \quad \text{Fe}^{III}$$

$$\text{Fe}^{III} \quad \text{Fe}^{III}$$

[^1O]O_2 data, as well as other spectroscopic evidence, are compatible with structure III, but the question was still open until the X-ray structure of oxyhemerythrin was further refined. The proposed structures of deoxyhemerythrin and oxyhemerythrin are:

$$\text{Fe}^{III} \quad \text{Fe}^{III}$$

Note that the hydrogen atoms cannot be located at this level of resolution and so the hydrogen bond shown is merely one suggestion for the possible stabilization of the peroxo ion.

Another oxygen-containing pigment is confusingly named hemocyanin, which contains neither the heme group nor the cyanide ion; the name simply means "blue pigment."
The reduction of mono-coordinated molecular nitrogen to ammonia in a protic environment.

Fuel-saving way to make fertilizer

Fuel break-through

More progress in nitrogen fixation

Cheaper nitrogen by 1990

Basic life process created in UK lab


The Times (Jan. 3, 1975)

The Guardian (Jan. 3, 1975)

New Scientist (Jan. 9, 1975)

Farmer's Weekly (Jan. 10, 1975)

The Province (British Columbia, Jan. 15, 1975)

With each retelling the story grew, until by the time it reached British Columbia, it appeared that the press was almost able in 12 days to duplicate what is recorded as a 6-day event in Genesis! The result: disappointment when scientists are not able to meet expectations benefit neither them nor the public (but that, too, is good copy for the popular press!).

There are several bacteria and blue-green algae that can fix molecular nitrogen in vivo. In Vivo Nitrogen Fixation

Both free-living species and symbiotic species are involved. There are the strictly aerobic species Chaolesidium paratermonium, facultative aerobes like Klebsiella pneumoniae, and strict aerobes like Azotobacter vinelandii. Even in the aerobic forms it appears that the nitrogen fixation takes place under essentially anaerobic conditions (see below). The most important nitrogen-fixing species are the mutualistic species of Rhizobium living in root nodules of various species of legumes (clover, alfalfa, beans, peas, etc.).

The active enzyme in nitrogen fixation is nitrogenase. It is not a unique enzyme but appears to differ somewhat from species to species. Nevertheless the various enzymes are very similar. Two proteins are involved. The larger protein is an a₂b₃ complex having a molecular weight of 57,000-73,000. It contains an Fe₄S₉ cluster containing molybdenum and iron (ca. 1 Mo, 7-8 Fe, and 4-6 S). Recombination of the cofactor with inactive nitrogenase restores the activity.

The ultimate source of reductive capacity is pyruvate, and the electrons are transferred via ferredoxin (see page 911) to nitrogen gas. Alternatively, since the enzyme is rich in ferredoxin-type clusters, there should be a ready flow of electrons, and the molybdenum may stay in the one or two oxidation states that most readily bind dinitrogen and its intermediate reductants. The overall catalytic cycle may resemble that shown in Eq. 19.38.

A schematic diagram for the formation of dinitrogen compounds, including the sources of materials and energy, and the overall reactions, is given in Fig. 19.25. Note the presence of leghemoglobin. This is a monomeric oxygen-binding molecule rather closely resembling myoglobin. It is felt that the leghemoglobin binds any oxygen that is present very tightly and thus protects the nitrogenase, which cannot be present in the presence of oxygen. On the other hand, it allows a reservoir of oxygen for respiration to supply energy to keep the fixation process going.

The structure of nitrogenase has now been determined. It is thought that the coordination sphere consists of several sulfur atoms at distances of about 235 pm. As Mo=O-O double bond, so common in complexes of Mo(IV) and Mo(VI), is not present. There are other heavy atoms, perhaps iron, nearby (ca. 270 pm). The ultimate source of reductive capacity is pyruvate, and the electrons are transferred via ferredoxin (see page 911) to nitrogenase. There is some evidence, not strong, that Mo(III) is involved. Two Mo(III) atoms cycling through Mo(VI) would provide the six electrons necessary for reduction of dinitrogen. Alternatively, since the enzyme is rich in ferredoxin-type clusters, there should be a ready flow of electrons, and the molybdenum may stay in the one or two oxidation states that most readily bind dinitrogen and its intermediate reductants. The overall catalytic cycle may resemble that shown in Eq. 19.38.

Note added in proof: The structure of the Fe-Mo cofactor cited in Footnote 97 has led these authors to suggest that the molybdenum does not directly participate in binding the diatomic molecule. The Mo is already six coordinate with three S atoms, two O atoms from a homocitrate anion, and one N atom from a histidine in the protein chain. Therefore, in Eq. 19.38 the N₂ is probably bound to an Fe-S cluster in place of Mo.

Cheaper nitrogen by 1990 (Jan. 10, 1975)

New Scientist

Fuel-breakthrough (Jan. 3, 1975)

The Times

Fuel-saving way to make fertilizer (Jan. 3, 1975)

Fuel break-through (Jan. 3, 1975)

More progress in nitrogen fixation (Jan. 9, 1975)

Cheaper nitrogen by 1990 (Jan. 10, 1975)

Basic life process created in UK lab

The Biochemistry of Iron

It is impossible to cover adequately the chemistry of various elements in biological systems in a single chapter. Before discussing the salient points of other essential and trace elements, the biochemistry of iron will be discussed briefly.

The Biochemistry of Iron


The Times (Jan. 3, 1975)

The Guardian (Jan. 3, 1975)

New Scientist (Jan. 9, 1975)

Farmer's Weekly (Jan. 10, 1975)

The Province (British Columbia, Jan. 15, 1975)


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The Times (Jan. 3, 1975)

The Guardian (Jan. 3, 1975)

New Scientist (Jan. 9, 1975)

Farmer's Weekly (Jan. 10, 1975)

The Province (British Columbia, Jan. 15, 1975)
blood**; whereas hemoglobin turns bright red upon oxygenation, the chromophore (Ca^+Cu^II) in colorless deoxyhemocyanin turns bright blue. Hemocyanin is found in many species in the Mollusca and Arthropoda. The gross molecular structures of the hemocyanins of the two phyla are quite different, though both bind dioxygen cooperatively, and spectroscopic evidence indicates that the dioxygen-binding centers are similar. The dioxygen binding site appears to be a pair of copper atoms, each bound by three histidine ligands (Fig. 19.12). The copper is in the +1 oxidation state in the deoxy form and +2 in the oxy form.

The structure of oxyhemocyanin has recently been determined. It presents yet a third mode of binding between oxygen-carrying metal atoms and the dioxygen molecule. The latter oxidizes each copper(II) to copper(III) and is in turn reduced to the peroxide ion (O_2^-). The two copper(II) atoms are bridged by one peroxide ion with unusual μ-η^-2:η^-2 bonds, i.e., each oxygen atom is bonded to both copper atoms.

The parallels and differences among hemoglobin, hemerythrin, and hemocyanin illustrate the ways in which evolution has often solved what is basically the same problem in different ways in different groups of animals.**

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![Fig. 19.12 The copper-dioxygen binding site in hemocyanin from Panulirus interruptus. The copper atoms are indicated by open circles, the histidines by pentagons, and the protein chains by ribbons. (From Volbeda, A.; Holm, W. G. J. J. Mol. Biol. 1989, 206, 240-279. Reproduced with permission.)](image-url)
Metallothioneins

We have seen that heavy metals can replace essential metals in enzymes and destroy the enzymatic activity. In addition, by coordinating to sulfur-bearing amino acids in the protein chain they might cause an enzyme to be "bent out of shape" and lose its activity. Protection of enzymes from toxic metals is thus requisite for their proper function. Searching for this purpose is a group of proteins that have the following characteristics: (1) The molecular weights are about 6000 with 64 to 66 amino acids. (2) One-third (20) of these amino acids are cysteine [HSC(=CH(NH2)COOH)] residues, grouped in Cys-Cys-Cys = Cys groups (X = a separating amino acid). (3) None of the cysteines are linked by S-S bridges (cystine). (4) There are few if any histidines or amino acids with aromatic side chains. (5) With such a high percentage of amino acids bearing thiol groups and "clumped" along the protein chain, the thionelins are able to bind several metal ions per molecule, preferentially the softer metals such as Zn$^{2+}$, Cd$^{2+}$, Pb$^{2+}$, Ag$^+$, etc. Metalloclothioneins containing Zn$^{2+}$ and Cd$^{2+}$ helpfully, possibly important in the transport of these essential elements, but the evidence is mostly negative. On the other hand, the binding of heavy metals such as cadmium and mercury suggests a protective function against these toxic metals. Indeed, increased amounts of thionelins are found in the liver, kidney, and spleen after exposure to them. Furthermore, it can be demonstrated that cell lines that fail to produce thionelins are extremely sensitive to cadmium poisoning while "over-producers" have enhanced protection. It is suggested that the binding of thionelins to cadmium and other heavy metals, with extremely high stability constants, is one of protection alone; perhaps the reduced binding of copper, an essential metal but one toxic in high concentrations, serves as a "buffering function" of providing copper for enzymes but not at levels sufficiently high to be toxic. The question of whether the weaker binding of the less toxic zinc serves a similar function, or "just happens," is moot.

For 2 cations such as zinc$^{2+}$ and cadmium$^{2+}$ or metallothionein molecule contains up to seven metal atoms. X-ray studies indicate that the metal atoms are in approximately tetrahedral sites bound to the cysteine sulfur atoms. The soft mercury$^{2+}$ ion has a higher affinity for sulfur and will displace cadmium from metallothionein. At first the mercury ions occupy tetrahedral sites, but as the number increases, the geometries of the metal sites and protein change until about nine (Hg$^{2+}$) atoms are bound in a linear (S—Hg—S) fashion.93 Up to twelve + 1 cations such as copper(II) and silver(I) can bind per molecule, indicating a coordination number higher than four, probably three (see Problem 12.34).

An intriguing problem about which we know very little is the mechanism of metal identification by the body that triggers its response, as in the case of the build-up of metallothionein upon exposure to toxic metals. Perhaps the best understood of the metalloregulatory proteins is MerR that protects bacteria from mercurial toxicity. It is a repressor-type DNA-binding protein. It contains up to seven metal atoms. X-ray studies indicate that the metal atoms are in approximately tetrahedral sites bound to the cysteine sulfur atoms. The soft mercurial ion has a higher affinity for sulfur and will displace cadmium from metallothionein. At first the mercury ions occupy tetrahedral sites, but as the number increases, the geometries of the metal sites and protein change until about nine (Hg$^{2+}$) atoms are bound in a linear (S—Hg—S) fashion.93 Up to twelve + 1 cations such as copper(II) and silver(I) can bind per molecule, indicating a coordination number higher than four, probably three (see Problem 12.34).

A repressor-type DNA-binding protein. It contains up to seven metal atoms. X-ray studies indicate that the metal atoms are in approximately tetrahedral sites bound to the cysteine sulfur atoms. The soft mercurial ion has a higher affinity for sulfur and will displace cadmium from metallothionein. At first the mercury ions occupy tetrahedral sites, but as the number increases, the geometries of the metal sites and protein change until about nine (Hg$^{2+}$) atoms are bound in a linear (S—Hg—S) fashion.93 Up to twelve + 1 cations such as copper(II) and silver(I) can bind per molecule, indicating a coordination number higher than four, probably three (see Problem 12.34).


Nitrogen Fixation

An enzyme system of particular importance is that which promotes the fixation of atmospheric dinitrogen. This is of considerable interest for a variety of reasons. It is a very important step in the nitrogen cycle, providing available nitrogen for plant nutrition. It is an intriguing process since it occurs readily in various bacteria, nitrogen-fixing algae, yeasts, and in symbiotic bacteria-legume associations under mild conditions. However, nitrogen fixation remains resistant to artificial chemical attack, even under stringent conditions.

Molecular nitrogen, N$_2$, is so unresponsive to ordinary chemical reagents that it has been characterized as "almost as inert as a noble gas."99 The very large triple bond energy (943 kJ mol$^{-1}$) tends to make the activation energy prohibitively large. Thus, in spite of the fact that the overall enthalpy of formation of ammonia is exothermic by about 39.9 kJ mol$^{-1}$, the common Haber process requires about 20 MPa pressure and 500 °C temperature to proceed, even in the presence of the best Haber catalyst. In addition to the purely pragmatic task of furnishing the huge supply of nitrogen compounds necessary for industrial and agricultural uses, we can easily imagine the possibility of discovering processes that will work under less drastic conditions. We know that they exist. We can watch a clover plant growing at 100 kPa and 25 °C!

In Vitro Nitrogen Fixation

The discovery that dinitrogen was capable of forming stable complexes with transition metals (Chapter 1) led to extensive investigation of the possibility of fixation via such complexes. An important development was the discovery that certain phosphine complexes of molybdenum and tungsten containing dinitrogen readily yield ammonia in acidic media.99

$$\text{[MoCl}_5\text{(thd)}_2 + 3e^- + \text{NH}_3 + \text{H}_2\text{O}]^- \rightarrow \text{[MoCl}_5\text{(thd)}_2^{-1} + 3\text{Cl}^-} \quad (19.36)$$

$$\text{[MoCl}_5\text{(dpe)}_2 + 6\text{H}^+ + 2\text{NH}_3 + 2\text{MoO}_4^{2-}] \quad (19.37)$$

where thd = tetrahydrofuran and dpe = 1,2-bis(diethylphosphino)ethane. Ph,PCH$_2$CH$_2$PPH$_2$. Both reactions take place at room temperature and atmospheric pressure. The reducing agent is a Grignard reagent. This reaction sequence is important because it models the in vivo nitrogenase systems that appear to employ molybdenum. We should not conclude, however, that ambient temperature and pressure reactions are likely to replace the Haber Bosch process. Despite the fact that the latter requires high temperature and pressure, it is efficient and well entrenched, and it can produce large volumes of product in short time periods. With respect to the former processes, it is certain that the chemist will not be able to keep pace with the lively imagination of the chemist. As an interesting aside on the inherent instability of the scientist to match ever increasing expectations, the reader is directed to the following selection of titles and headlines. The first is the title of the initial research report by Chatt's group in England and the remainder are headlines of various reports of it in the popular press:

The three most important redox systems in bioinorganic chemistry are: (1) high spin, tetrahedral Fe(II)/Fe(III) in rubredoxin, ferredoxin, etc.; (2) low spin, octahedral Fe(II)/Fe(III) in the cytochromes; and (3) pseudotetrahedral Cu(I)/Cu(II) in the blue copper proteins, such as stellacyanin, plastocyanin, and azurin. Gray has pointed out that these redox centers are ideally adapted for electron transfer in that no change in spin state occurs. Thus there is little or no movement of the ligands—the Franck-Condon activation barriers will be small.

The structure of plastocyanin (Fig. 19.14) is especially instructive in this regard. Copper(II) is $d^9$ and thus provides no ligand field stabilization energy in any geometry. Because it is relatively small (74 pm), it is usually found in a tetrahedral environment. In contrast, copper(I) is $d^9$ and is usually octahedrally coordinated with Jahn–Teller distortion, often to the point of square planar coordination. In the case of plastocyanin, the copper is situated in a "flattened tetrahedron" of essentially C$_4$ symmetry, "halfway" between the two idealized geometries. This facilitates electron transfer compared to a system that might be at the tetrahedral extreme or at the square planar extreme: Energetically, either of the latter would require reorganization to react with the intended target species and not be "short-circuited" by reacting uselessly with the wrong redox agent.

The determination of the structures of biologically important copper-containing redox systems illustrates the multiplicity of techniques that can be brought to bear on structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structural bioinorganic chemistry. Ultimately, one would like to have a highly refined structur...
In biological systems the two-electron reduction may be accomplished by NADH and flavin adenine dinucleotide (FAD). The methyl donor is N⁵-methyltetrahydrololate (CH₃-THF). The Co(III) corrinoid (methylcobalamin) can then participate in biomethylation reactions:

\[
\text{CH}_3\text{-THF} \rightarrow \text{B}_{12}(\text{Co}^\text{II}) \rightarrow \text{methionine} \rightarrow \text{homocysteine}
\]  (19.33)

Certain bacteria can methylate not only sulfur in organic compounds but also various heavy metal ions such as Hg, As, Ti, Pb, Sn, Au, Pd, and Pt in anerobic sludges. Thus, heavy metal ions can form inorganic mercury compounds methylmercury cation, CH₃Hg⁺, may be formed from inorganic mercury compounds. It is believed that the reaction starts with homolytic cleavage of the cobalt-carbon bond (at a cost of perhaps 100 kJ mol⁻¹) to yield a Co(I) atom and a 5'-deoxyadenosyl radical. This radical then abstracts a hydrogen atom (in Eq. 19.35 from the methyl group). Migration of the —C(0)SR group takes place, followed by return of the hydrogen atom from 5'-deoxyadenosine to the substrate. This regenerates the 5'-deoxyadenosine radical, which can recombine with the Co(III) atom to form the coenzyme.

B₁₂ is unusual in several ways. The ability to form a metal-carbon bond in a biological system appears to be unique. These are nature's only organometallic compounds. It is the only vitamin known to contain a metal. It appears to be synthesized exclusively by bacteria. It is not found in higher plants, and although it is essential for all higher animals, it must be obtained from food sources, hence its designation as a "vitamin." The fitness of cobalamin to serve its biochemical functions has been variously ascribed to different factors by different authors. Certainly, the existence of three oxidation states, Co(I), Co(II), and Co(III), in aqueous (and hence biological) media is necessary. This, in itself, may eliminate the earlier transition metals (without accessible + I oxidation states) and copper (Cu(I) is strongly oxidizing). In addition, we have seen that 18e⁰ systems are ideal for oxidative addition/reductive elimination reactions. It has also been suggested that the flexibility of the corrin ring allows changes in conformation that may be beneficial. In this regard it may be noted that the cobalt porphyrin analogues of B₁₂ cannot be reduced to Co(I) in aqueous solution. Hence the corrin ring was selected in place of porphyrin in the evolution of the B₁₂ cobalt complexes.

It is believed that the reaction starts with homolytic cleavage of the cobalt-carbon bond (at a cost of perhaps 100 kJ mol⁻¹) to yield a Co(III) atom and a 5'-deoxyadenosine radical. This radical then abstracts a hydrogen atom (in Eq. 19.35 from the methyl group). Migration of the —C(0)SR group takes place, followed by return of the hydrogen atom from 5'-deoxyadenosine to the substrate. This regenerates the 5'-deoxyadenosine radical, which can recombine with the Co(III) atom to form the coenzyme.

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89 This reaction of yesterday is currently being challenged—there is increasing evidence of other biological metal-carbon bonds, but, unlike B₁₂, most of the suspected compounds have been isolated and characterized.

electrons to unoccupied orbitals or to the continuum. By choosing X-ray frequencies near the X-ray edge of a particular element, atoms of that element can be excited to emit photoelectrons. The wave of each electron is backscattered by the nearest neighbors in proportion to the number and kind of the ligands and inversely proportional to the interatomic distance. If the backscattered wave is in phase with the original wave, reinforcement will occur, yielding a maximum in the X-ray absorption spectrum. Out-of-phase waves will cancel and give minima. The EXAFS spectrum consists, then, of the X-ray absorption plotted against the energy of the incident X-ray photon. The amplitudes and frequencies of the oscillations in the absorption are related to the number, type, and spacing of the ligands. Thus if one bombards heme with an X-ray frequency characteristic of an iron edge, it should, in principle, be possible to learn that there are four atoms of atomic number 7 equidistantly surrounding the iron atom.

Some EXAFS data for copper proteins are given in Table 19.2. Confirming data from X-ray crystallography are also listed where known. Copper is particularly well suited for study by electron paramagnetic resonance. At the simplest level, this method can distinguish between the presence of an odd electron (Cu$^{1+}$, EPR signal) and complete electron pairing (Cu$^{2+}$, no EPR signal). Ligands with nuclei having nonzero spins (such as nitrogen) will cause hyperfine splittings proportional to the number of such atoms bonded to the copper(II) atom (see page 923 with respect to Cu$^{II}$-substituted carbamoylpeptide A). Finally, a study of the hyperfine splitting, some of it resulting from the copper atom's nonzero nuclear spin, can provide geometric information (see below).

Analysis of ligand field and charge transfer absorption bands can provide information concerning the geometry of the copper site and the nature of the ligand, though mostly of a qualitative sort; values for bond angles and bond lengths cannot be quantified. It is often useful in this regard to attempt the synthesis and structural determination of model compounds and to try to match their properties with those of the active sites in the metalloproteins. These efforts, combined frequently with theoretical calculations of the same properties, often allow predictions to be made concerning the nature of the active sites. For example, while the structures of azurin and plastocyanin have been determined by X-ray crystallography, that of the related blue copper protein stellacyanin has not because suitable crystals have not yet been grown. Spectral studies have indicated that three of the four ligands (His, His, Cys) are the same in plastocyanin and stellacyanin, but that the latter does not contain the methionine ligand found in the former. A combination of electron paramagnetic resonance and electronic spectral data with self-consistent-field calculations has indicated that the unknown fourth ligand in stellacyanin provides a stronger field than does methionine. It presumably results in a shorter Cu–X bond as well as a flattening of the geometry more towards a square planar arrangement.

The synthesis of model compounds has proved to be an interesting challenge. The Cu$^{2+}$ ion is a sufficiently strong oxidizing agent to couple two sulfhydryl groups:

$$2\text{RSH} \rightarrow \text{RS} - \text{SR} + 2\text{H}^+ \quad (19.20)$$

Thus any simple attempt to let thiolate coordinate to Cu$^{II}$ will result in persulfides and Cu(I).

$$2\text{L}_2\text{Cu}^{II}\text{RSH} \rightarrow \text{L}_2\text{Cu}^{II}\text{SH} + 2\text{L}_2\text{Cu}^{II}$$

As shown in Eq. 19.21, it is thought that this reaction takes place through a dimeric, bridged intermediate of coordination number 5. Copper tends to form a maximum of five strong bonds and two weak ones (Chapter 11). As shown in Eq. 19.21, it is thought that this reaction takes place through a dimeric, bridged intermediate of coordination number 5. Copper tends to form a maximum of five strong bonds and two weak ones (Chapter 11).

$$2\text{L}_2\text{Cu}^{II}\text{RSH} \rightarrow \text{L}_2\text{Cu}^{II}\text{SH} + 2\text{L}_2\text{Cu}^{II}$$

As shown in Eq. 19.21, it is thought that this reaction takes place through a dimeric, bridged intermediate of coordination number 5. Copper tends to form a maximum of five strong bonds and two weak ones (Chapter 11). For a comprehensive discussion, see Solomon, E. I.; Baldwin, M. J.; Lowery, M. D.; Solomon, E. I. Annu. Rev. Biochem. 1991, 60, 591-591. This discussion of the study of blue copper proteins has necessarily been brief. For a comprehensive discussion, see Solomon, E. I.; Baldwin, M. J.; Lowery, M. D. Chem. Rev. 1992, 92, 525-535.

$^{4}$ See Chapter 7. Copper(I) undergoes Jahn-Teller distortion when six-coordinate and tends to form four strong bonds and two weak ones (Chapter 11).

This enzyme catalyzes the oxidation of xanthine to uric acid:

\[
\text{Xanthine} \rightarrow \text{Mo} \rightarrow 2\text{Fe}_2\text{S}_2 \rightarrow \text{FAD} \rightarrow \text{O}_2
\]  \hspace{1cm} \text{(19.29)}

The electron flow may be represented as:

\[
\text{Xanthine} \rightarrow \text{Mo} \rightarrow 2\text{Fe}_2\text{S}_2 \rightarrow \text{FAD} \rightarrow \text{O}_2
\]  \hspace{1cm} \text{(19.30)}

Uric acid is the chief end product of purine metabolism in primates, birds, lizards, and snakes. An inborn metabolic error in humans results in increased levels of uric acid and its deposition as painful crystals in the joints. This condition (gout) may be treated by the drug allopurinol which is also oxidized by xanthine oxidase to allo-xanthine (dashed line in Eq. 19.29). However, alloxanlhine binds so tightly to the molybdenum that the enzyme is inactivated, the catalytic cycle broken, and uric acid formation is inhibited. The extra stability of the alloxanthine complex may be a result of strong N—H---N hydrogen bonding by the nitrogen in the 8-position:

\[
\text{This structure resembles the hydrogen bonded transition state for the nucleophilic attack of hydroxide ion (Eq. 19.29) where the hydrogen bond promotes the attack on the carbon. With a nitrogen atom at the 8-position there is no way for the alloxanthine to leave.}^{63}
\]

A closely related enzyme is aldehyde oxidase. It also contains two (Mo/2Fe_2S_2/FAD) units with a molecular weight of about 300,000. It converts acetalddehyde to acetic acid via electron flow:

\[
\text{Acetalddehyde} \rightarrow \text{Mo(VI)} \rightarrow 2\text{Fe}_2\text{S}_2 \rightarrow \text{FAD} \rightarrow \text{O}_2
\]  \hspace{1cm} \text{(19.31)}

When ethanol is consumed, the initial metabolic product is the extremely poisonous acetalddehyde, which is kept in low concentration by the oxidase-catalyzed conversion to harmless acetic acid. The drug Antabuse, used for treating alcoholism, is a sulfon-containing ligand, disulfiram:

\[
\text{S} \hspace{1cm} \text{S} \hspace{1cm} \text{S} \hspace{1cm} \text{S} \hspace{1cm} \text{S}
\]

\[
\text{Et}_{2}\text{N}—\text{C}—\text{S}—\text{S}—\text{C}—\text{NEt}_2
\]

In the body, Antabuse inhibits acetalddehyde oxidase, presumably via the soft-soft molybdenum-sulfur interaction.\(^{64}\) Any alcohol ingested will be converted to acetalddehyde which, in the absence of a pathway to destroy it, will build up with severely unpleasant effects, discouraging further consumption.

In 1948 an "anti-pernicious anemia factor" was isolated, crystallized, and named vitamin B_12 or cyanocobalamin. The molecule is built around a corrin ring containing a cobalt(III) atom. The corrin ring is a modified porphyrin ring in which one of the =CH— bridges between two of the pyrrole-type rings is missing, contracting the ring. The fifth and sixth coordination sites on the cobalt are filled by a nitrogen atom from an imidazole ring and a cyanide ion. The latter is an artifact of the isolation procedure and is not present in the biological system, where the sixth position appears to hold a loosely bound water molecule.

\[
\text{Vitamin B}_{12}\text{ may be reduced by one electron ("vitamin B}_{12}'\) or two electrons ("vitamin B}_{12}"') to form the Co(I) and Co(II) complexes, respectively.}^{65}\]

\[
[\text{B}_{12}\text{(Co)I} + \text{CH}_3\text{I} \rightarrow [\text{B}_{12}\text{(CoII)}—\text{CH}_3]^+ + \text{I}^- \hspace{1cm} \text{(19.32)}
\]

The above surmise is based on the known chemistry between molybdenum and sulfur-containing ligands. It has been suggested that disulfiram inhibits the enzyme by oxidizing essential sulfhydryl groups to form internal S—S bonds (see Vallari. R. C.; Pietruszko, R. Science 1982, 216, 637). Disulfiram is also used to prevent renal toxicity from platinum when cis-diamminedichloroplatinum (II) (see page 938) is used to treat neoplasms and trypanosomiasis (see Wysor, M. S.; Zwelling, L. A.; Sanders, J. E.; Grcnan, M. M. Science 1982, 217, 434-456). The complexing agent is thought to be dicthyldithiocarbamate, a metabolite of disulfiram.

\[
\]

\[
\text{The r stands for "reduced" and the s for "super-reduced." The letter r may seem to be something of an exaggeration until one recalls that the predominant coordination chemistry of cobalt is that of Co(III), with less for Co(II), and very little for other oxidation states.}
\]

\[
\text{See Chapter 15 with respect to the basicity of metals in low oxidation states and oxidative addition reactions.}
\]
The photosynthetic process in green plants consists of splitting the elements of water, followed by reduction of carbon dioxide:

\[ \text{H}_2\text{O} \rightarrow [\text{4H}^+] + \frac{1}{2}\text{O}_2 \]  

where [\text{4H}^+] does not imply free atoms of hydrogen but a reducing capacity of four equivalents. The details of the reactions involved in photosynthesis are not known, although the broad outlines are fairly clear. In all dioxygen-producing organisms ranging from cyanobacteria to algae to higher plants, there are two coupled photosynthetic systems, PS I and PS II. The two differ in the type of chlorophyll present and in the accessory chemicals for processing the trapped energy of the photon. The primary product of PS I is reduced carbon, and the primary product of PS II is energy in the form of two moles of ATP with molecular oxygen as a chemical by-product.

In addition to the chlorophyll molecules at the reaction centers of PS I and PS II, there are several other pigments associated with the light-harvesting complexes. Among these are carotenoids, open-chain tetrapyrrole pigments, and others. These serve dual roles of protecting the cell from light radiation and at the same time harvesting much of the light energy and funneling it into the reaction centers.

The energy of an absorbed photon in either PS I or PS II initiates a series of redox reactions (see Fig. 19.16). System I produces a moderately strong reducing species (\textit{RED}_\text{i}) and a moderately strong oxidizing species (\textit{OX}_\text{i}). System II provides a stronger oxidizing agent (\textit{OX}_\text{II}) and a weaker reducing agent (\textit{RED}_\text{II}). \textit{OX}_\text{i} is responsible for the production of molecular oxygen in photosynthesis. A manganese complex, probably containing four atoms of manganese, is attached to a protein molecule. It reduces \textit{OX}_\text{i}, which is recycled for use by another excited chlorophyll molecule in PS II. In the redox reactions the manganese shuttle between two oxidation states with each manganese atom increasing (and subsequently decreasing) its oxidation state by one unit, but it is not known with absolute certainty what these oxidation states are.

In the reduced form the oxidation states may be as low as three Mn(II) and one Mn(III), but they are more likely to be three Mn(II) and one Mn(IV). A suggested scheme for this redox chemistry is shown in Fig. 19.17 in which the active site cycles between a cubane-like and an adamantane-like configuration. There have been several other suggestions concerning these structures, including the "butterfly clusters" and other modifications of the Mn configuration.

The chlorophyll ring system is a porphyrin in which a double bond in one of the pyrrole rings has been reduced. A fixed cyclooctatetraene ring is also present. In addition, bacteriochlorophyll is similar but has a double bond in a second pyrrole ring reduced, and it has a substituent acetyl group in place of a vinyl group. Chlorophyll absorbs low-energy light in the red region (-600-700 nm). The exact frequency depends on the nature of the substituents.

First, there is extensive conjugation of the porphyrin ring. This lowers the energy of the electronic transitions and shifts the absorption maximum into the red. The Cu-S bonds are about 10 pm longer than those in plastocyanin but about the same as those in cytochrome c oxidase.

Finally, a pseudotetrahedral complex more closely resembling the copper site in cytochrome c oxidase.

**Photosynthesis**

\[ [\text{N}_2\text{Cu}]^{2+} + \text{HSCH}_2\text{COO}^- \rightarrow \text{N}_2\text{CuSCH}_2\text{COO}^- + \text{H}^+ \]  

(19.22)

In addition, several other suggestions concerning these structures, including the "butterfly clusters" and other modifications of the Mn configuration.67

---

63 Adenosine triphosphate, an important energy-rich species in metabolism.
and $N_2^+$, none of which is known for exceptional softness, are bound with exceptional strength. They are, however, isoelectronic and isostructural with the reactants and products of the enzyme reaction, CO$_2$, CO$_3^{2-}$, and HCO$_3^-$, respectively. The explanation appears to be a tailoring of the structure of the enzyme molecule to form a pocket about 450 pm long next to the zinc ion, perhaps containing an additional positive center, to stabilize ions of appropriate size.

Although some mechanisms illustrate the carbon dioxide coordinated directly to the zinc atom, this is highly unlikely. The infrared asymmetric stretch for carbon dioxide is found at 2343.5 cm$^{-1}$ in the bound enzyme compared with 2321 cm$^{-1}$ for the free molecule, hardly compatible with a strong interaction of one oxygen atom and not the other. The visible spectrum of the Co$^{2+}$-substituted enzyme shows very small shifts upon binding CO$_2$, again incompatible with strong oxygen-metal interactions.

The zinc atom is thought to be considerably more acidic in carbonic anhydrase than in the other. The visible spectrum of the Co$^{2+}$-substituted enzyme shows very small shifts upon binding CO$_2$, again incompatible with strong oxygen-metal interactions.

It may operate either clockwise (as drawn) to hydrate carbon dioxide, or counterclockwise to release carbon dioxide (from the hydrogen carbonate anion) from

![Diagram of enzyme mechanism](image)

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19. The Inorganic Chemistry of Biological Systems

Photoevolution of dioxygen. [Modified from 987, Si, 4586. Reproduced with permission!]

19.17 One proposal for the involvement of Mn centers in the

Fig. 19.17 One proposal for the involvement of Mn centers in the photoevolution of dioxygen. [Modified from Brodersen, G. W.; Crabtree, R. H. Proc. Natl. Acad. Sci. U. S. A. 1987, 84, 4266. Reproduced with permission.]

19.18 Structure of chlorophyll. The long alkyl chain at the bottom is the phytyl group.

Fig. 19.18 Structure of chlorophyll. The long alkyl chain at the bottom is the phytyl group.

the region of visible light. Conjugation also helps to make the ring rigid, and thus less energy is wasted in internal thermal degradation (via molecular vibrations). The maximum intensity of light reaching the earth's surface is in the visible region; ultraviolet light is absorbed in the earth's atmosphere by species such as dioxygen and ozone (trioxygen), infrared light is absorbed by carbon dioxide, water etc. The absorption spectra of photosynthetic systems fall nicely within that portion of the sun's spectrum that reaches the earth. Some of the energy of the light not absorbed by the chlorophyll itself is captured by accessory pigments. In the octave of light from

Enzymes are the catalysts of biological systems. They not only control the rate of reactions but, by favoring certain geometries in the transition state, can lower the activation energy for the formation of one product rather than another. The basic structure of enzymes is built of proteins. Those of interest to the inorganic chemist are composed of a protein structure (called an apoenzyme) and a small prosthetic group, which may be either a simple metal ion or a complexed metal ion. For example, heme is the prosthetic group in hemoglobin. A reversibly bound group that combines with an enzyme for a particular reaction and then is released to combine with another is termed a coenzyme. Both prosthetic groups and coenzymes are sometimes called cofactors.

To illustrate the structure of an enzyme and its relation to function, consider carboxypeptidase A. This pancreatic enzyme cleaves the carboxyl terminal amino acid from a peptide chain by hydrolyzing the amide linkage:

\[
\text{Pro-Leu-Glu-Phe} \rightarrow \text{Pro-Leu-Glu} + \text{phenylalanine (19.26)}
\]

Enzymes are the catalysts of biological systems. They not only control the rate of reactions but, by favoring certain geometries in the transition state, can lower the activation energy for the formation of one product rather than another. The basic structure of enzymes is built of proteins. Those of interest to the inorganic chemist are composed of a protein structure (called an apoenzyme) and a small prosthetic group, which may be either a simple metal ion or a complexed metal ion. For example, heme is the prosthetic group in hemoglobin. A reversibly bound group that combines with an enzyme for a particular reaction and then is released to combine with another is termed a coenzyme. Both prosthetic groups and coenzymes are sometimes called cofactors.

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Inhibition and Poisoning

The study of the factors that enable an apoenzyme to select the appropriate metal ion is of importance to the proper understanding of enzyme action. The factors that favor the formation of certain complexes in the laboratory should also be important in biological systems. For example, the Irving-Williams series and the hard-soft acid-base principles should be helpful guides. Thus we expect to find the really hard metal ions [Group IA (1); Group IIA (2)] preferring ligands with oxygen donor atoms. The somewhat softer metal atoms of the first transition series (Cu to Zn) may prefer coordination to nitrogen atoms (cf. Fig. 9.5). The important thiol group, —SH, should have a particularly strong affinity for soft metal ions.

The usual structural principles of coordination chemistry such as the chelate effect, the preference for five- and six-membered rings, and the stability of certain ring conformations should hold in biological systems. In addition, however, enzymes present structural effects not observed in simpler complexes. An interesting example is carbonic anhydrase which catalyzes the interconversion of carbon dioxide and carbonates. Like carboxypeptidase, carbonic anhydrase has one zinc atom per molecule (with a molecular weight of ~30,000), in this case coordinated to three histidine residues (His 54, His 96, His 199) and a water molecule or hydroxide ion. The active site (Fig. 19.23) contains other amino acids that may function through hydrogen bonding, proton transfer, etc. The relative binding power of the zinc ion towards halide ions is reversed in the enzyme (I^- > Br^- > Cl^- > F^-) compared with the free Zn^{2+} ions (F^- > CPO > Br^- > I^-). This reversal could be interpreted as some sort of "softening" effect on the zinc by the apoenzyme were it not that the soft ligand CN^- is bound equally well by the free ion as by the complex.

Furthermore, NO^- CNCP, coordinates to the zinc atom. All hydrogen atoms have been omitted for clarity.

18 There are three human isozymes of carbonic anhydrase that differ slightly in amino acid composition, and so the sequencing numbers for the histidines differ among them.
19 It should be noted that this discussion is based on a comparison of the equilibrium constants of enzymic cyanide complexation versus aqueous zinc-cyanide complexations. Cyanide has a high affinity for the soft zinc ion under both conditions (stability constant of [Zn(CN)\textsubscript{4}]^{2-} = 7.7 x 10^{17}), hence it should not be concluded that there is any lack of affinity for cyanide in the enzyme.
The enzyme consists of a protein chain of 307 amino acid residues plus one Zn$^{2+}$ ion to yield a molecular weight of about 34,600. The molecule is roughly egg-shaped, with a maximum dimension of approximately 5000 pm and a minimum dimension of about 3800 pm (Fig. 19.21a). There is a cleft on one side that contains the zinc ion, the active site. The metal is coordinated approximately tetrahedrally to two nitrogen atoms and an oxygen atom from three amino acids (His 69, Glu 72, His 169) in the protein chain.
The fourth coordination site is free to accept a pair of electrons from a donor atom in the substrate to be cleaved. The enzyme is thought to act through coordination of the zinc atom to the carbonyl group of the amide linkage. In addition, a nearby hydrophobic pocket envelops the organic group of the amino acid to be cleaved (Fig. 19.21) and those amino acids with aromatic side groups react most readily. Accompanying these events is a change in conformation of the enzyme. The arginine side chain moves about 200 pm closer to the carboxylate group of the substrate, and the phenolic group of the tyrosine comes within hydrogen bonding distance of the imido group of the C-terminal amino acid, a shift of 1200 pm. The hydrogen bonding to the free carboxyl group (by arginine) and the amide linkage (by tyrosine) not only holds the substrate to the enzyme but helps break the N–C bond. Nucleophilic displacement of the amide group by an attacking carboxylate group from a glutamate group could form an anhydride link to the remainder of the peptide chain. Hydrolysis of this anhydride bond could then complete the cycle and regenerate the original enzyme. More likely, the glutamate acts indirectly by polarizing a water molecule (Fig. 19.22b) that attacks the amide linkage.

This example illustrates the basic key-and-lock theory first proposed by Emil Fischer in which the enzyme and substrate fit each other sterically. However, there is more to enzymatic catalysis than merely bringing reactants together. There is good evidence that the enzyme also encourages the reaction by placing a strain on the bond to be broken. Evidence comes from spectroscopic studies of enzymes containing metal ions that, unlike Zn$^{2+}$, show d-d transitions. The spectrum of the enzyme containing such a metal ion provides information on the microsymmetry of the site of the metal. For example, Co$^{2+}$ can replace the Zn$^{2+}$ and the enzyme retains its activity. The spectrum of carboxypeptidase A(Co$^{2+}$) is "irregular" and has a high absorptivity (extinction coefficient), indicating that a regular tetrahedron is not present. The distortion presumably aids the metal to effect the reaction. It has been suggested that the metal in the enzyme is peculiarly poised for action and that this lowers the energy of the transition state. The term entatic has been coined to describe this state of the metal in an enzyme.

The substitution of a different metal into an enzyme provides a very useful method for studying the immediate environment of the metal site. In addition to the use of Co$^{2+}$ for spectral studies, appropriate substitution allows the use of physical methods such as electron paramagnetic resonance (Co$^{2+}$, Cu$^{2+}$), the Mössbauer effect (Fe$^{2+}$), proton magnetic resonance relaxation techniques (Mn$^{2+}$), or X-ray crystallography (with a heavy metal atom to aid in the structure solution).