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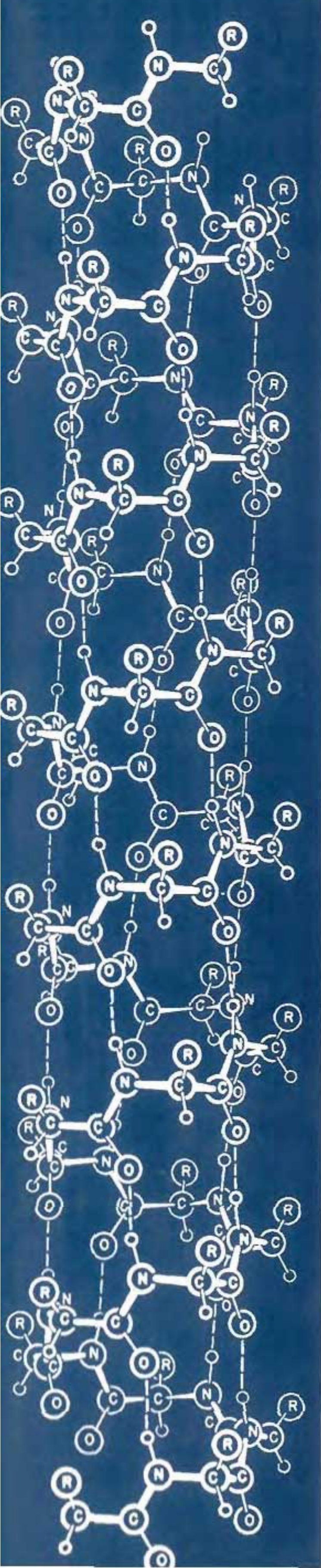

LINUS PAULING

Selected Scientific Papers

VOLUME I

World Scientific

LINUS
PAULING

Selected Scientific Papers

VOLUME I

Physical Sciences

WORLD SCIENTIFIC SERIES IN 20TH CENTURY CHEMISTRY

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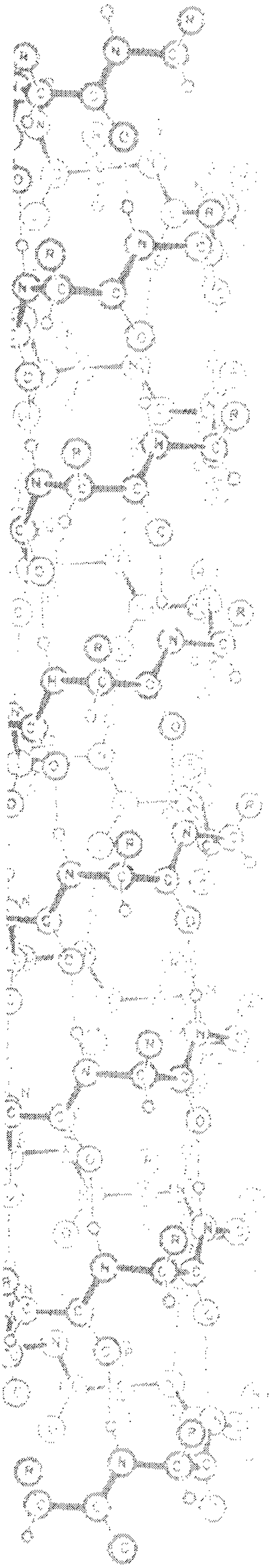

LINUS PAULING

Selected Scientific Papers

VOLUME I

Physical Sciences

Editors

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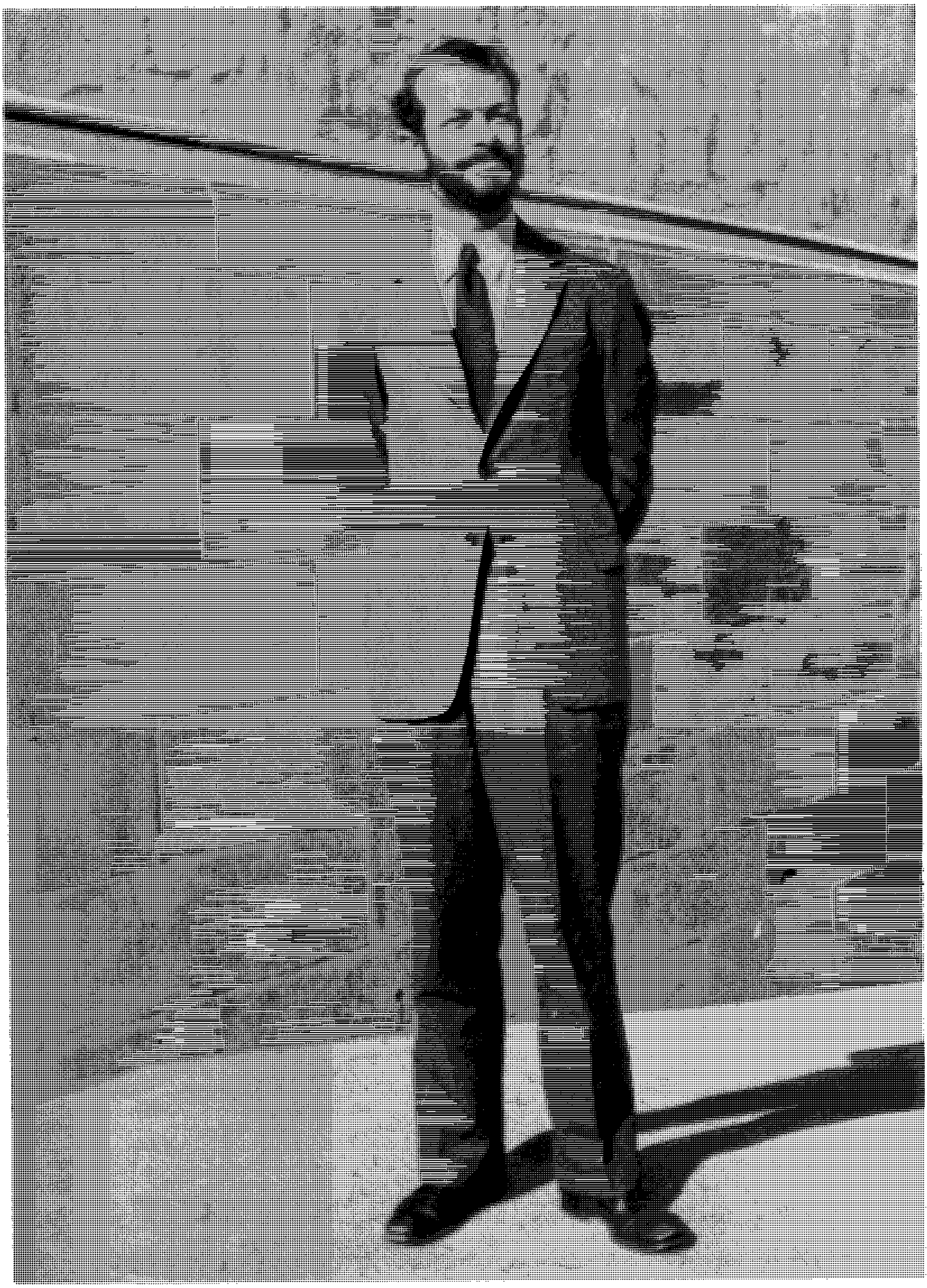

FOREWORD

Linus Pauling is widely considered to be the most influential chemist of the 20th century and one of the greatest scientists of all time. He made important contributions over an enormously broad range of scientific subjects, including quantum chemistry, structural chemistry, structural crystallography, mineralogy, biochemistry, molecular biology, molecular medicine, and biological evolution. For his research into the nature of the chemical bond and its application to the structures of complex substances he was awarded the Nobel Prize in Chemistry for 1954. This research changed the science of chemistry in a fundamental way, and later the science of biology as well. In 1963 he was awarded the Nobel Peace Prize for his work striving to eliminate the possibility of nuclear war. He is the only person ever to receive two unshared Nobel Prizes. He became widely known also for his public advocacy of the nutritional benefits of large doses of vitamin C and other vitamins. He died in 1994 at the age of 93.

When I came to Caltech in 1976, there was one name which, in my mind, is to chemistry what the Great Pyramid of Cheops (Khufu) is to the world. That name was Pauling. Caltech had a great pharaoh of chemistry, with a dynasty spanning over forty years. It was at Caltech where Linus made his major contributions to chemistry—especially the nature of the chemical bond, elucidating the concepts of hybridization, resonance, and electronegativity from studies of numerous crystal and molecular structures by x-ray and electron diffraction. His major contributions to biology included the α-helix structure of polypeptide molecules and the concept of molecular disease. Caltech was the mecca of molecular structure. While there was a strained period at the time he left Caltech in 1964, Linus told me on several occasions of his highest admiration for the California Institute of Technology. This respect is mutual. Linus Pauling will always be remembered as one of the most distinguished members of our faculty, for his science, teaching, and leadership. Jack Dunitz puts it well when he says (in Chapter 18): "his name will be remembered as long as there is a science of chemistry." I might add biology too!

The present two-volume work is an anthology of Linus Pauling's most significant and influential scientific papers. The volumes are testimony to the extraordinary contributions of this giant and to his impact. They enable the reader to see in exact facsimile many of the original works upon which his fame as a scientist rests. These works represent a monumental contribution — a must for chemists, biologists, and scientists in general who want to understand the roots of important concepts in modern science, the foundations for which were laid down by Linus Pauling.

We are indebted to the Pauling family for preparing this anthology, and to World Scientific Publishing Company for accepting my initial suggestion that such an anthology be published. It will help assure that the scientific work of Linus Pauling is well preserved and available, and that this work, like the Great Pyramid, is not forgotten!

Ahmed H. Zewail
Linus Pauling Professor of Chemistry and Physics
California Institute of Technology
May 15, 1999

PREFACE

Shortly before his death on 19 August 1994 at his home on the California coast, Professor Linus Pauling was contacted by World Scientific Publishing Company with the proposal that the Company republish in book form a selection of his scientific writings. He agreed and his four children agreed to act as editors. The editorial process of selecting and assembling the papers to be included had, however, only just begun at the time of his death. The task of studying and considering the more than 1000 publications and selecting a limited number from this wealth of material was daunting. Pauling is reported to have said "the selection is easy—print them all." But World Scientific wanted a more selective approach that would concentrate on the more important papers and avoid escalating the price out of reach.

With the family in mourning, the project languished for a time despite encouragement from admirers of Pauling and his scientific work. It was restarted by Barclay Kamb, who took on the job of Editor-in-Chief and moved the project forward to completion, albeit with many delays. (Barclay Kamb is Pauling's son-in-law, colleague, former Ph.D. student, and Caltech professor of geology and geophysics.)

Editorial functions in the preparation of this work were as follows: son Peter Pauling Ph.D. was Editor of Part I (see General Introduction), grandson Alexander (Sasha) Kamb Ph.D. was Editor of Part III, son Linus Pauling Jr. M.D. was Editor of Part IV, daughter Linda Pauling Kamb B.A. was Editor of photographic illustrations and curator of the original publications, and Barclay Kamb Ph.D. was Editor of Part II, author of the General Introduction, and Chief Editor and coordinator of all components. The Editor of each Part had responsibility for the selection of papers for inclusion in his Part and wrote the Introduction for that Part. The final selection and the editing of the Introductions were done by the Chief Editor. Linda Kamb chose the photographs (mostly from her own collection), helped write the captions for them, and carried out the arduous search for original offprints of the selected papers. (Sadly, son Crellin Pauling Ph.D. could not contribute to the completion of the project, dying aged 60 on 27 July 1997.)

In view of the Editors' limited knowledge of the many scientific fields in which Linus Pauling worked and published, several specialists in various fields were asked to serve as Advisors for the selection of papers and in some cases to help with the writing of the introductions to the Parts. The Advisors were:

Prof. Jack D. Dunitz Ph.D., F.R.S., Professor of Chemistry, Eidgenössische Technische Hochschule, Zürich, Switzerland

Dr. Justine Garvey Ph.D.,Visiting Associate, Division of Biology, California Institute of Technology, Pasadena, California

Dr. Zelek Herman Ph.D., Senior Research Scientist, Linus Pauling Institute of Science and Medicine, Palo Alto, California

Dr. Richard Marsh Ph.D., Senior Research Associate Emeritus, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California

Prof. Harden McConnell Ph.D., Professor of Chemistry, Stanford University, Stanford, California

Mrs. Dorothy Munro, Assistant to Linus Pauling, Linus Pauling Institute of Science and Medicine, Palo Alto, California

Prof. Ray Owen Ph.D., Professor of Biology Emeritus, California Institute of Technology, Pasadena, California

Prof. Alexander Rich M.D., Professor of Biology, Massachusetts Institute of Technology, Cambridge, Massachusetts

Prof. Verner Schomaker Ph.D., Professor of Chemistry Emeritus, University of Washington, Seattle, Washington (deceased)

Prof. Ahmed Zewail Ph.D., The Linus Pauling Professor of Chemistry, California Institute of Technology, Pasadena, California

The Editors express their sincere thanks to the Advisors for their invaluable help. They thank Professor Jack Dunitz for contributing the biographical memoir of Linus Pauling that he wrote originally for the Royal Society of London.

Our thanks go also to the Caltech photo lab (Richard Gomez) for much help in preparing the photographic illustrations for this work, to Ramesh Krishnamurthy of Special Collections, Oregon State University, for providing many of the original offprints, and to Kathy Lima, Denise Darrell and Anthony Pauling Kamb for word and data processing.

An American chemist came through University College London to visit me perhaps 30 years ago and mentioned a discussion with a graduate student. The subject may have been "hybrid bond orbitals" or "resonance" but it does not matter. The student said that the nature of the chemical bond came from Genesis. My visitor said: It did not; it came from Linus Pauling. In 70 years young chemists have forgotten from where the ideas, knowledge, and methods came. The Editors and Advisors hope that this republication will not only be a recollection but will also be a valuable asset in the education of scientists.

My view of Linus Pauling is necessarily different to that of others. For one thing, there is genetics, although my view of genetics is Thomas Hunt Morgan and fruit flies, and the Caltech maize genetics farm. For another, we were thrown into each other's company by force of logistic circumstances from 10 February 1931 until 1952 when I left home. The "bond" and communication ("resonance") grew stronger and stronger until 19 August 1994.

Peter Jeffress Pauling
Abergwenlais Mill
Wales, UK
14 December 1998

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BRIEF CONTENTS

VOLUME I — PHYSICAL SCIENCES

VOLUME II — BIOMOLECULAR SCIENCES

Part V. Summary of Linus Pauling's Life and Scientific Work

GENERAL INTRODUCTION

Linus Pauling's published writings number some 1200 in all, of which about 850 are scientific papers and books, produced over the period 1923–1994. In the present pair of volumes, we the editors endeavor to place before you a substantial selection of Pauling's published contributions to science, reproduced from the original publications. Within the scope of some 1400 pages the selection aims to present Pauling's most important and influential scientific papers and the papers that best convey his imaginative style of scientific thinking and the considerable gamut of scientific subjects that he tackled. His writings on subjects outside the scope of science—on social, humanitarian, and political subjects—are presented in the book *Linus Pauling in His Own Words,* edited by Barbara Marinacci (1995), and in *Linus Pauling on Peace,* by Marinacci and Krishnamurthy (1998). The biographies by Thomas Hager (1995, 1998) and by Ted and Ben Goertzel (1995) provide detailed background material on Pauling's life and the context of his writings.

The selected scientific papers, listed in tables of contents, as explained below, are organized into four major subject groupings, designated Parts I to IV. Part I contains papers on the nature of the chemical bond, the subject for which Pauling was first and foremost acclaimed in the scientific world and for which he was awarded the Nobel Prize for Chemistry in 1954. (His second Nobel Prize, for Peace, awarded in 1963, relates to his writings in the social, humanitarian, and political areas mentioned above.) Part II contains papers on the atomic structure of molecules and crystals, which provided much of the observational evidence on which Pauling's concepts of the chemical bond in Part I were based. Part II also contains papers in which the principles of quantum mechanics, which provided the theoretical basis for many of Pauling's concepts of the chemical bond in Part I, were applied by him to understand the physical properties of molecules and crystals. The pervasive role of quantum mechanics, which was developed by physicists in the 1920's, during the early years of Pauling's career, makes somewhat blurry the distinction between the subject matter of Parts I and II, but the papers in Part I concentrate on conceptual and theoretical aspects of chemical bonding while the concentration in Part II is on observational and empirical evidence and on physical properties as distinct from chemical bonding. Part III contains a major new thrust in Pauling's research that began to develop in the late 30's and culminated in the 50's — the structure and function of large molecules of biological importance, particularly proteins. The bridge to Part III was the application of concepts and observational methods of Parts I and II to small organic molecules that are building blocks for the large molecules of biological importance. Finally, Part IV contains papers on biomedical subjects, beginning with Pauling's much-cited 1949 discovery of molecular disease, which is considered by biologists and medical scientists to be among his greatest and most influential contributions to science. Part IV includes papers on nutritional (orthomolecular) medicine, which was the focus of much of Pauling's research effort in his later years. Parts I and II are in Volume I of this two-volume anthology, and Parts III and IV are in Volume II.

To provide a sharper guide to the different subject areas of Pauling's scientific research and writing, beyond the rather broad division into Parts I to IV, the 144 selected papers are further subdivided into seventeen chapters. Each chapter begins with a table of contents listing the selected papers contained in that chapter. This is followed by the actual papers, reproduced in exact facsimile from the original publications indicated by the citations in the table of contents. (In these citations, the by-line is omitted for single-author papers by Pauling.) The selected papers are presented in an arbitrary sequence that is primarily subject-matter oriented and secondarily chronological. The significance of the subdivision into chapters is briefly explained and the relationships between the chapters are discussed in an introduction at the beginning of each Part. Particularly important papers are noted but it is beyond the scope of the introductions to discuss each paper. However, we hope that the commentary provided will make the individual papers sufficiently self-explanatory by indicating their context.

The papers were selected from the list of Pauling's scientific publications given in Appendix III, which is derived from a complete list of Pauling's publications prepared by Z. S. Herman and D. B. Munro (1996) as noted below. The basis for selection is the editors' judgement as to the scientific interest and importance of each paper and its representativeness for papers in its subject area, in relation to an overall limitation on the number of pages. A few selections were made to display collaborative work with students or more senior colleagues. In subject areas of the most importance, such as the nature of the chemical bond, the structure and function of proteins, and molecular disease, the selected papers constitute a substantial fraction of Pauling's published papers in these subject areas, whereas in other areas, the selected fraction is smaller. We have tried to select representative papers from all scientific areas that Pauling was interested in and wrote about, but in some cases, interesting papers could not be included for lack of space. The selection was made with the help of a number of advisors, acknowledged in the Preface.

We have included only four selections from Pauling's several books, because it would be impractical to include more within the space limitation and because our main objective is to document Pauling's science as it emerged and first impacted the scientific world rather than as it appeared in later retrospectives. Two selections are from Pauling's *The Nature of the Chemical Bond,* which has been called the twentieth century's most important book in chemistry (for example, it was cited 16,027 times in the period 1955–1983). The third is a passage from Pauling and Wilson's *Introduction to Quantum Mechanics,* which has trained generations of quantum chemists and is said to be the longest-lived quantum-mechanics textbook in terms of length of time in print. The fourth book selection is a concluding summary from Cameron and Pauling's book on vitamin C and cancer. In a few cases we have included retrospective papers, which are placed at the end of the appropriate chapters, except for the 1954 Nobel Lecture, which is placed at the beginning of Chapter 1 where it provides an introductory overview of Pauling's contributions to the nature of the chemical bond. Many more of his retrospective scientific writings are presented and discussed in *Linus Pauling in His Own Words,* edited by Barbara Marinacci (1995).

Except for *Introduction to Quantum Mechanics,* we have likewise not included selections from Pauling's several textbooks, beginning in 1930 with *The Structure of Line Spectra* (with Samuel Goudsmit) and blossoming fully in 1947 with *General Chemistry,* an introductory textbook that for the first time presented chemistry in the light of chemical bonding theory and was widely influential in the teaching of chemistry at the first-year university level. Pauling was a charismatic and spellbinding teacher and lecturer. The scope of the anthology does not include Pauling's teaching, but hints of it will be found in the photographic illustrations (explained below).

Included as a final chapter (Part V, Chapter 18) is a compact, science-oriented biography "Linus Carl Pauling" from the *Biographical Memoirs of Fellows of the Royal Society of London* by Jack D. Dunitz (1996). This work summarizes Pauling's contributions to science and assesses their significance and impact, as judged by a leading structural chemist who knew Pauling well. It thus provides a frame of reference in which the original papers in this anthology can be studied and evaluated retrospectively. It also places Pauling's scientific work in the broader context of his life as a whole.

The selected papers in the present anthology are numbered from SP 1 to SP 144 in the somewhat arbitrary sequence in which they are presented. Throughout the two volumes the selected papers are identified by "Selected Paper number", with the prefix "SP". The SP designation is used to forestall confusion between the SP numbers used in the main text and the other numbers used in Chapter 18 (the *Biographical Memoir*) and in the appendices. Appendix I is a conversion table between the SP numbers and the citation numbers that are used in Chapter 18 to refer to Pauling's papers. Appendix I also gives, for each citation number in Chapter 18, the corresponding publication number assigned in the complete list of Pauling's publications by Z. S. Herman and D. B. Munro (1996). These publication numbers, which appear also in Appendices II and III, have the format [*y*-*n*], where *y* is the year of publication and *n* is the number of the publication in that year, counted sequentially by date of publication. (In Chapter 18, the *y*-*n* is enclosed by round brackets instead of the square brackets used elsewhere.)

Most of the selected papers contain reference citations to other Pauling papers, some selected for inclusion here and some not. To help the reader make use of these citations, a citation index of the selected papers is included as Appendix II. It enables any selected paper (represented by its SP number) to be found in the anthology from a reference to it in another paper. Its Herman-Munro publication number [*y*-*n*] is also given.

Appendix III, as noted above, contains a full listing of Pauling's scientific papers, from which the selected papers were chosen. The entries are gathered into seventeen Groups 1–17 that correspond in subject matter one-for-one with chapters 1–17 of the main text, plus three additional Groups as explained later. By perusing the group lists of paper titles in Appendix III, the reader can get an idea of the wealth of material that Pauling contributed to science, from which the selected papers are drawn as outstanding examples. The selected papers are identified by an asterisk in Appendix III. Further explanation is given at the beginning of Appendix III.

A collection of photographs is included, showing Linus Pauling with many of his colleagues over the years. The photos are arranged in a sequence approximating the sequence of chapters in the text. Photos generally representative of the 20's, 30's, and into the 40's are in Volume I near the end of Part I; they relate mostly to Pauling's scientific work in Parts I and II. Photos generally from the 40's and especially the 50's are grouped near the end of Part III, to which they generally relate, and those from the 60's onward are grouped near the end of Part IV.

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PART I

THE CHEMICAL BOND

INTRODUCTION TO PART I

THE CHEMICAL BOND

The 38 papers collected in Part I present Linus Pauling's concepts of the forces that bond atoms together in molecules and crystals. These papers had great impact on chemistry because they showed for the first time how the structural features of chemical bonding, such as the angles between the bonds in a molecule, could be rationally understood and even predicted. The first paper in the collection is Pauling's 1954 Nobel Lecture, which gives an introductory overview of the subject from Pauling's perspective at the time of his first Nobel Prize.

The papers of Part I are grouped into four chapters, corresponding to the four principal types of chemical bonding that Pauling recognizes—covalent, ionic, metallic, and hydrogen bonding. Pauling's contributions to understanding the chemical bond are particularly great in the case of covalent bonding (Chapter 1), for which the bonding forces are explained by quantum mechanics, a theory that was just being discovered by physicists in the 20's when Pauling began his career. His published participation in the development of the basic quantum mechanical theory of covalent bonding begins with SP 3 (Selected Paper number 3), which is largely a review of others' work but contains in Section VI.*b*. (pp. 190–196) Pauling's application of first-order perturbation theory to obtain an approximate solution of the Schrödinger quantum mechanical wave equation for the one-electron bond in the hydrogen molecular ion—the covalent bond of greatest simplicity for quantum mechanical calculations. This use of the perturbation method (or the related "variation method"), which came to be known as the *valence bond method*, served as Pauling's basic approach in many subsequent molecular quantum mechanical calculations, represented here by SP 7, SP 8, SP 10, SP 12, and SP 16 in Chapter 1, and by SP 31 in Chapter 3. These papers are all characterized by setting up a *secular equation* for the molecule of interest and solving it to obtain an approximate bond energy and wave function for the molecule, based on a certain type of trial wave function with adjustable coefficients that are determined from the solution of the secular equation. The method is best explained in Pauling and Wilson's book *Introduction to Quantum Mechanics* (SP 15), and for that reason, as well as to give the flavor of this classic text, a passage from Section 42 of the book is included here, amplifying upon the treatment of the hydrogen molecular ion in SP 3. Pauling preferred the valence bond method to its chief alternative, the molecular orbital method, but he used the latter where he considered it appropriate (SP 13, SP 17). A full explanation of these quantum mechanical methods would require also Sections 24, 26, 43, and 46 of the textbook, but these are too extensive to include here.

Pauling's most distinctive and valuable contributions to chemical quantum mechanics are in semiquantitative theoretical constructions of bond orbitals—patterns of localization of electrons involved in forming shared-electron covalent bonds quantum mechanically. Many of these contributions appeared in SP 5, entitled "The nature of the chemical bond". Pauling considered SP 5 to be his greatest paper. Papers SP 2 and SP 4 are short "previews" of it. Pauling's method of constructing bond orbitals is to make mathematical combinations of electron orbitals of the type present in the isolated hydrogen atom. In the early papers, this is called "changing the quantization", or "breaking the quantization", or "destroying the *s-p* quantization", but in later papers (e.g. SP 11), it is called "*bond orbital hybridization*". The hybrid orbitals in Pauling's method control the directions of the bonds and the angles between bonds, hence his treatment of bond orbitals is called the quantum mechanics of directed valence. Quantum mechanical calculations in support of the hybridization concept are carried out in SP 16. Material on hybridization from the original paper SP 5 appears without amplification in some subsequent papers, such as SP 11 and SP 18, but in later years, Pauling returned to develop the subject somewhat further, as in papers SP 20 and SP 21.

A second feature central to Pauling's thinking about the chemical bond is his concept of *quantum mechanical resonance*, according to which a given molecular structure may be interpreted as being formed by the superposition or combination of two or more differently bonded structures, among which the molecule is said to resonate. Resonance is involved also in the hybridization of bond orbitals and in the electron exchange that takes place in the covalent bond itself. The resonance concept pervades the papers in Chapter 1, and if anything, its importance grows in Pauling's thinking through the years (e.g. SP 18). It is summarized in SP 22, at the end of Chapter 1. The summary acknowledges that the resonance concept is somewhat controversial, and it addresses objections that have been raised.

Three other important concepts should be mentioned: (1) The *magnetic criterion for bond type*, developed in detail in SP 5 and often referred to in later papers. (2) The relationship between *covalent bond length* and *bond character*, covered in SP 11 and in SP 60 (Chapter 7). (3) The *electroneutrality principle* introduced in SP 18. Concepts (2) and (3) played a very important role in many of Pauling's subsequent interpretations of bonding in molecules and crystals (e.g. SP 19). The magnetic criterion (1), based on the paramagnetic property of substances interpreted in terms of hybrid bond orbitals and electron spin, enabled Pauling to distinguish between different types of bonds formed by transition-metal atoms in crystals.

The concept of bonding between electrically charged ions, contained in Chapter 2, is based mainly on classical rather than quantum physics and was already developed to a considerable extent before Pauling took it up—it was his first venture into the nature of the chemical bond. SP 23 makes quantum-mechanically based improvements in the way *ionic radii* are assigned empirically from observed interatomic distances in ionic crystals, and it puts forward a new table of ionic radii that supersedes the older, entirely empirical tables. (Analogous to the ionic radii are the various *covalent radii* developed later, for covalent bonding, in SP 11.) SP 24 promulgates Pauling's celebrated *rules for the structure of ionic crystals*, which had great impact and are still frequently cited. Comparably great in its impact is Pauling's concept of an *electronegativity scale* of the elements (SP 26) and the relation of electronegativity differences to *partial ionic character* of covalent bonds (SP 25). The electronegativity scale is based on thermochemical data on bond strengths (SP 26), not on quantum mechanical theory.

Pauling's concept of the metallic bond (Chapter 3) is closely related to his concept of the covalent bond, adding the feature of *incoherent resonance of valence bonds* over the variety of possible bond positions characteristic of metal structures (SP 31), and adding the presence of a *metallic orbital* that facilitates the bond resonance (SP 28). Two other added features, which pervade Pauling's interpretations of metallic and intermetallic structures both in Chapter 3 and in Chapter 6 (Part II), are the concept of *fractional bonds*, and the *dependence of metal-metal interatomic distance on (fractional) bond number* (SP 29, SP 32). Although his work on the metallic bond reached a culmination in the forties with SP 31, Pauling continued to develop the theory in later years, particularly along statistical lines (e.g. SP 33, SP 34). Paper [83-8] (in Group 1 of Appendix III) elicited some noteworthy interest, being covered in a full-page article "Linus Pauling discovers a new chemical bond" in *The New Scientist* (Vol. 100, No. 1382, p. 342, Nov. 3, 1983; article by Lionel Milgrom).

Chapter 4 starts with a passage from *The Nature of the Chemical Bond* (SP 35) summarizing Pauling's concept of the hydrogen bond. The concept is exemplified by the hydrogen bonding in two crystals (SP 36, SP 37) and in Pauling's predicted structure of liquid water (SP 38). The structure of ice (SP 73, in Chapter 9, Part II) could well be included here also, as another quite important example of hydrogen bonding, but it is placed in Chapter 9 because of the special significance of the concept of residual entropy, which it demonstrates. In view of their largely observational content, SP 36 and SP 37 could on the other hand be placed in Chapter 5, Part II, as examples of ionic bonding, because Pauling considered the hydrogen bond to be largely electrostatic in nature (hence ionic). However, they are included here because they help to illuminate the concepts of hydrogen bonding in SP 35. In SP 35 (on p. 453) Pauling explains that although largely ionic, the hydrogen bond has appreciable covalent character (about 5%). This concept is noteworthy because of a recent report of its confirmation by inelastic x-ray scattering experiments on ice (see article entitled "Linus Pauling got it right...again" in *The New Scientist*, Vol. 1261, No. 2170, p. 17, 1999).

Pauling's concept of the hydrogen bond enabled him to recognize the great importance of hydrogen bonds in proteins, influencing through internal interactions the conformation of the polypeptide chain (Part III, Chapter 13) and providing localized external interactions with other molecules (Chapters 13 and 14). Detailed features of the hydrogen bond, particularly its asymmetry, also play an important role in the entropy and other properties of ice, as shown in SP 73, Chapter 9, Part II. Hydrogen bonding is also important in Pauling's theory of anesthesia (Part IV, Chapter 16, SP 129), which is based on the theory of water structure in SP 38, and incidentally illustrates Pauling's liking for the pentagonal dodecahedron as a structural element (see Photo 28).

Chapter 1

COVALENT BONDING, RESONANCE, AND BOND-ORBITAL HYBRIDIZATION

Contents

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MODERN STRUCTURAL CHEMISTRY.

Nobel Lecture — December 11, 1954.

By LINUS PAULING.

A century ago the structural theory of organic chemistry was developed. FRANKLAND in 1852 suggested that an atom of an element has a definite capacity for combining with atoms of other elements — a definite valence. Six years later KEKULÉ and COUPER, independently, introduced the idea of valence bonds between atoms, including bonds between two carbon atoms, and suggested that carbon is quadrivalent. In 1861 BUTLEROV, making use for the first time of the term "chemical structure", stated clearly that the properties of a compound are determined by its molecular structure and reflect the way in which atoms are bonded to one another in the molecules of the compound. The development of the structure theory of organic chemistry then progressed rapidly, and this theory has been of inestimable value in aiding organic chemists to interpret their experimental results and to plan new experiments.

A most important early addition to organic structure theory was made by the first Nobel Laureate in Chemistry, VAN'T HOFF, who in 1874 recognized that the optical activity of carbon compounds can be explained by the postulate that the four valence bonds of the carbon atom are directed in space toward the corners of a tetrahedron.

The structure theory of inorganic chemistry may be said to have been born only fifty years ago, when WERNER, Nobel Laureate in Chemistry in 1913, found that the chemical composition and properties of complex inorganic substances could be explained by assuming that metal atoms often coordinate about themselves a number of atoms different from their valence, usually four atoms at the corners either of a tetrahedron or of a square coplanar with the central atom, or six atoms at the corners of an octahedron. His ideas about the geometry of inorganic complexes were completely verified twenty years later, through the application of the technique of x-ray diffraction.

After the discovery of the electron many efforts were made to develop an electronic theory of the chemical bond. A great contribution was made in 1916 by GILBERT NEWTON LEWIS, who proposed that the chemical bond, such as the single bond between two carbon atoms or a carbon atom and a hydrogen atom represented by a line in the customary structural formula for ethane, consists of a pair of electrons held jointly by the two atoms that are bonded together. LEWIS also suggested that atoms tend to assume the electronic configuration of a noble gas, through the sharing of electrons with other atoms or through electron transfer, and that the eight outermost electrons in an atom with a noble-gas electronic structure are arranged tetrahedrally in pairs about the atom. Applications of the theory and additional contributions were made by many chemists, including IRVING LANGMUIR and NEVIL VINCENT SIDGWICK.

After the discovery of quantum mechanics in 1925 it became evident that the quantum mechanical equations constitute a reliable basis for the theory of molecular structure. It also soon became evident that these equations, such as the SCHRÖDINGER wave equation, cannot be solved rigorously for any but the simplest molecules. The development of the theory of molecular structure and the nature of the chemical bond during the past twenty-five years has been in considerable part empirical — based upon the facts of chemistry — but with the interpretation of these facts greatly influenced by quantum mechanical principles and concepts.

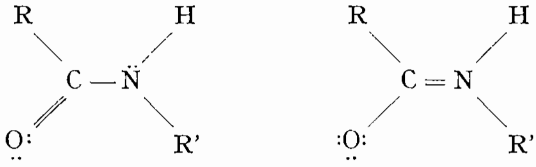
The solution of the wave equation for the hydrogen molecule-ion by Ø. BURRAU (Det Kgl. Danske Vid. Selsk. Math.-fys. Meddelelser, 7, 14 (1927)) completely clarified the question of the nature of the one-electron bond in this molecule-ion. Two illuminating quantum mechanical discussions of the shared-electron-pair bond in the hydrogen molecule were then simultaneously published, one by HEITLER and LONDON (Z. Physik, *44*, 455 (1927)), and the other by E. U. CONDON (Proc. Nat. Acad. Sci. U. S., *13*, 466 (1927)). In the approximate solution of the wave equation for the hydrogen molecule by HEITLER and LONDON a wave function is used that requires the two electrons to be separated, each being close to one of the two nuclei. The treatment by CONDON permits the electrons to be distributed between the two nuclei independently of one another, each occupying a wave function similar to BURRAU's function for the hydrogen-molecule ion. CONDON's treatment is the prototype of the molecular-orbital treatment that has been extensively applied in the discussion of aromatic and conjugated molecules, and HEITLER and LONDON's treatment is the prototype of the valence-bond method. When the effort is made to refine the two treatments they tend to become identical.

These early applications of quantum mechanics to the problem of the nature of the chemical bond made it evident that in general a covalent bond, involving the sharing of a pair of electrons between two atoms, can be formed if two electrons are available (their spins must be opposed, in order that the bond be formed), and if each atom has available a stable electronic orbital for occupancy by the electrons.

The equivalence of the four bonds formed by a carbon atom, which had become a part of chemical theory, was not at first easily reconciled with the quantum mechanical description of the carbon atom as having one $2s$ orbital and three $2p$ orbitals in its outer shell. The solution to this difficulty was obtained when it was recognized that as a result of the resonance phenomenon of quantum mechanics a tetrahedral arrangement of the four bonds of the carbon atom is achieved(1). The carbon atom can be described as having four equivalent tetrahedral bond orbitals, which are hybrids of the s and p orbitals. Further study of this problem led to the discovery of many sets of hybrid bond orbitals, which could be correlated with bond angles, magnetic moments, and other molecular properties (2). In particular it was found that sp^3, dsp^2, and d^2sp^3 hybrid orbitals correspond respectively to the tetrahedral, square planar, and octahedral configurations of inorganic complexes that had been discovered by Werner. Conclusions as to the utilization of atomic orbitals in bond formation can be drawn from experimental values of magnetic moments. For example, the theory of the dsp^2 square complexes of bipositive nickel, palladium, and platinum requires that these substances be diamagnetic. The square complexes of bipositive palladium and platinum had been recognized by Werner and their structure verified by Dickinson (J. Am. Chem. Soc., *44*, 2404 (1922)); but the assignment of the square configuration to the complexes of nickel which are diamagnetic had not been made until the development of the new theory.

Further detailed information about the chemical bond resulted from a consideration of the energy of single bonds in relation to the relative electronegativity of the bonded atoms (3). It was found that the elements can be assigned electronegativity values such as to permit the rough prediction of the heats of formation of compounds to which chemical structures involving only single bonds are conventionally assigned, and that many of the properties of substances can be discussed in a simple way with the use of the electronegativity values of the elements.

The idea that the properties of many organic compounds, especially the aromatic compounds, cannot be simply correlated with a single valence-bond structure, but require the assignment of a somewhat more complex electronic structure, was developed during the period 1923 to 1926 by a number of chemists, including Lowry, Lapworth, Robinson, and Ingold in England, Lucas in the United States, and ARNDT and EISTERT in Germany. It was recognized that the properties of aromatic and conjugated molecules can be described by the use of two or more valence-bond structures, as reflected in the names, the theory of mesomerism and the theory of intermediate states, proposed for the new chemical theory. In 1931 SLATER, E. HÜCKEL, and others recognized that these theories can be given a quantum mechanical interpretation: an approximate wave function for a molecule of this sort can be set up as the sum of wave functions representing the hypothetical structures corresponding to the individual valence-bond structures. The molecule can then be described as having a structure that is a hybrid of the individual valence-bond structures, or as resonating among these structures, and the theory itself is now usually called the resonance theory of chemical structure. Very many quantitative calculations, approximate solutions of the wave equation, for aromatic and conjugated molecules have been made, with results that are in general in good agreement with experiment. Perhaps more important than the quantitative calculations is the possibility of prediction by simple chemical arguments. For example, the amide group, an important structural feature of proteins, can be described as resonating between two structures, one with the double bond between the carbon atom and the oxygen atom, and the other with the double bond between the carbon atom and the nitrogen atom(4):



General arguments about the stability of alternative structures indicate that the structure with the double bond between carbon and oxygen should contribute somewhat more to the normal state of the amide group than the other structure; experience with other substances and acquaintance with the results of quantum mechanical calculations suggest the ratio 60 % : 40 % for the respective contributions of these structures. A 40 % contribution of the structure with the double bond between the carbon atom and the nitrogen atom would confer upon this bond the property of planarity of the group of six atoms; the resistance to deformation from the planar configuration would be expected to be 40 % as great as for a molecule such as ethylene, containing a pure double bond, and it can be calculated that rotation of one end by 3° relative to the other end would introduce a strain energy of 100 cal/mole. The estimate of 40 % double-bond character for the C—N bond is supported by the experimental value of the bond length, 1.32 Å., interpreted with the aid of the empirical relation between double-bond character and interatomic distance (5). Knowledge of the structure of amides and also of the amino acids, provided by the theory of resonance and verified by extensive careful experimental studies made by R. B. COREY and his coworkers, has been of much value in the determination of the structure of proteins.

In the description of the theory of resonance in chemistry there has been a perhaps unnecessarily strong emphasis on its arbitrary character. It is true, of course, that a description of the benzene molecule can be given, in quantum mechanical language, without any reference to the two Kekulé structures, in which double bonds and single bonds alternate in the ring. An approximate wave function for the benzene molecule may be formulated by adding together two functions, representing the two Kekulé structures, and adding other terms, to make the wave function approximate the true wave function for the molecule more closely, or it may be constructed without explicit introduction of the wave functions representing the two Kekulé structures. It might be possible to develop an alternative simple way of discussing the structure of the amide group, for example, that would have permitted chemists to predict its properties, such as planarity; but in fact no simple way of discussing this group other than the way given above, involving resonance between two valence-bond structures, has been discovered, and it seems likely that the discussion of complex molecules in terms of resonance among two or more valence-bond structures will continue in the future to be useful to chemists, as it has been during the past twenty years.

The convenience and usefulness of the concept of resonance in the discussion of chemical problems are so great as to make the disadvantage of the element of arbitrariness of little significance. Also, it must not be forgotten that the element of arbitrariness occurs in essentially the same way in the simple structure theory of organic chemistry as in the theory of resonance — there is the same use of idealized, hypothetical structural elements. In the resonance discussion of the benzene molecule the two Kekulé structures have to be described as hypothetical: it is not possible to synthesize molecules with one or the other of the two Kekulé structures. In the same way, however, the concept of the carbon-carbon single bond is an idealization. The benzene molecule has its own structure, which cannot be exactly composed of structural elements from other molecules. The propane molecule also has its own structure, which cannot be composed of structural elements from other molecules — it is not possible to isolate a portion of the propane molecule, involving parts of two carbon atoms and perhaps two electrons in between them, and say that this portion of the propane molecule is the carbon-carbon single bond, identical with a portion of the ethane molecule. The description of the propane molecule as involving carbon-carbon single bonds and carbon-hydrogen single bonds is arbitrary; the concepts themselves are idealizations, in the same way as the concept of the Kekulé structures that are described as contributing to the normal state of the benzene molecule. Chemists have found that the simple structure theory of organic chemistry and also the resonance theory are valuable, despite their use of idealizations and their arbitrary character.

Other extensions of the theory of the chemical bond made in recent years involve the concept of fractional bonds. Twenty-five years ago it was discovered that a simple theory of complex crystals with largely ionic structures, such as the silicate minerals, can be developed on the basis of the assumption that each cation or metal atom divides its charge or valence equally among the anions that are coordinated about it (6). For example, in a crystal of topaz, $Al_2SiO_4F_2$, each silicon atom is surrounded by a tetrahedron of four oxygen atoms, and each aluminum atom is surrounded by an octahedron of four oxygen atoms and two fluorine atoms. The valence of silicon, 4, is assumed to be divided among four bonds, which then have the bond number 1 — they are single bonds. The valence of aluminum, 3, is divided among six bonds, each of which is a half bond. A stable structure results when the atoms are arranged in such a way that each anion, oxygen or fluorine, forms bonds equal to its valence. In topaz each oxygen atom forms one single bond with silicon and two half bonds with aluminum, whereas each fluorine atom forms only two half bonds with aluminum. The distribution of the valences hence then corresponds to the bivalence of oxygen and the univalence of fluorine. It was pointed out by W. L. BRAGG that if the metal atoms are idealized as cations (Si^{++++} and Al^{+++}) and the oxygen and fluorine atoms as anions (O^{--} and F^{-}), this distribution corresponds to having the shortest possible lines of force between the cations and the anions — the lines of force need to reach only from a cation to an immediately adjacent anion, which forms part of its coordination polyhedron. Occasionally ionic crystals are found in which there are small deviations from this requirement, but only rarely are the deviations larger than one quarter of a valence unit.

Another application of the concept of fractional valence bonds has been made in the field of metals and alloys. In the usual quantum mechanical discussion of metals, initiated by W. PAULI (Z. Physik, *41*, 81 (1927)) and SOMMERFELD (Naturwiss., *15*, 825 (1927)), the assumption was made that only a small number of electrons contribute significantly to the binding together of the metal atoms. For example, it was customary to assume that only one electron, occupying a 4*s* orbital, is significantly involved in the copper-copper bonds in the metal copper. Sixteen years ago an analysis of the magnetic properties of the transition metals was made that indicated that the number of bonding electrons in the transition metals is much larger, of the order of magnitude of six (7). Iron, for example, can be described as having six valence electrons, which occupy hybrid d^3sp^2 orbitals. The six bonds, corresponding to these six valence electrons, resonate among the fourteen positions connecting an iron atom with its fourteen nearest neighbors. The bonds to the eight nearest neighbors have bond number approximately 5/8, and those to the six slightly more distant neighbors have bond number 1/6. In gamma iron, where each atom is surrounded by twelve equally distant neighbors, the bonds are half bonds. The concept that the structure of metals and intermetallic compounds can be described in terms of valence bonds that resonate among alternative positions, aided by an extra orbital on most or all of the atoms (the metallic orbital), has been found of value in the discussion of the properties of these substances (8). The resonating-bond theory of metals is supported especially strongly by the consideration of interatomic distances in metals and intermetallic compounds (9).

The iron atom has eight electrons outside of the argon shell of eighteen. Six of these electrons are assumed, in the resonating-valence-bond theory, to be valence electrons, and the remaining two are atomic electrons, occupying 3*d* orbitals, and contributing two Bohr magnetons to the magnetic moment of the atom. A theory of the ferromagnetism of iron has recently been developed (10), in which, as suggested by Zener (Phys. Rev., *81*, 440 (1951)), the interaction producing the Weiss field in the ferromagnetic metal is an interaction of the spin moments of the atomic electrons and uncoupled spins of some of the valence electrons. It has been found possible to use spectroscopic energy values to predict the number of uncoupled valence electrons, and hence the saturation magnetic moment for iron: the calculation leads to 0.26 uncoupled valence electrons per atom, and saturation magnetic moment 2.26 Bohr magnetons, which might be subject to correction by two or three percent because of the contribution of orbital moment. The experimental value is 2.22. A calculated value of the Curie temperature in rough agreement with experiment is also obtained.

The valence theory of metals and intermetallic compounds is still in a rather unsatisfactory state. It is not yet possible to make predictions about the composition and properties of intermetallic compounds with even a small fraction of the assurance with which they can be made about organic compounds and ordinary inorganic compounds. We may, however, hope that there will be significant progress in the attack on this problem during the next few years.

Let us now return to the subject of the structural chemistry of organic substances, especially the complex substances that occur in living organisms, such as proteins. Recent work in this field (11) has shown the value of the use of structural arguments that go beyond those of the classical structure theory of organic chemistry. The interatomic distances and bond angles in the polypeptide chains of proteins are precisely known, the bond distances to within about 0.02 Å and the bond angles to within about 2°. It is known that the amide groups must retain their planarity; the atoms are expected not to deviate from the planar configuration by more than perhaps 0.05 Å. There is rotational freedom about the single bonds connecting the alpha carbon atom with the adjacent amide carbon and nitrogen atoms, but there are restrictions on the configurations of the polypeptide chain that can be achieved by rotations about these bonds: atoms of different parts of the chain must not approach one another so closely as to introduce large steric repulsion, and in general the N—H and O atoms of different amide groups must be so located relative to one another as to permit the formation of hydrogen bonds, with $N—H \cdots O$ distance equal to 2.79 ± 0.10 Å and with the oxygen atom not far from the N—H axis. These requirements are stringent ones. Their application to a proposed hydrogen-bonded structure of a polypeptide chain cannot in general be made by the simple method of drawing a structural formula; instead, extensive numerical calculations must be carried out, or a model must be constructed. For the more complex structures, such as those that are now under consideration for the polypeptide chains of collagen and gelatin, the analytical treatment is so complex as to resist successful execution, and only the model method can be used. In order that the principles of modern structural chemistry may be applied with the power that their reliability justifies, molecular models must be constructed with great accuracy. For example, molecular models on the scale 2.5 cm = 1 Å have to be made with a precision better than 0.01 cm.

We may, I believe, anticipate that the chemist of the future who is interested in the structure of proteins, nucleic acids, polysaccharides, and other complex substances with high molecular weight will come to rely upon a new structural chemistry, involving precise geometrical relationships among the atoms in the molecules and the rigorous application of the new structural principles, and that great progress will be made, through this technique, in the attack, by chemical methods, on the problems of biology and medicine.

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THE SHARED-ELECTRON CHEMICAL BOND

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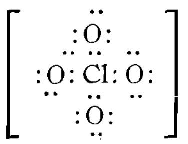
With the development of the quantum mechanics it has become evident that the factors mainly responsible for chemical valence are the Pauli exclusion principle and the Heisenberg-Dirac resonance phenomenon. It has been shown[1,2] that in the case of two hydrogen atoms in the normal state brought near each other the eigenfunction which is symmetric in the positional coördinates of the two electrons corresponds to a potential which causes the two atoms to combine to form a molecule. This potential is due mainly to a resonance effect which may be interpreted as involving an interchange in position of the two electrons forming the bond, so that each electron is partially associated with one nucleus and partially with the other. The so-calculated heat of dissociation, moment of inertia, and oscillational frequency[2] of the hydrogen molecule are in approximate agreement with experiment. London[3] has recently suggested that the interchange energy of two electrons, one belonging to each of two atoms, is the energy of the non-polar bond in general. He has shown that an antisymmetric (and hence allowed) eigenfunction symmetric in the coordinates of two electrons can occur only if originally the spin of each electron were not paired with that of another electron in the same atom. The number of electrons with such unpaired spins in an atom is, in the case of Russell-Saunders coupling, equal to $2s$, where s is the resultant spin quantum number, and is closely connected with the multiplicity, $2s + 1$, of the spectral term. This is also the number of electrons capable of forming non-polar bonds. The spins of the two electrons forming the bond become paired, so that usually these electrons cannot be effective in forming further bonds.

It may be pointed out that this theory is in simple cases entirely equivalent to G. N. Lewis's successful theory of the shared electron pair, advanced in 1916 on the basis of purely chemical evidence. Lewis's electron pair consists now of two electrons which are in identical states except that their spins are opposed. If we define the chemical valence of an atom as the sum of its polar valence and the number of its shared electron pairs, the new theory shows that the valence must be always even for elements in the even columns of the periodic system and odd for those in the odd columns. The shared electron structures assigned by Lewis to molecules such as H_2, F_2, Cl_2, CH_4, etc., are also found for them by London. The quantum mechanics explanation of valence is, moreover, more detailed and correspondingly more powerful than the old picture. For example, it leads to the result that the number of shared bonds possible for an atom of the first row is not greater than four, and for hydrogen not greater than one; for, neglecting spin, there are only four quantum states in the L-shell and one in the K-shell.

A number of new results have been obtained in extending and refining London's simple theory, taking into consideration quantitative spectral and thermochemical data. Some of these results are described in the following paragraphs.

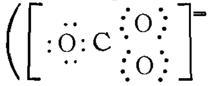
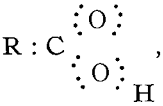
It has been found that a sensitive test to determine whether a compound is polar or non-polar is this: If the internuclear equilibrium distance calculated for a polar structure with the aid of the known properties of ions agrees with the value found from experiment, the molecule is polar; the equilibrium distance for a shared electron bond would, on the other hand, be smaller than that calculated. Calculated[4] and observed values of the hydrogen-halogen distances in the hydrogen halides are in agreement only for HF, from which it can be concluded that HF is a polar compound formed from H^+ and F^- and that, as London had previously stated, HCl, HBr, and HI are probably non-polar. This conclusion regarding HF is further supported by the existence of the hydrogen bond. The structure $\left[:\ddot{\underset{..}{F}}:H:\ddot{\underset{..}{F}}:\right]^-$ for the acid fluoride ion and a similar one for H_6F_6 are ruled out by Pauli's principle, if the shared pairs be of London's type. The ionic structure $:\ddot{\underset{..}{F}}:^-\ H^+\ :\ddot{\underset{..}{F}}:^-$, in which the proton holds the two fluoride ions together by electrostatic forces (including polarization), is, of course, allowed. This conception of the hydrogen bond, requiring the presence of a proton, explains the observation that only atoms of high electron affinity (fluorine, oxygen, and nitrogen) form such bonds.

Compounds of septivalent chlorine probably contain chlorine with a polar valence of +3 and with four shared electron bonds. Thus the perchlorate ion would be formed from $\cdot\dot{\underset{\cdot}{Cl}}\cdot^{+3}$ and $4\cdot\ddot{\underset{..}{O}}:^-$ and would have the structure



$$\left[\begin{array}{c} :\ddot{O}: \\ :\ddot{\underset{..}{O}}:\ddot{\underset{..}{Cl}}:\ddot{\underset{..}{O}}: \\ :\underset{..}{O}: \end{array}\right]^-$$

. This structure is, of course, also possible for FO_4^-, inasmuch as there are positions for four (and only four) unpaired electrons in the *L*-shell of fluorine. London assumed that septivalent chlorine had a polar valence of zero and seven shared electron bonds, and pointed out in explanation of the non-existence of valences other than one for fluorine that seven unpaired *L*-electrons cannot occur. This simple explanation, however, does not make impossible fluorine with a polar valence of +3 and with four shared bonds; the non-existence of higher valences of fluorine must accordingly instead be explained on energetic considerations, and is connected with its very large ionization potentials.

In the case of some elements of the first row the interchange energy resulting from the formation of shared electron bonds is large enough to change the quantization, destroying the two sub-shells with $l = 0$ and $l = 1$ of the *L*-shell. Whether this will or will not occur depends largely on the separation of the *s*-level ($l = 0$) and the *p*-level ($l = 1$) of the atom under consideration; this separation is very much smaller for boron, carbon, and nitrogen than for oxygen and fluorine or their ions, and as a result the quantization can be changed for the first three elements but not for the other two. The changed quantization makes possible the very stable shared electron bonds of the saturated carbon compounds and the relatively stable double bonds of carbon, which are very rare in other atoms, and in particular are not formed by oxygen. This rupture of the *l*-quantization also stabilizes structures in which only three electron pairs are attached to one atom, as in molecules containing a triple bond ($N_2 = \dot{:}N:N\dot{:}$), the carbonate, nitrate, and borate ions  $\left(\left[:\ddot{O}:C\genfrac{}{}{0pt}{}{:O:}{:O:}\right]^{=}\right.$, etc.), the carboxyl group,  $R:C\genfrac{}{}{0pt}{}{:O:}{:O:H}$, and similar compounds. It has further been found that as a result of the resonance phenomenon a tetrahedral arrangement of the four bonds of the quadrivalent carbon atom is the stable one.

Electron interactions more complicated than those considered by London also result from the quantum mechanics, and in some cases provide explanations for previously anomalous molecular structures.

It is to be especially emphasized that problems relating to choice among various alternative structures are usually not solved directly by the application of the rules resulting from the quantum mechanics; nevertheless, the interpretation of valence in terms of quantities derived from the consideration of simpler phenomena and susceptible to accurate mathematical investigation by known methods now makes it possible to attack them with a fair assurance of success in many cases.

The detailed account of the material mentioned in this note will be submitted for publication to the *Journal of the American Chemical Society.*

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[2] Y. Sugiura, *Ibid.*, **45**, 484 (1927).

[3] F. London, *Ibid.*, **46**, 455 (1928).

[4] L. Pauling, *Proc. Roy. Soc.*, **A114**, 181 (1927). In this paper it was stated that the consideration of polarization of the anion by the cation would be expected to reduce the calculated values; a number of facts, however, indicate that with ions with the noble gas structure the effect of polarization on the equilibrium distance is small.

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THE APPLICATION OF THE QUANTUM MECHANICS TO THE STRUCTURE OF THE HYDROGEN MOLECULE AND HYDROGEN MOLECULE-ION AND TO RELATED PROBLEMS

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I. INTRODUCTION

Many attempts were made to derive with the old quantum theory structures for the hydrogen molecule, H_2, and the hydrogen molecule-ion, H_2^+, in agreement with the experimentally observed properties of these substances, in particular their energy contents. These were all unsuccessful, as were similar attempts to derive a satisfactory structure for the helium atom. It became increasingly evident that in these cases the straightforward application of the old quantum theory led to results definitely incompatible with the observed properties of the substances, and that the introduction of variations in the quantum rules was not sufficient to remove the disagreement. (For a summary of these applications see, for example, Van Vleck (1).) This fact was one of those which led to the rejection of the old quantum theory and the origination of the new quantum mechanics. The fundamental principles of the quantum mechanics were proposed by Heisenberg (2) in 1925. The introduction of the matrix algebra (3) led to rapid developments. Many applications of the theory were made, and in every case there was found agreement with experiment. Then the wave equation was discovered by Schrödinger (4), who developed and applied his wave mechanics independently of the previous work. Schrödinger's methods are often considerably simpler than matrix methods of calculation, and since it has been shown (5) that the wave mechanics and the matrix mechanics are mathematically identical, the wave equation is generally used as the starting point in the consideration of the properties of atomic systems, in particular of stationary states.

The physical interpretation of the quantum mechanics and its generalization to include aperiodic phenomena have been the subject of papers by Dirac, Jordan, Heisenberg, and other authors. For our purpose, the calculation of the properties of molecules in stationary states and particularly in the normal state, the consideration of the Schrödinger wave equation alone suffices, and it will not be necessary to discuss the extended theory.

In the following pages, after the introductory consideration of the experimentally determined properties of the hydrogen molecule and molecule-ion, a unified treatment of the application of the quantum mechanics to the structure of these systems is presented. In the course of this treatment a critical discussion will be given the numerous and scattered pertinent publications. It will be seen that in every case the quantum mechanics in contradistinction to the old quantum theory leads to results in agreement with experiment within the limit of error of the calculation. It is of particular significance that the straightforward application of the quantum mechanics results in the unambiguous conclusion that two hydrogen atoms will form a molecule but that two helium atoms will not; for this distinction is characteristically chemical, and its clarification marks the genesis of the science of sub-atomic theoretical chemistry.

II. THE OBSERVED PROPERTIES OF THE HYDROGEN MOLECULE AND MOLECULE-ION

The properties of the hydrogen molecule and molecule-ion which are the most accurately determined and which have also been the subject of theoretical investigation are ionization potentials, heats of dissociation, frequencies of nuclear oscillation, and moments of inertia. The experimental values of all of these quantities are usually obtained from spectroscopic data; substantiation is in some cases provided by other experiments, such as thermochemical measurements, specific heats, etc. A review of the experimental values and comparison with some theoretical results published by Birge (7) has been used as the basis for the following discussion.

The ultraviolet absorption spectrum of hydrogen was analyzed by Dieke and Hopfield (8). They identified the three lowest

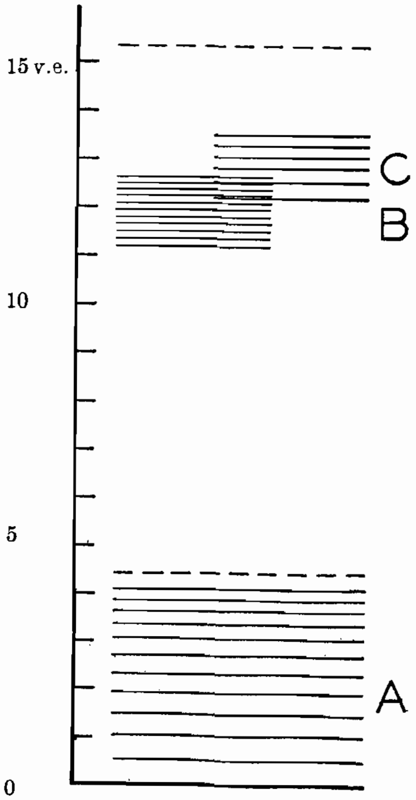

FIG. 1. ENERGY LEVEL DIAGRAM FOR THE THREE LOWEST ELECTRONIC STATES OF THE HYDROGEN MOLECULE, SHOWING SUCCESSIVE OSCILLATIONAL LEVELS

electronic states, indicated in figure 1 by the symbols A, B, and C, and for each a number of states of oscillation of the nuclei, also shown in the figure. In addition there is a fine-structure of each oscillational state due to rotation of the molecule. A number of these levels were independently obtained by Witmer (9) from the analysis of the Lyman bands. Richardson (10) has analyzed bands in the visible, and on the basis of comparison of the oscillational and rotational fine-structure has identified the lower states of some of these bands with Dieke and Hopfield's *B* and *C* states. The upper levels of Richardson's bands correspond to an electron in successive excited states, and by means of an assumed Rydberg formula Birge has carried out the extrapolation to ionization, and has obtained for the ionization potential of the hydrogen molecule the value

$$I_{H_2} = 15.34 \pm 0.01 \text{ volts}$$

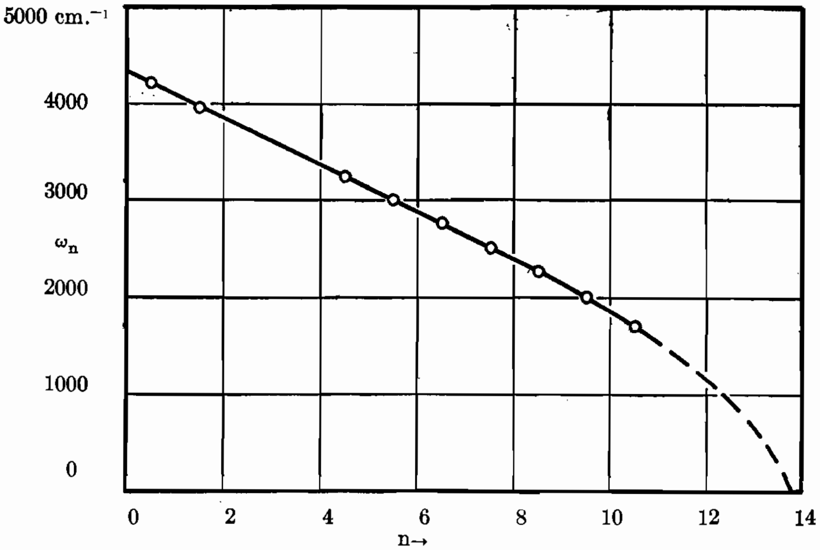

FIG. 2. THE OSCILLATIONAL FREQUENCY FOR THE NORMAL STATE OF THE HYDROGEN MOLECULE AS A FUNCTION OF THE OSCILLATIONAL QUANTUM NUMBER

The area under the curve gives the heat of dissociation

He also states that he has verified this value by means of the heat of dissociation of various excited states of the molecule as obtained by extrapolating the oscillational levels in the way described below.

Ionization by electron impact has been shown (11) to occur at about 16.1 volts. Condon has given the explanation of the discrepancy between this and the band spectrum value in terms of a general phenomenon discovered and interpreted by Franck (12). We shall see later that the equilibrium internuclear distance for H_2 is about 0.75 Å, and for H_2^+, 1.06 Å. When H_2 in the normal state is ionized by electron impact to H_2^+ the nuclei do not have time to move, but are left some distance from their new equilibrium positions. As a result large nuclear oscillations occur, estimated by Condon to correspond to about 1 volt-electron of oscillational energy; and this energy in addition to the ionization energy must be supplied by the impacting electron.

The best experimental value of the heat of dissociation of H_2 is that obtained by Witmer (9) by extrapolating the oscillational levels of the normal state of the molecule to dissociation. The restoring force acting on the two nuclei becomes smaller as the nuclei get farther apart, and as a result the oscillational frequency in successive oscillational states becomes smaller and smaller. For H_2 in the normal state this oscillational frequency

$$\omega_n = \frac{1}{h}\frac{\partial E_n}{\partial n}$$

is represented in figure 2 for values of n, the oscillational quantum number,[1] from 0 to 11. The curve was extrapolated by Witmer as shown by the dotted line; the area under it is equal to the heat of dissociation, and gives

$$D_{H_2} = 4.34 \pm 0.1 \text{ volt-electrons}$$

It is of interest to note that dissociation, represented in figure 1 by the dotted line, is very close to the highest observed oscillational-rotational state. Indeed the oscillational and rotational energy of the highest observed level was 4.10 v.e. (94,600 cal/mole), which must be a lower limit to the heat of dissociation.

The value 4.34 v.e. is equal to 100,000 cal/mole. Thermochemical measurements are in satisfactory agreement with this spectroscopic result. Thus Isnardi's experiments (13) on the thermal conductivity of partially dissociated hydrogen give, with the computational error discovered by Wohl (14) corrected, a

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[1] The true oscillational quantum number has the values 1/2, 3/2, 5/2,... For convenience we shall use in this paper the integers obtained by subtracting $\frac{1}{2}$ from these values, unless specific mention is made of an alternative procedure.

value between 96,765 and 102,257 cal/mole. Langmuir's most recent value from his similar measurements (15) is 97,000 cal/mole.

From the rotational fine-structure of the A levels Hori (16) obtained the value

$$I_o = 0.467 \times 10^{-40} \text{ g. cm.}^2$$

for the moment of inertia of the molecule in the normal state, corresponding to an equilibrium internuclear distance

$$r_o = 0.76 \text{ Å}$$

TABLE 1

The properties of the hydrogen molecule

		E_e,cm^{-1}	n^*	ω_0,cm^{-1}	r_0,Å.
1	1^1S(A)	0	0.9396	4264	0.76
2	2^1S(B)	90083	1.7920	1325	1.55
3	2^3P	(94735)	(1.9281)	2390	0.97
4	2^3S	94906.7	1.9337	2593.82	1.08
5	2^1P	(95469)	(1.9526)		
6	C	99086	2.0882	2380	1.06
7	3^3S	111427	2.9261		
8	3^3P	111518.1	2.9365	2306.94	1.136
9	3^1P	111656.8	2.9526	2373.89	
10	4^3P	117169.9	3.9395	2276.45	1.145
11	4^1P	117216.9	3.9526	2325.6(?)	
12	5^3P	119744.2	4.941	2251	1.168
13	6^3P	121130.2	5.942	2229 (?)	1.166
14	7^3P	121961.0	6.942		
15	8^3P	122498.3	7.942		
16	H_2^+	124237		2247	(1.06)

This result is independently verified by Dennison (17) who has recently given a satisfactory theory of the specific heat of hydrogen. The observed specific heat as interpreted by Dennison requires that I_0 be equal to 0.464×10^{-40} g. cm.^{2}. The very recent measurements by Cornish and Eastman (18) of the specific heat of hydrogen from the velocity of sound are said to agree very well with Dennison's theory if I_0 be given the value of 0.475×10^{-40} g. cm.^{2}.

The oscillational frequency of the nuclei in H_2 in the normal state was calculated by Birge from the measurements of Witmer, Dieke and Hopfield, and Hori to be

$$\omega_{H_2} = 4264 \text{ cm.}^{-1}$$

By extrapolating the observed oscillational frequencies for various excited states of H_2 forming a part of a Rydberg series, Birge obtained for H_2^+ in the normal state the value

$$\omega_{H_2^+} = 2247 \text{ cm.}^{-1}$$

A summary of information regarding various electronic states of the hydrogen molecule is given in table 1, quoted from Birge.

The symbols in the second column represent the electronic state; in particular the first number is the total quantum number of the excited electron. We shall see later that in one case at least the symbol is probably incorrect. The third column gives the wave-number of the lowest oscillational-rotational level, the fourth the effective quantum number, the fifth and sixth the oscillational wave-number and the average internuclear distance for the lowest oscillational-rotational level. The data for H_2^+ were obtained by extrapolation, except r_0, which is Burrau's theoretical value (Section VIa).

The interrelation of these quantities and comparison with theoretical results will be discussed in the following sections of this paper.

III. THE HYDROGEN ATOM

The wave equation representing a conservative Newtonian dynamical system is

$$\Delta\psi + \frac{8\pi^2}{h^2}(W - V(q_k))\,\psi = 0 \qquad (1)$$

with the conditions that ψ, the wave function or eigenfunction, be everywhere continuous, single-valued, and bounded. W and $V(q_k)$ are the energy constant and the potential energy; and the differential operations are with respect to coördinates whose line-element is given by

$$ds^2 = 2T(q_k, \dot{q}_k)\,dt^2,$$

in which T is the kinetic energy expressed as a function of the velocities. Only certain functions satisfy these requirements in any given case; to each there corresponds a characteristic value of the energy constant W. For a hydrogen-like atom with fixed nucleus of charge Ze the potential energy is $-\frac{Ze^2}{r}$, and the wave equation is

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}\left(W + \frac{Ze^2}{r}\right)\psi = 0 \tag{2}$$

On writing for the eigenfunction

$$\psi_{nlm} = X_{nl}(r)\, Y_{lm}(\vartheta)\, Z_m(\varphi), \tag{3}$$

the wave equation can be resolved into three total differential equations, with the solutions (4) (19)

$$X_{nl}(r) = \left\{\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)!}{2n\,[(n+l)\,!]^3}\right\}^{\frac{1}{2}} e^{-\frac{\xi}{2}}\, \xi^l\, L_{n+l}^{(2l+1)}(\xi)$$

with

$$\left.\begin{aligned} \xi &= \frac{2Z}{na_0}r, \quad a_0 = \frac{h^2}{4\pi^2 me^2} = 0.529\ \text{Å}. \\ Y_{lm}(\vartheta) &= \left\{(l+\tfrac{1}{2})\frac{(l-m)\,!}{(l+m)\,!}\right\}^{\frac{1}{2}} P_l^m(\cos\vartheta) \\ Z_m(\varphi) &= \frac{1}{\sqrt{2\pi}}e^{im\varphi} \end{aligned}\right\} \tag{4}$$

$L_{n+l}^{(2l+1)}(\xi)$ represents the $(2l+1)^{\text{th}}$ derivative of the $(n+l)^{\text{th}}$ Laguerre polynomial (20); and $P_l^m(\cos\vartheta)$ is Ferrers' associated Legendre function of the first kind, of degree l and order m. $Y_{lm}\,Z_m$ thus constitutes a tesseral harmonic (21). The ψ's are in this form orthogonal and normalized, so that they fulfill the conditions

$$\int \psi_{nlm}\,\psi_{n'l'm'}\,d\Omega = \begin{cases} 1 \text{ for } n = n',\ l = l',\ m = m' \\ 0 \text{ otherwise} \end{cases} \tag{5}$$

in which $d\Omega$ is the element of volume. The parameter n, the principal quantum number, can assume the values 1, 2, 3, . . . ;

l, the analogue of the azimuthal quantum number, the values 0, 1, 2, . . . n–1; and m, the magnetic quantum number, the values 0, ± 1, ± 2, . . . $\pm l$.

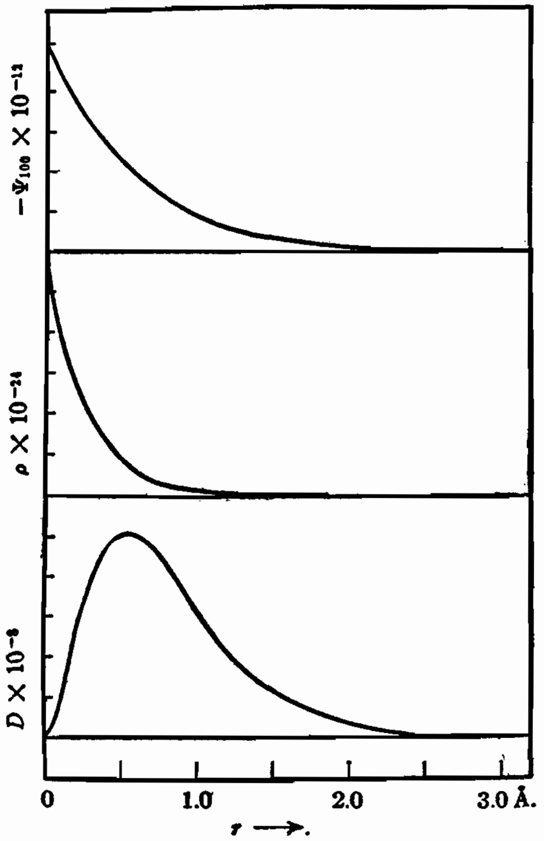

FIG. 3

The eigenfunction ψ_{100}, the electron density $\rho = \psi^2_{100}$, and the electron distribution function $D = 4 \pi r^2 \rho$ of the normal hydrogen atom as functions of the distance r from the nucleus.

The normal state of the atom is that with $n = 1, l = 0, m = 0$. The corresponding eigenfunction is

$$\psi_{100} = \sqrt{\frac{Z^3}{\pi a_0^3}}\, e^{-\frac{\xi}{2}} \tag{6}$$

The quantity ψ^2 as a function of the coördinates is interpreted as the probability of the corresponding microscopic state of the system; in this case the probability that the electron occupies a certain position relative to the nucleus. It is seen from equation 6 that in the normal state the hydrogen atom is spherically symmetrical, for ψ_{100} is a function of r alone. The atom is furthermore not bounded, but extends to infinity; the major portion is, however, within a radius of about $2a_0$ or 1Å. In figure 3 are represented the eigenfunction ψ_{100}, the average electron density $\rho = \psi^2_{100}$ and the radial electron distribution $D = 4\pi r^2\rho$ for the normal state of the hydrogen atom.

The energy values correponding to the various stationary states are found from the wave equation to be those deduced originally by Bohr with the old quantum theory; namely,

$$W_{nlm} = -\frac{2\pi^2 m e^4 Z^2}{n^2 h^2} = -\frac{Z^2 e^2}{2 n^2 a_0}. \tag{7}$$

The energy of the normal state of hydrogen is

$$W_H = -\frac{e^2}{2 a_0} = -13.54 \text{ v.e.} \tag{8}$$

I_H, the ionization potential of hydrogen, accordingly is equal to 13.54 volts.

This simplified treatment does not account for the fine-structure of the hydrogen spectrum. It has been shown by Dirac (22) that the assumption that the system conform to the principles of the quantum mechanics and of the theory of relativity leads to results which are to a first approximation equivalent to attributing to each electron a spin; that is, a mechanical moment and a magnetic moment, and to assuming that the spin vector can take either one of two possible orientations in space. The existence of this spin of the electron had been previously deduced by Uhlenbeck and Goudsmit (23) from the empirical study of line spectra. This result is of particular importance for the problems of chemistry.

IV. THE PERTURBATION THEORY OF THE QUANTUM MECHANICS. THE RESONANCE PHENOMENON

The first-order perturbation theory of the quantum mechanics (4, III) is very simple when applied to a non-degenerate state of a system; that is, a state for which only one eigenfunction exists. The energy change W^1 resulting from a perturbation function f is just the quantum mechanics average of f for the state in question; i.e., it is

$$W^1 = \int f \psi^2 \, d\Omega \tag{9}$$

As an example we may calculate the energy of the helium atom in its normal state (24). Neglecting the interaction of the two electrons, each electron is in a hydrogen-like orbit, represented by equation 6; the eigenfunction of the whole atom is then ψ_{100} (1) ψ_{100} (2), where (1) and (2) signify the first and the second electron. The perturbation function is the electronic interaction $\frac{e^2}{r_{12}}$; and the perturbation energy is

$$W^1 = \int\int \frac{e^2}{r_{12}} \psi^2_{100}(1) \, \psi^2_{100}(2) \, d\Omega_1 \, d\Omega_2 \tag{10}$$

in which subscripts refer to the two electrons. This integral has the value $\frac{5}{8}\frac{Ze^2}{a_0}$. The energy of the unperturbed system was (equation 7) $-\ 2\frac{Z^2e^2}{2a_0} = -108.4$ v.e., giving a total energy of $-\ \frac{11}{4}\frac{e^2}{a_0}$ or -74.5 v.e. The experimentally determined value is -78.8 v.e. Thus the first-order approximation reduces the discrepancy from 29.6 v.e. to -4.3 v.e. A more accurate theoretical calculation (25) has led to -77.9 v.e.

If the unperturbed system is degenerate, so that several linearly independent eigenfunctions correspond to the same energy value, then a more complicated procedure must be followed. There can always be found a set of eigenfunctions (the zeroth order eigenfunctions) such that for each the perturbation energy is given by equation 9; and the perturbation theory provides the method for finding these eigenfunctions (4, III). This result is of importance for systems containing two or more electrons. Let us consider, for example, an excited helium atom. Neglecting the interaction of the two nuclei the system may be described by saying that the electrons are in two different orbits, represented by the hydrogen-like eigenfunctions ψ and φ, say. The eigenfunction for the atom is, then, $\psi\ (1)\ \varphi\ (2)$. But on interchanging the electrons to give $\psi\ (2)\ \varphi\ (1)$ the energy of the system is unchanged, so that the system is degenerate. The perturbation theory leads to the result that the correct eigenfunctions are not $\psi\ (1)\ \varphi\ (2)$ and $\varphi\ (1)\ \psi\ (2)$, but rather

$$\Psi_S = \frac{1}{\sqrt{2}} \{\psi\ (1)\ \varphi\ (2) + \varphi\ (1)\ \psi\ (2)\} \tag{11a}$$

and

$$\Psi_A = \frac{1}{\sqrt{2}} \{\psi\ (1)\ \varphi\ (2) - \varphi\ (1)\ \psi\ (2)\} \tag{11b}$$

Ψ_S is said to be symmetric in the coördinates of the two electrons, for interchanging them leaves the eigenfunction unchanged, while Ψ_A is antisymmetric, for interchanging the electrons changes the sign of the eigenfunction.

Substitution of these eigenfunctions in equation 9 leads to the result

$$\begin{aligned} W^1{}_S &= H_{11} + H_{12} \\ W^1{}_A &= H_{11} - H_{12} \end{aligned} \tag{12}$$

with

$$\begin{aligned} H_{11} &= \int\int\int \psi^2(1)\ \varphi^2(2)\ d\Omega_1\ d\Omega_2 \\ H_{12} &= \int\int\int \psi\ (1)\ \varphi\ (1)\ \psi\ (2)\ \varphi\ (2)\ d\Omega_1\ d\Omega_2. \end{aligned}$$

If the electrons did not change positions; that is, if $\psi\ (1)\ \varphi\ (2)$ or $\varphi\ (1)\ \psi\ (2)$ were the correct eigenfunction, the perturbation energy would be H_{11} alone. The added or subtracted term H_{12} results from one electron jumping from one orbit (ψ) to the other (φ) at the same time that the other electron makes the reverse jump. For this reason $\pm H_{12}$ is called the interchange or resonance energy. This phenomenon, called the interchange or resonance phenomenon, was discovered by Heisenberg and Dirac (26).

There is no classical analogue of it save the trivial case of the resonance of two similar harmonic oscillators.

The interchange energy of electrons is in general the energy of the non-polar or shared-electron chemical bond.

V. THE PROPERTIES OF MOLECULES ACCORDING TO THE QUANTUM MECHANICS

The procedure to be followed in the theoretical discussion of the structure of molecules has been given by Born and Oppenheimer (27), who applied the perturbation theory (to the fourth order) to a system of nuclei and electrons. They showed that the electronic energy is first to be calculated for various arrangements of the nuclei fixed in space. The stable state will then be that for which the so-calculated electronic energy added to the internuclear energy is a minimum. The nuclei will then undergo oscillations about their equilibrium positions, with the electronic and nuclear energy as the restoring potential; and the molecule as a whole will undergo rotations about axes passing through its center of mass.

The justification was also given for the assumption made originally by Franck (12) that during an electron transition the nuclei retain the configuration characteristic of the initial state. These results were true for classical mechanics and the old quantum theory, and had been assumed without proof by many people before the work of Born and Oppenheimer was published.

VI. THE HYDROGEN MOLECULE-ION

a. Numerical solution of the wave equation

The system to be considered consists of two nuclei and one electron. For generality let the nuclear charges be $Z_A e$ and $Z_B e$. From Born and Oppenheimer's results it is seen that the first step in the determination of the stationary states of the system is the evaluation of the electronic energy with the nuclei fixed an arbitrary distance apart. The wave equation is

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}\left(W + \frac{Z_A e^2}{r_A} + \frac{Z_B e^2}{r_B}\right)\psi = 0 \qquad (13)$$

in which r_A and r_B represent the distance of the electron from nucleus A and nucleus B respectively. If elliptic coördinates ξ, η, and φ, defined by the equations

$$\left.\begin{aligned} \xi &= \frac{r_A + r_B}{r_{AB}} \\ \eta &= \frac{r_A - r_B}{r_{AB}} \\ \varphi &= \cos^{-1} \frac{\mathrm{x}}{\sqrt{\mathrm{x}^2 + \mathrm{y}^2}} \end{aligned}\right\} \quad (14)$$

in which r_{AB} in the internuclear distance, be introduced, the partial differential equation becomes separable into three total differential equations. For introducing

$$\psi = \Xi\,(\xi)\; \mathrm{H}\,(\eta)\; \Phi\,(\varphi), \qquad (15)$$

it reduces to

$$\frac{\mathrm{d}^2\Phi}{\mathrm{d}\varphi^2} = m^2\,\Phi \qquad (16a)$$

$$\frac{\mathrm{d}}{\mathrm{d}\xi}\left[(\xi^2 - 1)\frac{\mathrm{d}\Xi}{\mathrm{d}\xi}\right] + \left(-\lambda\,\xi^2 + 2\,\rho\,\xi + \frac{m^2}{\xi^2 - 1} + \mu\right)\Xi = 0 \qquad (16b)$$

$$\text{with} \quad 1 \leqq \xi \leqq \infty$$

and

$$\frac{\mathrm{d}}{\mathrm{d}\eta}\left[(1 - \eta^2)\frac{\mathrm{dH}}{\mathrm{d}\eta}\right] + \left(\lambda\eta^2 - 2\,\mathrm{b}\eta + \frac{m^2}{1 - \eta^2} - \mu\right)\mathrm{H} = 0 \qquad (16c)$$

$$\text{with} \quad -1 \leqq \eta \leqq +1$$

in which

$$\lambda = -\frac{2\,\pi^2\,m\,r_{AB}^2\,W}{h^2} = \rho^2\frac{W}{4\,W_{\mathrm{H}}}$$

$$\rho = \frac{r_{AB}\,(Z_A + Z_B)}{2\,a_0}$$

$$\mathrm{b} = \frac{r_{AB}\,(Z_A - Z_B)}{2\,a_0}$$

and m, λ, and μ are undetermined parameters. The solutions of Equation 16a are known; in order that Φ be an eigenfunction m must assume only the values 0, ±1, ±2, . . . Similarly in order for Ξ and H to be eigenfunctions λ and μ must assume specific values, with the accompanying determination of the energy constant W as a function of the nuclear separation r_{AB}.

Many efforts have been made to solve these equations analytically, but so far they have all been unsuccessful, and little has been published regarding them. Some unsatisfactory work has been reported by Alexandrow (28). Very recently a short report of a paper read by Wilson before the Royal Society has appeared (29). It is probable, in view of the vigor with which it is being attacked, that the problem will be solved completely before very long.

The problem has already been solved for the normal state of the hydrogen molecule-ion ($Z_A = Z_B = 1$) by the use of numerical methods. A rather complete account of these calculations of Burrau (30) will be given here, since the journal in which they were published is often not available.

The numerical solution of the equations was carried out in the following way. For the lowest state m is equal to 0, and for hydrogen, with $Z_A = Z_B = 1$, b = 0. Introducing new variables $\sigma_\xi = -\frac{1}{\Xi}\frac{d\Xi}{d\xi}$ and $\sigma_\eta = -\frac{1}{H}\frac{dH}{d\eta}$, Equations 16b and 16c become

$$\frac{d\,\sigma_\xi}{d\,\xi} = \sigma_\xi^2 - \frac{\lambda\,\xi^2 - 2\,(\rho - \sigma_\xi)\,\xi - \mu}{\xi^2 - 1} \qquad (16b')$$

and

$$\frac{d\,\sigma_\eta}{d\,\eta} = \sigma_\eta^2 - \frac{\lambda\,\eta^2 + 2\,\sigma_\eta\,\eta - \mu}{1 - \eta^2} \qquad (16c')$$

For a given value of λ, σ_η is expanded as a power series satisfying Equation 16c′ about the points $\eta = 0$ and $\eta = 1$ (or -1). It is found that these series coincide at $\eta = 1/2$ only when μ has a certain value. In this way a relation between λ and μ is found.

For each value of μ a similar treatment is given Equation 16b′, resulting in the determination of the corresponding value of ρ, and hence of the relation between W and ρ. The results of the calculation are given in table 2, taken directly from Burrau. The electronic energy is given in the third column. To it must be added the internuclear energy $\frac{e^2}{r_{AB}} = -\frac{2W_H}{\rho}$ (fourth column) to obtain the total energy given in the fifth column.

The relation between W and ρ is shown in figure 4; that for W_{total} in figure 5. It is seen that the equilibrium distance of the nuclei is $\rho = 2.0 \pm 0.1$, or $r_o = 1.06 \pm 0.05$ Å. The corresponding total energy is $W_{total} = 1.204 \pm 0.002\ W_H$ or -16.30 ± 0.03 v.e. To this there is to be added the oscillational energy $\frac{1}{2}h\omega_o$ of the lowest oscillational state. The frequency ω_o is obtained from the curvature of the W_{total} curve, and leads to $\frac{1}{2}h\omega_o = 0.14$ v.e. according to Condon, who corrected an error made by Burrau (Condon's value is reported by Birge (7)). The energy of $H_2{}^+$ in the normal state is thus

TABLE 2

Energy of the hydrogen molecule-ion

ρ	λ	$\frac{W}{W_H} = \frac{4\lambda}{\rho^2}$	$\frac{2}{\rho}$	$\frac{W_{total}}{W_H}$
0.0	0.000	4.000	∞	∞
1.0	0.724	2.896	2.000	0.896
1.3	1.119	2.648	1.538	1.110
1.6	1.559	2.436	1.250	1.186
1.8	1.870	2.309	1.111	1.198
2.0	2.204	2.204	1.000	1.204
2.2	2.552	2.109	0.909	1.200
2.4	2.917	2.025	0.833	1.192
2.95	3.995	1.836	0.678	1.158
∞		1.000	0.000	1.000

$$W_{H_2{}^+} = -16.16 \pm 0.03 \text{ v.e.}$$

It is now possible to check the relation

$$I_{H_2} + I_{H_2{}^+} = D'_{H_2} + 2\,I_H,$$

in which D'_{H_2} is the dissociation potential of hydrogen. With $I_{H_2} = + 15.34$ v. (Section 2), and $I_H = + 13.54$ v. This equation leads to

$$D_{H_2} = 4.42 \text{ v.e.} = 102000 \text{ cal/mol.}$$

for the energy of dissociation of the hydrogen molecule. This is within the limit of error equal to the band spectrum value 4.34

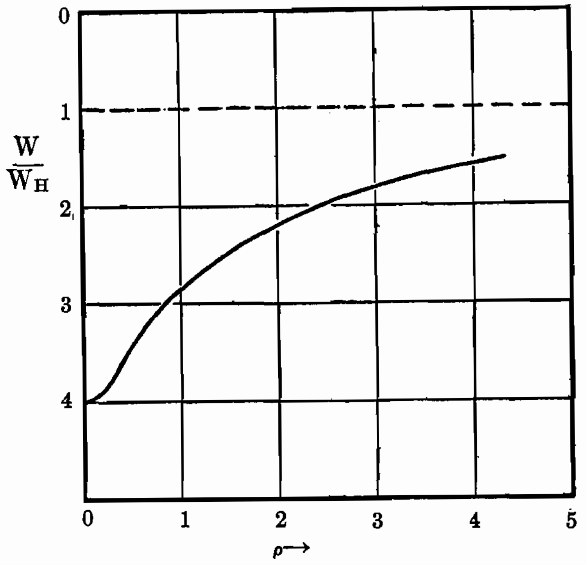

FIG. 4. THE ELECTRONIC ENERGY OF THE HYDROGEN MOLECULE-ION IN THE NORMAL STATE AS A FUNCTION OF THE DISTANCE BETWEEN THE TWO NUCLEI (BURRAU)

± 0.10 v.e., and is to be accepted as the most accurate determination of the heat of dissociation of hydrogen.

The heat of dissociation of H_2^+ into H and H^+ is

$$D_{H_2^+} = W_H - W_{H_2^+} = 2.62 \text{ v.e.}$$

No direct determination of this quantity has been made.

The value 2247 cm^{-1} for ω_0 for H_2^+ obtained by Birge (table 1) leads to $\frac{1}{2}h\omega_0 = 0.141$ v.e., in very good agreement with the theoretical 0.14 v.e.

The average electron density ψ^2 as a function of position was also found by Burrau. For the normal state ψ^2 is represented in figure 6, in which the contour lines pass through points of relative density 1.0, 0.9, 0.8, . . . 0.1. The second curve represents the values of ψ^2 along the line passing through the two nuclei. (ψ^2 is cylindrically symmetrical about this line). It will be seen that the electron is most of the time in the region between the two nuclei, and can be considered as belonging to them both, and forming a bond between them.

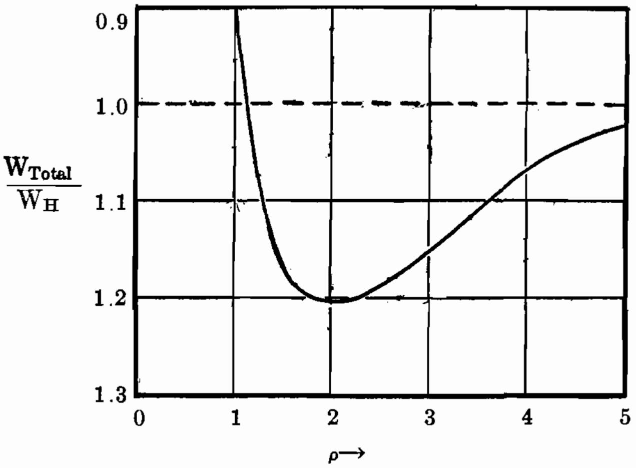

FIG. 5. THE TOTAL ENERGY OF THE HYDROGEN MOLECULE-ION AS A FUNCTION OF ρ (BURRAU)

b. Application of the first-order perturbation theory

Although no new numerical information regarding the hydrogen molecule-ion can be obtained by treating the wave equation by perturbation methods, nevertheless it is of value to do this. For perturbation methods can be applied to many systems for which the wave equation can not be accurately solved, and it is desirable to have some idea of the accuracy of the treatment. This can be gained from a comparison of the results of the perturbation method of the hydrogen molecule-ion and of Burrau's accurate numerical solution. The perturbation treatment assists, moreover, in the physical interpretation of the forces operative in the formation of the ion; for the electronic energy is obtained as the sum of terms each of which can be related without difficulty to a visualisable process of interaction of the nuclei and the electron.

A hydrogen atom and a proton serve as the starting point of the calculation. With the nuclei a distance r_{AB} apart, and with the electron attached to the nucleus A to form a hydrogen atom, the zero$^{\text{th}}$ order eigenfunction is

$$\psi = \sqrt{\frac{Z^3}{\pi a_0^3}}\, e^{-\frac{\xi_A}{2}}, \quad \xi_A = \frac{2\,Z_A}{a_0}\, r_A \qquad (17a)$$

and the action of nucleus B on the electron is the perturbation.

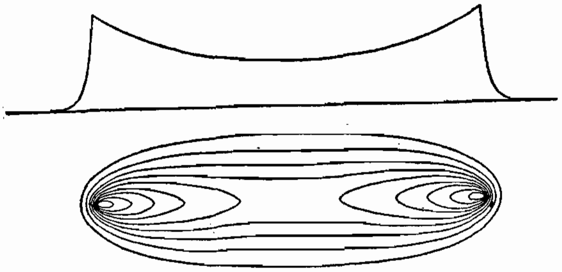

Fig. 6. The Electron Density ψ^2 for the Hydrogen Molecule-ion in the Normal State (Burrau)

The contour lines represent in section places of relative density 1.0, 0.9, 0.8, ..0.1. The density at points along a line drawn through the nuclei is given above.

But the configuration with the electron on nucleus B and with the eigenfunction

$$\varphi = \sqrt{\frac{Z^3}{\pi a_0^3}}\, e^{-\frac{\xi_B}{2}}, \quad \xi_B = \frac{2\,Z_B}{a_0}\, r_B \qquad (17b)$$

corresponds to the same energy. The unperturbed system is thus degenerate. There is, however, no perturbation function for the system as a whole, for in each case the interaction between the electron and the more distant nucleus produces the perturbation; and accordingly the usual theory for degenerate systems cannot be directly applied. It is instead found that on carrying out the treatment used in the derivation of the ordinary perturbation theory closely similar results are obtained. The correct zero$^{\text{th}}$ order eigenfunctions are linear aggregates of ψ and φ, and are, indeed, symmetric and antisymmetric in the two nuclei; they are

$$\Psi = \frac{1}{\sqrt{2 + 2\,S}}\,(\psi + \varphi) \tag{18a}$$

and

$$\Phi = \frac{1}{\sqrt{2 - 2\,S}}\,(\psi - \varphi) \tag{18b}$$

with

$$S = \int \psi\,\varphi\,\mathrm{d}\Omega = \mathrm{e}^{-\rho}\,(1 + \rho + \tfrac{1}{3}\,\rho^2), \tag{19a}$$

in which

$$\rho = \frac{Z}{a_0}\,r_{AB},\ \text{assuming}\ Z_A = Z_B = Z.$$

The radicals in the denominators are necessary in order that the new eigenfunctions be normalized. The wave equation (Equation 13) can now be written

$$\Delta\psi + \frac{8\pi^2 m}{h^2}\left(W_{\mathrm{H}} + W^1 + \frac{Z_A\,e^2}{r_A} + \frac{Z_B\,e^2}{r_B}\right)\psi = 0, \tag{20}$$

in which W^1 is the perturbation energy. It is found (see Heitler and London (39) for the detailed treatment of a similar problem) that the perturbation energy for the eigenfunction Ψ is given by the solution of the equation

$$\int \Psi \left\{\Delta\,\Psi + \frac{8\pi^2 m}{h^2}\left(W_{\mathrm{H}} + W^1 + \frac{Z\,e^2}{r_A} + \frac{Z\,e^2}{r_B}\right)\Psi\right\} \mathrm{d}\Omega = 0 \tag{21}$$

This leads to the result

$$W^1 = -\,e^2\,\frac{I_1 + I_2}{1 + S} \tag{22}$$

in which

$$I_1 = \int \frac{\psi^2}{r_A}\, d\Omega = \frac{Z}{a_0}\left\{\frac{1}{\rho} - e^{-2\rho}\left(1 + \frac{1}{\rho}\right)\right\} \tag{19b}$$

and

$$I_2 = \int \frac{\psi\,\varphi}{r_A}\, d\Omega = \frac{Z}{a_0}\, e^{-\rho}\,(1 + \rho). \tag{19c}$$

The total energy, including the internuclear term, is then

$$W_{\text{Total}} = W_H - e^2\,\frac{I_1 + I_2}{1 + S} + \frac{e^2}{r_{AB}} \tag{23}$$

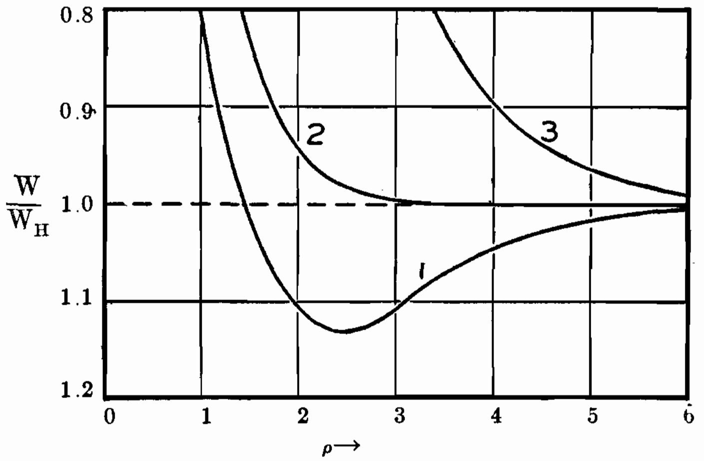

FIG. 7.

Curve 1 represents the total energy of the hydrogen molecule-ion as calculated by the first-order perturbation theory; curve 2, the naïve potential function obtained on neglecting the resonance phenomenon; curve 3, the potential function for the antisymmetric eigenfunction, leading to elastic collision.

In figure 7 is shown the so-calculated total energy W_{total} for H_2^+ as a function of ρ. Comparison with figure 5 shows that the perturbation curve is too high; the force holding the ion together is too small. Equilibrium occurs at $\rho = 2.5$ or $r_0 = 1.32$ Å (correct value, 1.06 Å), and the energy of the ion is then -15.30 v.e. (correct value, -16.30 v.e.).

The eigenfunction Ψ is represented qualitatively by figure 6, but is somewhat more extended, for the contracting influence of the second nucleus has not been taken into account.

It is of interest to calculate the energy corresponding to the single eigenfunction ψ (or φ); i.e., to find the interaction of a proton and a hydrogen atom that would result if the electron were not allowed to jump from one nucleus to the other. For this case

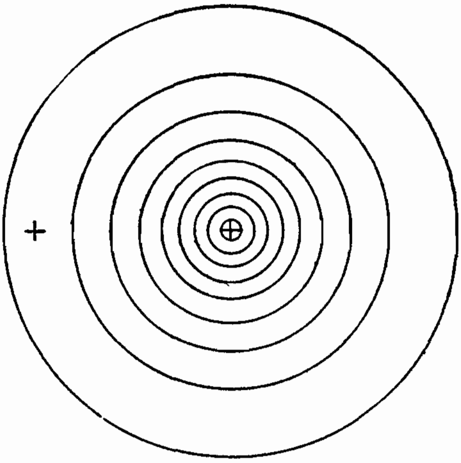

Fig. 8

The contour lines represent points of relative density 1.0, 0.9, 0.8,..0.1 for a hydrogen atom. This figure, with the added proton 1.06 Å from the atom, gives the electron distribution the hydrogen molecule-ion would have (in the zero$^{\text{th}}$ approximation) if the resonance phenomenon did not occur; it is to be compared with figure 6 to show the effect of resonance.

$$W^1 = -e^2 I_1$$

and

$$W_{\text{Total}} = W_{\text{H}} - e^2 I_1 + \frac{e^2}{r_{AB}}. \tag{24}$$

(The perturbation energy is here just the electrostatic energy calculated for the electron distribution given by ψ^2; it is in part this feature of the perturbation theory which led Schrödinger to proclaim that the electron is smeared through space, and which supports the present interpretation of ψ^2 as the probability that the electron will be in the selected region.) This naïve potential is also represented in figure 7. It leads to a repulsive force at all distances. The correct perturbation calculation given in Equation 23 differs from the naïve one in that it involves consideration of the interchange or resonance phenomenon, and leads to an attraction, giving an energy of formation of H_2^+ of about 1.62 v.e. (correct result from Burrau, 2.62 v.e.). We thus see that the fact that the electron can jump from one nucleus to the other—in other words, is shared between the two nuclei— is mainly responsible for the formation of the molecule-ion H_2^+ from H^+ and H. The way the electron distribution is affected by the resonance phenomenon is seen by comparing figure 6 with figure 8, which shows contour lines (of electron density ψ^2) for a hydrogen atom and a proton at the distance $\rho = 2$ (1.06 Å). This comparison is particularly effective in showing that the sharing of the electron between the two nuclei results from the resonance phenomenon.

This resonance energy leads to molecule formation only if the eigenfunction is symmetric in the two nuclei. The perturbation energy for the antisymmetric eigenfunction Φ is

$$W^1_A = -e^2\frac{I_1 - I_2}{1 - S}, \tag{25}$$

and the total energy,

$$W_{A\ \mathrm{Total}} = W_{\mathrm{H}} - e^2\frac{I_1 - I_2}{1 - S} + \frac{e^2}{r_{AB}}, \tag{26}$$

also shown in figure 7, leads to strong repulsion at all distances. This eigenfunction does not, then, give rise to a stable excited state of the hydrogen molecule-ion. Stable excited states will, however, correspond to the symmetric eigenfunctions relating to the various excited states of the hydrogen atom; and in each case (at least until deformation becomes very pronounced) not to the antisymmetric eigenfunctions. This is contrary to the qualitative scheme of levels given by Hund (31), who in a series of papers

(32) has considered the application of the quantum mechanics to molecules in general, with particular reference to molecular spectra.

The above perturbation treatment of the hydrogen molecule-ion has not before been published.

c. The second-order perturbation calculation

An attempt was made by Unsöld (33) to evaluate to the second-order the interaction of a proton and a hydrogen atom. He found, neglecting the resonance phenomenon, that the second-order perturbation energy is given approximately by the expression

$$W^2 = -\frac{9e^2}{4a_0}\left\{\frac{1}{\rho^4} + e^{-2\rho}\left(-\frac{4}{3}\rho + 2 + \frac{4}{3\rho} + \frac{1}{\rho^2} + \frac{2}{\rho^3} + \frac{1}{\rho^4}\right)\right.$$
$$\left. - e^{-4\rho}\left(1 + \frac{2}{\rho} + \frac{1}{\rho^2}\right) + \frac{8}{3}\rho^2\,\mathrm{E_i}\,(-2\rho)\right\}, \qquad (27)$$

in which $\mathrm{E_i}\ (-2\rho)$ represents the integral logarithm with the argument -2ρ. This expression is accurate for large values of ρ; for it then reduces to $-\frac{1}{2}\frac{e^2\alpha}{r^4_{AB}}$, in which α, the polarizability of a hydrogen atom, has the value 0.667×10^{-24} deduced from the second-order Stark effect energy (34).

Using this expression and the value given in Equation 24 for the first-order perturbation, Unsöld found that equilibrium would occur at $\rho = 1$, $r_0 = 0.53$ Å; and that the electronic energy of the hydrogen molecule-ion would then be $-1.205\ W_H$, or -16.31 v.e., in exact agreement with Burrau's value. This agreement is, however, misleading, and indeed the calculation is of no significance, for Unsöld neglected to consider the resonance phenomenon, making use instead of the naïve first-order perturbation. We may, however, attempt to rectify this by adding the second-order energy W^2 to the correct first-order energy of Equation 23. When this is done it is found that equilibrium occurs at $\rho = 1.2$, $r_0 = 0.64$ Å, and that the energy then is -17.95 v.e.

The results of Burrau's calculation, of the first-order perturbation treatment, and of the second-order treatment are given in table 3.

It will be seen that the second-order treatment leads to results which deviate more from the correct values than do those given by the first-order treatment alone. This is due in part to the fact that the second-order energy was derived without consideration of the resonance phenomenon, and is probably in error for that reason. The third-order energy is also no doubt appreciable. It can be concluded from table 3 that the first-order perturbation calculation in problems of this type will usually lead to rather good results, and that in general the second-order term need not be evaluated.

TABLE 3

The properties of the hydrogen molecule-ion

	ρ	r_0	$W_{H_2^+}$
Burrau	2.0	1.06Å	−16.30v.e.
First-order	2.5	1.32	−15.30
Second-order	1.2	0.64	−17.95

In dealing with problems of molecular structure it has been customary in the past to introduce the energy of polarization of one atom or ion by another ion in the form $-\frac{1}{2}\frac{e^2\alpha}{r^4_{AB}}$, and to give α the value it possesses in a uniform field. The form of Equation 27 shows that this is not a good representation of the polarization energy, for it gives values which are much too large at small distances. Indeed, if we attach this term to the first-order energy of Equation 23, it is found that the correct equilibrium distance $r_0 = 1.06$ Å results only if α be placed equal to 0.032×10^{-24}, which is only 5 per cent of the true polarizability of hydrogen. This indicates that in general better results will be obtained in the theoretical treatment of the structure of molecules by ignoring polarization completely than by introducing the usual expression for the polarization. As a matter of fact, it has already been pointed out by Fajans (35) that the experimental values of the heat of sublimation of the alkali halides agree better with those calculated by Reis (36), who neglected polarization, than with those of Born and Heisenberg (37), who took it into consideration. As a result of this it is probable that the numerous discussions of molecular structure based on polarization (38) are of only limited significance.

VII. THE HYDROGEN MOLECULE

a. Perturbation treatment of the interaction of two hydrogen atoms

The most satisfactory treatment which has been given the structure of the hydrogen molecule is that of Heitler and London

FIG. 9. DIAGRAMMATIC REPRESENTATION OF THE EIGENFUNCTIONS FOR TWO HYDROGEN ATOMS

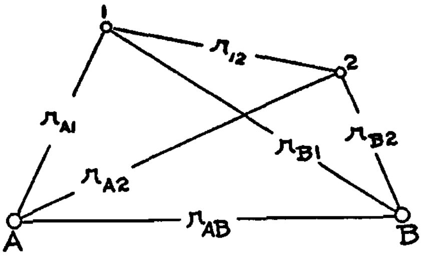

FIG. 10. DIAGRAM SHOWING THE SYMBOLS USED FOR THE VARIOUS INTERNUCLEAR AND INTERELECTRONIC DISTANCES

(39). The system to be treated consists of two nuclei A and B and two electrons 1 and 2. In the unperturbed state two hydrogen atoms are assumed, so that the zeroth-order energy is $2W_H$. If the first electron is attached to nucleus A and the second to nucleus B, the zeroth-order eigenfunction is ψ (1) φ (2), in which ψ and φ are the functions given in Equations 17a and 17b. The state obtained by interchanging the two electrons, φ (1) ψ(2), corresponds to the same zeroth-order energy, so that the system is degenerate, and must be treated in a way similar to that applied to the hydrogen molecule-ion in Section VIb.

The wave equation for the hydrogen molecule with fixed nuclei is

$$\Delta_1 \psi + \Delta_2 \psi + \frac{8\pi^2 m}{h^2} \left\{ 2\, W_H + W^1 + \frac{e^2}{r_{A_1}} + \frac{e^2}{r_{B_1}} + \frac{e^2}{r_{A_2}} + \frac{e^2}{r_{B_2}} - \frac{e^2}{r_{12}} - \frac{e}{r_{AB}} \right\} \psi = 0 \tag{28}$$

in which Δ_1 and Δ_2 represent the second differential operations with respect to the coördinates of the first and the second electron respectively, and the various r's refer to the distances indicated in figure 10. The correct zero$^{\text{th}}$-order eigenfunctions are found by the procedure of Section VIb to be the symmetric

$$\Psi_{H_2} = \frac{1}{\sqrt{2 + 2\, S^2}} \{\psi(1)\, \varphi(2) + \varphi(1)\, \psi(2)\} \tag{29a}$$

and the antisymmetric

$$\Phi_{H_2} = \frac{1}{\sqrt{2 - 2\, S^2}} \{\psi(1)\, \varphi(2) - \varphi(1)\, \psi(2)\} \tag{29b}$$

in which S is given by Equation 19a.

In this case, too, molecule formation results from the symmetric eigenfunction. The corresponding perturbation energy W^1 is obtained from an equation of the type of Equation 20 involving Ψ_{H_2} and the wave equation 28. It is

$$W^1 = \frac{e^2}{1 + S^2} \left\{ \frac{1 + S^2}{r_{AB}} + I_4 + I_6 - 2\, I_1 - 2\, S I_2 \right\} \tag{30}$$

in which I_1 and I_2 are given by Equations 19b and 19c, and I_4 and I_6 by

$$I_4 = \int\!\!\int \frac{\psi^2(1)\, \varphi^2(2)}{r_{12}}\, d\Omega_1\, d\Omega_2 = \frac{Z}{a_0} \left\{ \frac{1}{\rho} - e^{-2\rho} \left(\frac{1}{\rho} + \frac{11}{8} + \frac{3}{4}\rho + \frac{1}{6}\rho^2 \right) \right\} \tag{19d}$$

and

$$I_6 = \int\!\!\int \frac{\psi(1)\, \varphi(1)\, \psi(2)\, \varphi(2)}{r_{12}}\, d\Omega_1\, d\Omega_2$$

$$= \frac{Z}{5a_0}\left[-e^{-2\rho}\left(-\frac{25}{8}+\frac{23}{4}\rho+3\rho^2+\frac{1}{3}\rho^3\right)\right. \tag{31}$$

$$\left.+\frac{6}{\rho}\left\{S^2(\gamma+\log\rho)+S'^2\,\mathrm{E_i}(-4\rho)-2SS'\,\mathrm{E_i}(-2\rho)\right\}\right], \tag{19e}$$

in which $\gamma = 0.5772\ .\ .$ is Euler's constant, and $S' = e^{\rho}(1-\rho+\frac{1}{3}\rho^2)$.

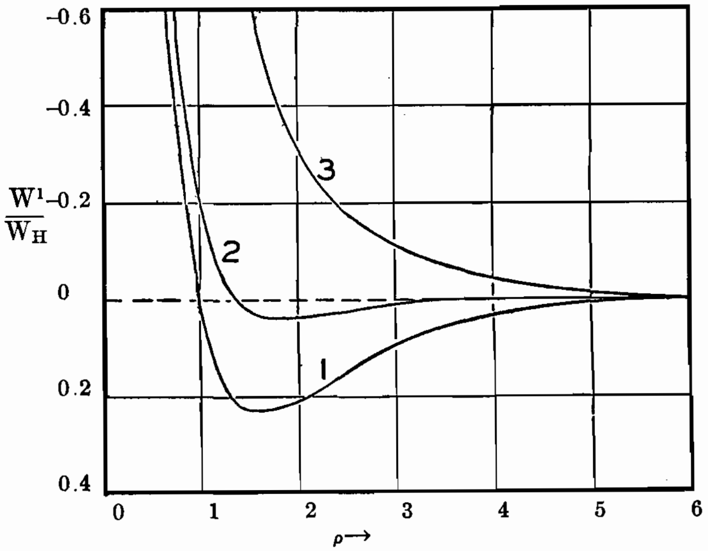

FIG. 11

Curve 1 shows the total energy for the normal state of the hydrogen molecule as given by the first-order perturbation theory; curve 2, the naïve potential function obtained by neglecting the resonance phenomenon; and curve 3, the potential function for the antisymmetric eigenfunction, corresponding to elastic collision.

The energy W^1 depends largely on the integral I_6, for which Heitler and London gave only an approximation. The difficult problem of carrying out this integration was solved by Sugiura (40), whose result is given in Equation 19e. W^1 is shown as a function of ρ in figure 11. It has a minimum at the equilibrium distance $\rho = 1.5$, at which $W^1 = -3.1$ v.e. The comparison of theory and experiment for the hydrogen molecule is shown in table 4. The general agreement is entirely satisfactory in view of the fact that only the first-order perturbation calculation has been made.

It is worthy of mention that the perturbation terms are actually larger than appears from W^1. Thus at $\rho = 1.5$ the term $\frac{e^2}{r_{AB}}$ has the value 18.1 v.e., so that the electronic perturbation energy is -21.3 v.e., which is to be compared with the experimental value -22.5 v.e. It is seen that the electronic perturbation energy is thus in error by only 5 per cent. Furthermore, we saw in Section VIb that the first-order perturbation calculation for the hydrogen molecule-ion gave an energy of dissociation of H_2^+ of 1.62 v.e., which is 1 v.e. smaller than Burrau's correct value. A similar error is to be expected for the hydrogen molecule; and, as a matter of fact, the calculated energy of dissociation is here 1.2 v.e. too small. We are hence justified in the belief that the accurate theoretical treatment of the hydrogen molecule would give results in complete agreement with experiment.

TABLE 4

Properties of the hydrogen molecule

	r_0	I_0	D_{H_2}	ω_0
Calculated..........	0.80 Å	0.53×10^{-40} g. cm.^{2}	3.2 v.e.	4800 cm.$^{-1}$
Observed............	0.76	0.48	4.42	4262

By bringing the nuclei into coincidence a helium atom in the normal state is formed; and a value for its energy can be obtained from the expression for the hydrogen molecule by neglecting the internuclear energy and by putting $\rho = 0$. It is found that $W_{\mathrm{He}} = -\frac{19}{8}e^2/a_0 = -64.3$ v.e., which lies considerably above the experimental value -78.8 v.e.; the error is in the same direction as that for $D_{H_2^+}$. A similar limiting calculation for the hydrogen molecule-ion gives $W_{\mathrm{He}^+} = -3e^2/2a_0 = -40.6$ v.e., instead of the correct value $-4W_{\mathrm{H}} = -54.16$ v.e. Thus for both He and He^+ this perturbation treatment is inaccurate. The treatment gives, however, 64.3 − 40.6 = 23.7 v. for the first ionisation potential of helium, which is in good agreement with the experimental 24.6 v. This agreement was adduced by Suguira as evidence of the accuracy of the perturbation treatment; but it is merely accidental.

If ψ (1) φ (2) or φ (1) ψ (2) alone were to be considered, the perturbation energy would be the electrostatic energy of two nuclei and two electrons distributed according to the probability functions ψ^2 and φ^2; namely,

$$W^1 = e^2\left\{\frac{1}{r_{AB}} + I_4 - 2\,I_1\right\} = \frac{e^2}{a_0}\,e^{-2\rho}\left(\frac{1}{\rho} + \frac{5}{8} - \frac{3}{4}\rho - \frac{1}{6}\rho^2\right) \quad (31)$$

This, the naïve potential function, is also shown in figure 11. It corresponds to a relatively small attraction, so that the conclusion can be drawn that in the hydrogen molecule the interchange energy of the two electrons is the principal cause of the forces leading to molecule formation.

b. The application to the hydrogen molecule of Burrau's numerical solution for the molecule-ion

If the interaction of the two electrons in the hydrogen molecule were small it could be neglected with respect to the electronic-nuclear interaction. Each electron would then be represented by an H_2^+ eigenfunction, and the electronic energy would be just twice that calculated by Burrau. The interelectronic energy could then be calculated as a perturbation; this would necessitate, however, a knowledge of Burrau's eigenfunctions in a form suitable for integration.

Lacking this knowledge, Condon (41) made use of the following semi-empirical method. The electronic energy of the helium atom is raised from $-4\ e^2/a_0 = -108.32$ v.e. (Burrau's value) to −78.8 v.e. (the experimental value) by the electronic interaction. If it be assumed that the interelectronic energy is to be raised to the same fractional value of the Burrau energy throughout the region corresponding to the normal state of the hydrogen molecule, there is obtained the electronic energy function shown in figure 12. Adding to this the electronic energy e^2/r_{AB}, it is found that equilibrium occurs at $r_o = 0.73$ Å, with $D_{H_2} = 4.3$ or 4.4 v.e. and $\omega_o = 7600$ cm.$^{-1}$. These values, except for ω_o, are in excellent agreement with the experimental ones.

This treatment is, however, of less significance than that of the preceding section, for it is more arbitrary and less confidence can be placed in it. In the first place, the interelectronic forces are not small, and it is to be expected that they will cause the electrons to tend to remain on different atoms, as is assumed in the previous treatment of Heitler and London. The assumption that the total electronic energy as calculated by Burrau should be reduced in a constant ratio is, moreover, without justification. It is definitely incorrect for ρ large; for the doubled Burrau energy then approaches the correct value $2W_H$. An assumption which might just as well be made and which is satisfactory both for $\rho = 0$ and for $\rho = \infty$ is that the difference between the doubled Burrau energy and $2W_H$ is to be reduced in a constant ratio; but it leads to the incorrect values $D_{H_2} = 8.0$ v.e. and $r_o = 0.90$ Å.

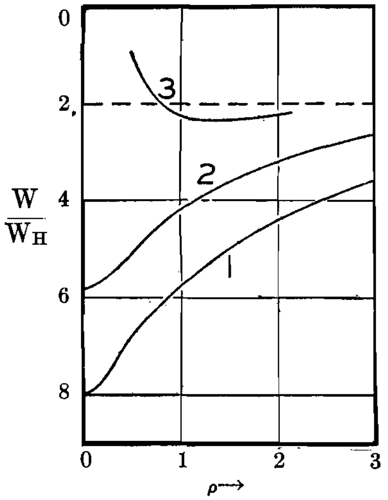

FIG. 12

Curve 1 shows the electronic energy of the hydrogen molecule neglecting interelectronic interaction (from Burrau's solution for the molecule-ion); curve 2, the electronic energy empirically corrected by Condon's method; and curve 3, the total energy of the hydrogen molecule, calculated by Condon's method.

c. The excited states of the hydrogen molecule

Excited states of the hydrogen molecule may be formed from a normal hydrogen atom and a hydrogen atom in various excited states.[2] For these the interelectronic interaction will be small, and the Burrau eigenfunction will represent the molecule in part with considerable accuracy. The properties of the molecule, in particular the equilibrium distance, should then approximate those of the molecule-ion; for the molecule will be essentially a molecule-ion with an added electron in an outer orbit. This is observed in general; the equilibrium distances for all known excited states but one (the second state in table 1) deviate by less than 10 per cent from that for the molecule-ion. It is hence probable that states 3, 4, 5, and 6 are formed from a normal and an excited atom with $n = 2$, and that higher states are similarly formed.

The exceptional state B has a very large equilibrium distance and small oscillational frequency, as has been pointed out by Birge (7). This suggests that the molecule is here not non-polar, but is a polar compound of H^+ and H^-. The electron affinity of hydrogen is probably negative, (about -1 kcal/mole (42)), and it is doubtful that a free negative hydrogen ion in the normal state can exist. The presence of another proton would, however, stabilize the structure, so that a polar hydrogen molecule could be formed. The unperturbed system is again degenerate, for both electrons may be attached to nucleus A or to nucleus B. The zero$^{\text{th}}$-order eigenfunction representing the most stable polar state of the molecule is

$$\frac{1}{\sqrt{2 + 2\,S^2}}\,\{\varphi(1)\,\varphi(2) + \psi(1)\,\psi(2)\}. \qquad (32)$$

The first-order perturbation theory in this case does not give good results, since the mutual interaction of two electrons on one nucleus is so large as to greatly deform the eigenfunctions; it leads

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[2] The calculation of the potential function for these states with the use of the method of Heitler and London is being made by Prof. E. C. Kemble (private communication to Dr. J. R. Oppenheimer).

to an equilibrium distance of about 1Å and an energy about 5 v.e. greater than the normal state. There is no energy level of the molecule in this region. The attempt to take into account the effect of deformation has led to the conclusion that both r_0 and the energy should be increased to values compatible with those observed for the first excited state *B*. Since a polar state is to be expected in this region and since *B* has properties explicable on this basis but not otherwise, the identification of the two may be made with some certainty.

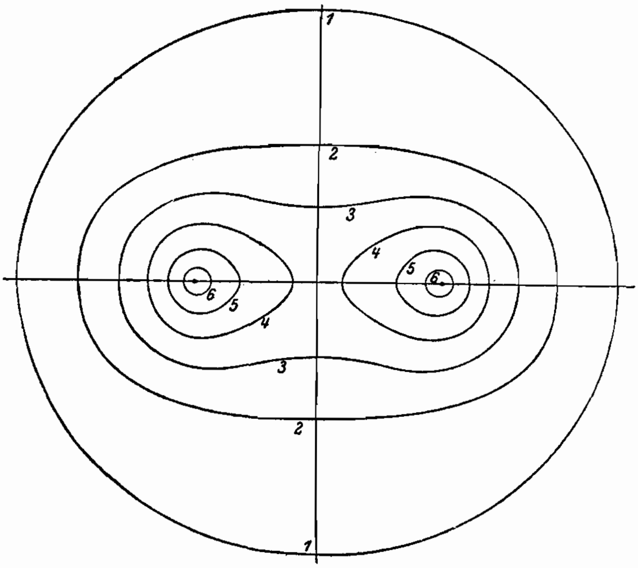

FIG. 13. QUALITATIVE REPRESENTATION BY CONTOURS OF ELECTRON DISTRIBUTION FOR TWO HYDROGEN ATOMS UNITING TO FORM A MOLECULE (LONDON)

We shall next consider whether or not the antisymmetric eigenfunction Φ_{H_2} for two hydrogen atoms (Equation 29b) would lead to an excited state of the hydrogen molecule. The perturbation energy is found to be

$$W^1 = \frac{e^2}{1 - S^2}\left\{\frac{1 - S^2}{r_{AB}} + I_4 - I_6 - 2\, I_1 + 2\, SI_2\right\} \tag{33}$$

This potential differs from that of Equation 30 in that the interchange energy has the opposite sign (and slightly different magnitude). As a result it corresponds to repulsion between the two atoms at all distances, and not to a stable state of the molecule (see figure 11). This result, which had been suggested as a possibility by Hund (31), was proved by Heitler and London. The existence of two potential functions representing the interaction of two normal hydrogen atoms is very remarkable and has, I believe, no classical interpretation. A certain feeling for the phenomenon results from the study of the distribution of the two electrons in the two cases (London, 46). In figure 13, representing the two hydrogen atoms in the process of forming a molecule, it is seen that the electrons tend to assume positions between the two nuclei, and form a bond between them—the shared electron-pair. But if the potential function represents elastic collision (the antisymmetric eigenfunction) the electrons take up positions on the outer sides of the atoms (fig. 14), with the result that the strong internuclear repulsion becomes effective.

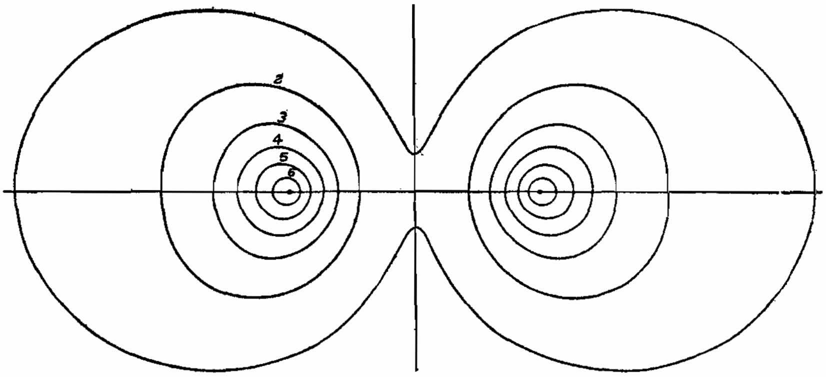

Fig. 14. The Electron Distribution for Two Hydrogen Atoms in Elastic Collision (London)

VIII. THE PAULI EXCLUSION PRINCIPLE. THE INTERACTION OF TWO HELIUM ATOMS

It was mentioned in Section III that the fine-structure of spectra arises from a phenomenon equivalent to a first approximation to that resulting from a spin of the electron. The spin moment of the electron can assume two orientations in space, which may be represented by spin eigenfunctions α and β. In the foregoing sections discussion has been given only to eigenfunctions referring to the electronic positions. A complete eigenfunction is the product of a positional eigenfunction and a spin eigenfunction, as $\psi\,\alpha$ or $\psi\,\beta$.

The observed structure of the spectra of many-electron atoms is entirely accounted for by the following postulate: *Only eigenfunctions which are antisymmetric in the electrons; that is, change sign when any two electrons are interchanged, correspond to existant states of the system.* This is the quantum mechanics statement (26) of the Pauli exclusion principle (43).

It is equivalent to saying that two electrons cannot occupy the same orbit. Thus there is no antisymmetric eigenfunction composed of ψ (1) α (1) and ψ (2) α (2), and no such state exists (for the helium atom, say). The allowed state is $\frac{1}{\sqrt{2}}\,\{\psi\,(1)\,\alpha\,(1)\,\psi\,(2)\,\beta\,(2) - \psi\,(1)\,\beta\,(1)\,\psi\,(2)\,\alpha\,(2)\}$; that is, in the normal state of the helium atom the two electrons have oppositely directed spins. Other consequences of the exclusion principle, such as that not more than two electrons can occupy the K-shell of an atom, follow directly.

In dealing with systems containing only two electrons we have not been troubled with the exclusion principle, but have accepted both symmetric and antisymmetric positional eigenfunctions; for by multiplying by a spin eigenfunction of the proper symmetry character an antisymmetric total eigenfunction can always be obtained. In the case of two hydrogen atoms there are three symmetric spin eigenfunctions α (1) α (2), β (1) β (2), and $\frac{1}{\sqrt{2}}\,\{\alpha\,(1)\,\beta\,(2) + \beta\,(1)\,\alpha\,(2)\}$, and one antisymmetric, $\frac{1}{\sqrt{2}}\{\alpha\,(1)\,\beta\,(2) - \beta\,(1)\,\alpha\,(2)\}$. The last is required to make the symmetric positional eigenfunction Ψ_{H_2} of Equation 29a conform to Pauli's principle, and the first three for the antisymmetric Φ_{H_2}. Since the a priori probability of each eigenfunction is the same, there are three chances that two hydrogen atoms will repel each other to one that they will attract.

But if the system contains more than two electrons explicit consideration must be given the spins. This is particularly evident in the problem of the interaction of two helium atoms. There are four individual eigenfunctions $\psi\alpha$, $\psi\beta$, $\varphi\alpha$, and $\varphi\beta$, which are to be occupied by the four electrons. The only eigenfunction allowed by Pauli's principle for the system is

$$\Psi_{\mathrm{He}_2} = a \begin{vmatrix} \psi(1)\,\alpha(1) & \psi(1)\,\beta(1) & \varphi(1)\,\alpha(1) & \varphi(1)\,\beta(1) \\ \psi(2)\,\alpha(2) & \psi(2)\,\beta(2) & \varphi(2)\,\alpha(2) & \varphi(2)\,\beta(2) \\ \psi(3)\,\alpha(3) & \psi(3)\,\beta(3) & \varphi(3)\,\alpha(3) & \varphi(3)\,\beta(3) \\ \psi(4)\,\alpha(4) & \psi(4)\,\beta(4) & \varphi(4)\,\alpha(4) & \varphi(4)\,\beta(4) \end{vmatrix} \tag{34}$$

(a is a factor of such value as to make the eigenfunction normalized.)

It will be seen that this is antisymmetric, for interchanging any two electrons is equivalent to interchanging two rows of the determinant, and hence to changing its sign.

Substitution of this eigenfunction in an expression of the type of Equation 21 permits the evaluation of the perturbation energy W^1, in the course of which use is made of the properties of orthogonality and normalization of the spin eigenfunctions; namely,

$$\left.\begin{array}{c} \int\alpha^2\,d\epsilon = \int\beta^2\,d\epsilon = 1 \\ \int\alpha\,\beta\,d\epsilon = 0. \end{array}\right\} \tag{35}$$

in which ϵ is the variable occurring in the spin eigenfunctions. The value of one further integral is also needed:

$$\begin{aligned} I_5 &= \iint \frac{\psi^2(1)\,\psi(2)\,\varphi(2)}{r_{12}}\,d\Omega_1\,d\Omega_2 \\ &= \frac{Z}{a_0}\left\{e^{-\rho}\left(\frac{5}{16\rho} + \frac{1}{8} + \rho\right) - e^{-3\rho}\left(\frac{5}{16\rho} + \frac{1}{8}\right)\right\}. \end{aligned} \tag{19f}$$

The potential function obtained is only approximately correct, for the eigenfunctions are in fact largely perturbed by the interelectronic interaction. There are no forces tending to molecule formation, but instead repulsion at all distances. The van der Waals' attractive force (which is very small for helium) does not appear, and the repulsive force is much larger than the actual one; these discrepancies are no doubt due to the inaccuracy of the calculation.

It is of interest to carry out the evaluation of the naïve potential function obtained from the eigenfunction ψ (1) α (1) ψ (2) β (2) φ (3) α (3) φ (4) β (4); i.e., with the neglect of the interchange energy of the electrons. This potential leads to a strong attractive force, with the formation of molecules He_2 with about 10,000 or 15,000 cal/mole dissociation energy. The resonance phenomenon is accordingly largely responsible for the very small van der Waals' forces in helium; without it the boiling point of helium would be around room temperature.

IX. OTHER RELATED PROBLEMS. THE EXTENSION OF THE THEORY

The interaction of two alkali metal atoms is to be expected to be similar to that of two hydrogen atoms, for the completed shells of the ions will produce forces similar to the van der Waals' forces of a rare gas. The two valence electrons, combined symmetrically, will then be shared between the two ions, the resonance phenomenon producing a molecule-forming attractive force. This is, in fact, observed in band spectra. The normal state of the Na_2 molecule, for example, has an energy of dissociation of 1 v.e. (44). The first two excited states are similar, as is to be expected; they have dissociation energies of 1.25 and 0.6 v.e. respectively.

In an atom of the second column of the periodic system, such as mercury, the two valence electrons are in the normal state s-electrons, and form a completed sub-group. Two such atoms would hence interact in a way similar to two helium atoms; the attractive forces would be at most very small. This is the case for Hg_2, which in the normal state has an energy of dissociation of only 0.05 v.e. But if one or both of the atoms is excited strong attractive forces can arise; and indeed the excited states of Hg_2 are found to have energies of dissociation of about 1 v.e.

Similarly two Hg^+ ions will attract each other with some force to form the stable Hg_2^{++} ion long recognized by chemists.

The application of the quantum mechanics to the interaction of more complicated atoms, and to the non-polar chemical bond in general, is now being made (45). A discussion of this work can not be given here; it is, however, worthy of mention that qualitative conclusions have been drawn which are completely equivalent to G. N. Lewis's theory of the shared electron pair. The further results which have so far been obtained are promising; and we may look forward with some confidence to the future explanation of chemical valence in general in terms of the Pauli exclusion principle and the Heisenberg-Dirac resonance phenomenon.

NOTE ADDED IN PROOF

Since the submission of this article for publication a number of pertinent papers have appeared.

A. H. Wilson (*Proc. Roy. Soc. London*, A **118,** 635 (1928); see also (29)) states that no functions satisfying the wave equation for the hydrogen molecule-ion and bounded everywhere exist. There are, however, solutions which become logarithmically infinite along the nuclear axis and are bounded elsewhere. These solutions would not be considered eigenfunctions if the usual definition is retained; but would be in case the restriction that the eigenfunction be bounded everywhere were replaced by the restriction that it be quadratically integrable. Wilson has made this assumption, and has found that the so-calculated properties of the hydrogen molecule-ion in the normal state are approximately those given by Burrau. An accurate treatment and the consideration of excited states have not been published.

A treatment of the hydrogen molecule by the Ritz method, applied to helium by Kellner (25), has been reported by S. C. Wang (*Phys. Rev.*, **31,** 579 (1928)). With this method the individual eigenfunctions ψ and φ (equation 29) are taken to be the hydrogen-like eigenfunctions of an atom with atomic number Z differing from unity. The value found for Z is 1.166, and the corresponding constants of the hydrogen molecule in the normal state are

$$r_0 = 0.75 \text{ Å}, I_0 = 0.459 \times 10^{-40} \text{ g. cm.}^2, D_{H_2} = 3.76 \text{ v.e.}, \omega_0 = 4900 \text{ cm}^{-1}.$$

Comparison with table 4 shows that these values are in somewhat better agreement with the observed ones than are Sugiura's.

B. N. Finkelstein and G. E. Horowitz (*Z. f. Physik*, **48**, 118 (1928)) have similarly applied the Ritz method to the hydrogen molecule-ion, obtaining the following values:

$$Z = 1.228, \rho \cong 2, r_0 \cong 1.06 \text{ Å}, W_{H_2^+} = -15.75 \text{ v.e.}$$

These results are better than those given by the perturbation theory (table 3).

F. R. Bichowsky and L. C. Copeland (*J. Am. Chem. Soc.*, **50**, 1315 (1928)) have made a direct determination of the heat of formation of molecular hydrogen, leading to the value $D_{H_2} = 105000 \pm 3500$ cal/mole.

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Quantum Mechanics and the Chemical Bond

Three years ago I announced in a short note[1] the discovery of some new results regarding the chemical bond. It was pointed out that under certain conditions the formation of chemical bonds by an atom can destroy the distinction between s and p eigenfunctions, and a criterion determining whether this change in quantization of the single-electron eigenfunctions will or will not take place was given. It was also announced that this change in quantization permits the formation of four equivalent tetrahedral bonds by carbon.

Since then a number of further results bearing on the nature of the chemical bond have been obtained; it is the purpose of this letter to call the attention of physicists to a paper in the April, 1931, issue of the Journal of the American Chemical Society in which they are given in detail. It was first shown from the quantum mechanics that the main resonance integrals for an electron-pair bond between two atoms involve only one single-electron eigenfunction on each atom. In consequence many properties of electron-pair bonds can be derived from a consideration of single-electron eigenfunctions alone. Thus it is shown that if $s-p$ quantization is not changed, the bonds formed by the p eigenfunctions will tend to be at right angles to one another. A very simple but powerful approximate *quantitative* treatment of bond strengths is given. With its aid it is shown that when $s-p$ quantization is broken through bond formation, the best bond eigenfunctions which can be formed from a combination of s and p eigenfunctions alone are tetrahedral eigenfunctions, so that the two, three, or four bonds formed will tend to make angles of 109°28′ with one another. This explains the tetrahedral angles found experimentally not only for quadricovalent carbon, nitrogen, silicon, etc., but also for tricovalent nitrogen, oxygen, etc. The tetrahedral eigenfunctions also allow free rotation about single bonds, but not about double bonds.

When d eigenfunctions as well as s and p are available for bond-eigenfunction formation a number of bond configurations are possible. One d eigenfunction with s and p permits the construction of only four strong bonds, *and these are directed towards the corners of a square.* Such a configuration has been shown to exist for bivalent palladium and platinum, and this theory predicts it also for bivalent nickel in $K_2Ni(CN)_4$ and for trivalent gold. Two d eigenfunctions give six strong bonds directed towards the corners of an octahedron; this configuration is found in many complexes.

It is also shown that in complex ions the orbital magnetic moments of electrons are extinguished through the interaction with surrounding atoms, so that the magnetic moment is due to the spin moments of unpaired electrons alone. Together with the results obtained regarding bond eigenfunctions, this leads to a complete theory of the magnetic moments of polyatomic molecules and complex ions. With its aid magnetic data have been shown to provide verification of many predictions regarding bond eigenfunctions; and in a number of doubtful cases magnetic data provide a basis for definite decision as to the type of bonds in a given complex.

These results have also permitted the formulation of a set of principles determining the structure of crystals containing electron-pair bonds, to be published in the Zeitschrift für Kristallographie.

Three of these results have been independently obtained by Slater and announced in a preliminary communication.[2] He points out the possibility of the formation of four equivalent tetrahedral bonds by a carbon atom (as I did in 1928), without giving the tetrahedral eigenfunctions and without recognizing that tetrahedral eigenfunctions are also important even when fewer than four bonds are formed; and mentions that this leads to restricted rotation about a double bond. Having apparently assumed the importance of one single-electron eigenfunction to bond formation, he also shows that p eigenfunctions should lead to 90° bond angles.

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April 7, 1931.

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[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 280]

THE NATURE OF THE CHEMICAL BOND. APPLICATION OF RESULTS OBTAINED FROM THE QUANTUM MECHANICS AND FROM A THEORY OF PARAMAGNETIC SUSCEPTIBILITY TO THE STRUCTURE OF MOLECULES

BY LINUS PAULING

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During the last four years the problem of the nature of the chemical bond has been attacked by theoretical physicists, especially Heitler and London, by the application of the quantum mechanics. This work has led to an approximate theoretical calculation of the energy of formation and of other properties of very simple molecules, such as H_2, and has also provided a formal justification of the rules set up in 1916 by G. N. Lewis for his electron-pair bond. In the following paper it will be shown that many more results of chemical significance can be obtained from the quantum mechanical equations, permitting the formulation of an extensive and powerful set of rules for the electron-pair bond supplementing those of Lewis. These rules provide information regarding the relative strengths of bonds formed by different atoms, the angles between bonds, free rotation or lack of free rotation about bond axes, the relation between the quantum numbers of bonding electrons and the number and spatial arrangement of the bonds, etc. A complete theory of the magnetic moments of molecules and complex ions is also developed, and it is shown that for many compounds involving elements of the transition groups this theory together with the rules for electron-pair bonds leads to a unique assignment of electron structures as well as a definite determination of the type of bonds involved.[1]

I. The Electron-Pair Bond

The Interaction of Simple Atoms.—The discussion of the wave equation for the hydrogen molecule by Heitler and London,[2] Sugiura,[3] and Wang[4] showed that two normal hydrogen atoms can interact in either of two ways, one of which gives rise to repulsion with no molecule formation, the other

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[1] A preliminary announcement of some of these results was made three years ago [Linus Pauling, *Proc. Nat. Acad. Sci.*, **14**, 359 (1928)]. Two of the results (90° bond angles for *p* eigenfunctions, and the existence, but not the stability, of tetrahedral eigenfunctions) have been independently discovered by Professor J. C. Slater and announced at meetings of the National Academy of Sciences (Washington, April, 1930) and the American Physical Society (Cleveland, December, 1930).

[2] W. Heitler and F. London, *Z. Physik*, **44**, 455 (1927).

[3] Y. Sugiura, *ibid.*, **45**, 484 (1927).

[4] S. C. Wang, *Phys. Rev.*, **31**, 579 (1928).

to attraction and the formation of a stable molecule. These two modes of interaction result from the identity of the two electrons. The characteristic resonance phenomenon of the quantum mechanics, which produces the stable bond in the hydrogen molecule, always occurs with two electrons, for even though the nuclei to which they are attached are different, the energy of the unperturbed system with one electron on one nucleus and the other on the other nucleus is the same as with the electrons interchanged. Hence we may expect to find electron-pair bonds turning up often.

But the interaction of atoms with more than one electron does not always lead to molecule formation. A normal helium atom and a normal hydrogen atom interact in only one way,[5] giving repulsion only, and two normal helium atoms repel each other except at large distances, where there is very weak attraction.[5,6] Two lithium atoms, on the other hand, can interact in two ways,[7] giving a repulsive potential and an attractive potential, the latter corresponding to formation of a stable molecule. In these cases it is seen that only when each of the two atoms initially possesses an unpaired electron is a stable molecule formed. The general conclusion that an electron-pair bond is formed by the interaction of an unpaired electron on each of two atoms has been obtained formally by Heitler[8] and London,[9] with the use of certain assumptions regarding the signs of integrals occurring in the theory. The energy of the bond is largely the resonance or interchange energy of two electrons. This energy depends mainly on electrostatic forces between electrons and nuclei, and is not due to magnetic interactions, although the electron spins determine whether attractive or repulsive potentials, or both, will occur.

Properties of the Electron-Pair Bond.—From the foregoing discussion we infer the following properties of the electron-pair bond.

1. *The electron-pair bond is formed through the interaction of an unpaired electron on each of two atoms.*
2. *The spins of the electrons are opposed when the bond is formed, so that they cannot contribute to the paramagnetic susceptibility of the substance.*
3. *Two electrons which form a shared pair cannot take part in forming additional pairs.*

In addition we postulate the following three rules, which are justified by the qualitative consideration of the factors influencing bond energies. An outline of the derivation of the rules from the wave equation is given below.

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4. *The main resonance terms for a single electron-pair bond are those involving only one eigenfunction from each atom.*

5. *Of two eigenfunctions with the same dependence on r, the one with the larger value in the bond direction will give rise to the stronger bond, and for a given eigenfunction the bond will tend to be formed in the direction with the largest value of the eigenfunction.*

6. *Of two eigenfunctions with the same dependence on θ and φ, the one with the smaller mean value of r, that is, the one corresponding to the lower energy level for the atom, will give rise to the stronger bond.*

Here the eigenfunctions referred to are those for an electron in an atom, and r, θ and φ are polar coördinates of the electron, the nucleus being at the origin of the coördinate system.

It is not proposed to develop a complete proof of the above rules at this place, for even the formal justification of the electron-pair bond in the simplest cases (diatomic molecule, say) requires a formidable array of symbols and equations. The following sketch outlines the construction of an inclusive proof.

It can be shown[10] that if Ψ is an arbitrary function of the independent variables in a wave equation

$$(H - W)\psi = 0$$

then the integral

$$E = \int \Psi^* H \Psi d\tau$$

called the variation integral, is always larger than W_0, the lowest energy level for the system. A function Ψ containing several parameters provides the best approximation to the eigenfunction ψ_0 for the normal state of the system when the variational integral is minimized with respect to these parameters. Now let us consider two atoms A and B connected by an electron-pair bond, and for simplicity let all the other electrons in the system be paired, the pairs being either lone pairs or pairs shared between A or B and other atoms. Let us assume that there are available for bond formation by atom A several single-electron eigenfunctions of approximately the same energy, and that the change in energy of penetration into the core is negligible compared with bond energy. Then we may take as single-electron eigenfunctions

$$\psi_{\mathrm{A}i} = \Sigma_k \, a_{ik} \, \psi^0_{\mathrm{A}k}$$

in which the a_{ik}'s are numerical coefficients and the $\psi^0_{\mathrm{A}k}$'s are an arbitrary set of single-electron eigenfunctions, such as those obtained on separating the wave equation in polar coördinates. From the $\psi_{\mathrm{A}i}$'s there is built up a group composed of atom A and the atoms to which it is bonded except atom B, such that all electrons are paired except one, corresponding to the eigenfunction $\psi_{\mathrm{A}i}$, say. From atom B a similar group with one unpaired electron is built. The interaction energy of these two groups can then be calculated with the aid of the variational equation through the substitution of an eigenfunction for the molecule built of those for the two groups in such a way that it has the correct symmetry character. The construction of this eingenfunction and evaluation of the integral would be very laborious; it will be noticed, however, that this problem is formally similar to Born's treatment[11] of the interaction of two atoms in S states, based on Slater's treatment of atomic eigenfunctions, and the value of E is found to be

$$E = W_{\mathrm{A}} + W_{\mathrm{B}} + J_E + J_X - \Sigma_Y J_Y - 2\Sigma_Z J_Z$$

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[10] A clear discussion is given by C. Eckart, *Phys. Rev.*, **36**, 878 (1930).

[11] M. Born, *Z. Physik*, **64**, 729 (1930).

Here W_A and W_B are the energies of the separate groups, and J_E represents the Coulomb interaction of A and B, neglecting resonance. The resonance term J_X corresponds to a permutation of the two AB bond electrons; J_Y corresponds to a permutation of the AB bond electron on B with a paired electron with similarly directed spin on A, or *vice versa;* and J_Z corresponds to a permutation of a paired electron on A with one on B. (For explicit expressions for these see Born.[11]) The resonance integrals J_X, J_Y and J_Z have been found to have negative signs in the case of simple molecules for which calculations have been made, and it is probable that these signs obtain in most cases. The resonance integrals depend qualitatively on what may be called the *overlapping* of the single-electron eigenfunctions involved; if ψ_A and ψ_B are two single-electron eigenfunctions, the product $\psi_A(1)\ \psi_B(2)\ \psi_A^*(2)\ \psi_B^*(1)$ occurs in the resonance integral corresponding to the permutation involving electrons 1 and 2, and the value of the integral increases as the magnitude of this product in the region between the two nuclei increases.

Now we vary the coefficients a_{ik} in such a way as to minimize E. W_A and W_B are not affected by this variation, and J_E is not changed in case that there is one electron for every eigenfunction in a subgroup on A, and is changed relatively slightly otherwise. The resonance integrals are, however, strongly affected by changing the coefficients. The positive sign preceding J_X requires that the two bond eigenfunctions ψ_A and ψ_B show the maximum overlapping in the region between the two nuclei, while the negative sign preceding J_Y requires the minimum overlapping between ψ_A and the eigenfunctions of B other than ψ_B, and between ψ_B and the eigenfunctions of A other than ψ_A. Hence the correct zeroth-order eigenfunctions for the atom A are such that one, the AB bond eigenfunction ψ_A, extends largely in the direction of atom B, while the other A eigenfunctions avoid overlapping with ψ_B. As a consequence the integral J_X is of large magnitude, while the integrals J_Y, because of the small overlapping of the eigenfunctions involved, are small.

An extension of this argument shows that the phenomenon of *concentration of the bond eigenfunctions* further increases the magnitude of J_X and decreases J_Y. The non-orthogonality of the bond eigenfunctions as well as certain second-order perturbations leads to a shrinkage of the region in which the bond eigenfunctions have appreciable values. This is strikingly shown by a comparison of H_2^+ and H; the volume within which the electron probability function $\psi\psi^*$ for H_2^+ is greater than one-tenth of its maximum value is found from Burrau's calculations to be 0.67 Å.^{3}, *less than 10% of its value 8.6 Å.^{3} for a hydrogen atom.*[12] This concentration of the bond eigenfunctions greatly increases their interaction with one another, and decreases their interaction with other eigenfunctions, a fact expressed in Rule 4. For double or triple bonds interactions among all four or six eigenfunctions must be considered.

s and p Eigenfunctions. Compounds of Normal Atoms.—As a rule s and p eigenfunctions with the same total quantum number in an atom do not differ very much in their mean values of r (the s levels lie lower because of greater penetration of inner shells), so that Rule 6 would not lead us to expect them to differ in bond-forming power. But their dependence on θ and φ is widely different. Putting

$$\begin{array}{lll} \Psi_{n0}(r,\theta,\varphi) = R_{n0}(r)\cdot s(\theta,\varphi) & \text{for } s \text{ eigenfunctions} & \\ \Psi_{n1}(r,\theta,\varphi) = R_{n1}(r)\cdot \left.\begin{array}{l} p_x(\theta,\varphi) \\ p_y(\theta,\varphi) \\ p_z(\theta,\varphi) \end{array}\right\} & \text{for } p \text{ eigenfunctions} & (1) \end{array}$$

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[12] Compare Fig. 6 with Fig. 7, which is drawn to half the scale of Fig. 6, of Linus Pauling, *Chem. Rev.*, **5**, 173 (1928).

the parts s, p_x, p_y, p_z of the eigenfunctions depending on θ and φ, normalized to 4π, are

$$\left.\begin{aligned} s &= 1 \\ p_x &= \sqrt{3}\sin\theta\cos\varphi \\ p_y &= \sqrt{3}\sin\theta\sin\varphi \\ p_z &= \sqrt{3}\cos\theta \end{aligned}\right\} \qquad (2)$$

Absolute values of s and p_x are represented in the xz plane in Figs. 1 and 2. s is spherically symmetrical, with the value 1 in all directions. $|p_x|$ consists of two spheres as shown (the x axis is an infinite symmetry axis), with the maximum value $\sqrt{3}$ along the x axis. $|p_y|$ and $|p_z|$ are similar, with maximum values of $\sqrt{3}$ along the y and z axis, respectively. From Rule 5 we conclude that *p electrons will form stronger bonds than s electrons*, and that *the bonds formed by p electrons in an atom tend to be oriented at right angles to one another.*

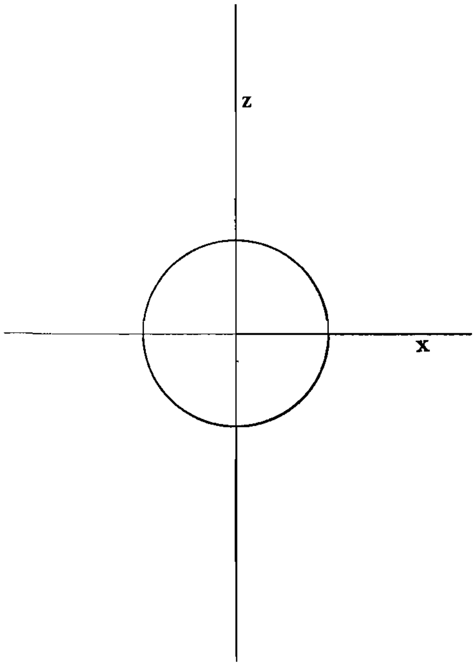
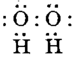


Fig. 1.—Polar graph of 1 in the xz plane, representing an s eigenfunction.

The second conclusion explains several interesting facts. Normal oxygen, in the state $2s^22p^4\,{}^3P$, contains two unpaired p electrons. When an atom of oxygen combines with two of hydrogen, a water molecule will result in which the angle formed by the three atoms is 90°, or somewhat larger because of interaction of the two hydrogen atoms. It has been long known from their large electric moment that water molecules have a kinked rather than a collinear arrangement of their atoms, and attempts have been made to explain this with rather unsatisfactory calculations based on an ionic structure with strong polarization of the oxygen anion in the field of the protons. The above simple explanation results directly from the reasonable assumption of an electron-pair bond structure and the properties of tesseral harmonics.

It can be predicted that H_2O_2, with the structure  $\underset{\text{H}}{:\ddot{\text{O}}}:\underset{\text{H}}{\ddot{\text{O}}}:$ involving bonds of p electrons, also consists of kinked rather than collinear molecules.

Nitrogen, with the normal state $2s^22p^3\,{}^4S$, contains three unpaired p

electrons, which can form bonds at about 90° from one another with three hydrogen atoms. The ammonia molecule, with the resulting pyramidal structure, also has a large electric moment.

The crystal skutterudite, $Co_4^{3+}(As_4^{4-})_3$, contains As_4^{4-} groups with a square configuration, corresponding to the structure $\left[\begin{matrix} :\ddot{As}:\ddot{As}: \\ :\underset{..}{As}:\underset{..}{As}: \end{matrix}\right]^{4-}$. This complex has bond angles of exactly 90°.

In the above discussion it has been assumed that the type of quantization has not been changed, and that *s* and *p* eigenfunctions retain their identity. This is probably true for H_2O and H_2O_2, and perhaps for NH_3 and As_4^{4-} also. A discussion of the effect of change of quantization on bond angles is given in a later section.

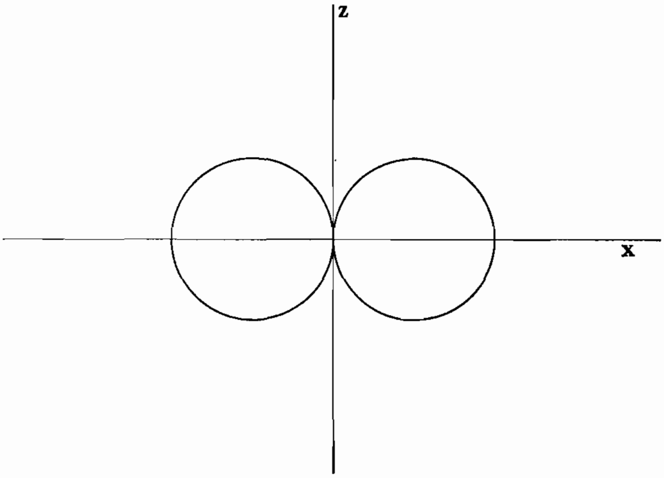


Fig. 2.—Polar graph of $|\sqrt{3}\sin\theta|$ in the *xz* plane, representing the p_x eigenfunction.

Transition from Electron-Pair to Ionic Bonds. The Hydrogen Bond.—In case that the symmetry character of an electron-pair structure and an ionic structure for a molecule are the same, it may be difficult to decide between the two, for the structure may lie anywhere between these extremes. The zero$^{\text{th}}$-order eigenfunction for the two bond electrons for a molecule MX (HF, say, or NaCl) with a single electron-pair bond would be

$$\Psi_{MX} = \frac{\psi_M(1)\,\psi_X(2) + \psi_M(2)\,\psi_X(1)}{\sqrt{2+2S^2}} \tag{3}$$

in which $S = \int \psi_M(1)\,\psi_X^*(1)\,d\tau_1$. The eigenfunction for a pure ionic state would be

$$\Psi_{M^+X^-} = \psi_X(1)\,\psi_X(2) \tag{4}$$

In certain cases one of these might approximate the correct eigenfunction closely. In other cases, however, it would be necessary to consider combinations of the two, namely

$$\Psi_+ = a\,\Psi_{MX} + \sqrt{1-a^2}\,\Psi_{M^+X^-}$$

and

$$\Psi_- = \sqrt{1-a^2}\Psi_{MX} - a\,\Psi_{M^+X^-} \qquad (5)$$

For a given molecule and a given internuclear separation a would have a definite value, such as to make the energy level for Ψ_+ lie as low as possible. If a happens to be nearly 1 for the equilibrium state of the molecule, it would be convenient to say that the bond is an electron-pair bond; if a is nearly zero, it could be called an ionic bond. This definition is somewhat unsatisfactory in that it does not depend on easily observable quantities. For example, a compound which is ionic by the above definition might dissociate adiabatically into neutral atoms, the value of a changing from nearly zero to unity as the nuclei separate, and it would do this in case the electron affinity of X were less than the ionization potential of M. HF is an example of such a compound. There is evidence, given below, that the normal molecule approximates an ionic compound; yet it would dissociate adiabatically into neutral F and H.[13]

But direct evidence regarding the value of a can sometimes be obtained. The hydrogen bond, discovered by Huggins and by Latimer and Rodebush, has been usually considered as produced by a hydrogen atom with two electron-pair bonds, as in $\left[:\underset{..}{\ddot{F}}:H:\underset{..}{\ddot{F}}:\right]^-$. It was later pointed out[1] that this is not compatible with the quantum mechanical rules, for hydrogen can have only one unpaired 1*s* electron, and outer orbits are so much less stable that strong bonds would not be formed. With an ionic structure, however, we would expect H^+F^- to polymerize and to add on to F^-, to give H_6F_6 and $[F^-H^+F^-]^-$; moreover, the observed coördination number 2 is just that predicted[14] from the radius ratio 0. Hence the observation that hydrogen bonds are formed with fluorine supports an ionic structure for HF. Hydrogen bonds are not formed with chlorine, bromine, and iodine, so that the bonds in HCl, HBr, and HI are to be considered as approaching the electron-pair type.

Hydrogen bonds are formed to some extent by oxygen ($(H_2O)_x$, ice, etc.) and perhaps also in some cases by nitrogen. The electrostatic structure for the hydrogen bond explains the observation that only these atoms of high electron affinity form such bonds, a fact for which no explanation was given by the older conception. It is of interest that there is considerable

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[13] There would, however, be a certain probability, dependent on the nature of the eigenfunctions, that actual non-adiabatic dissociation would give ions rather than atoms, and this might be nearly unity, in case the two potential curves come very close to one another at some point. See I. v. Neumann and E. Wigner, *Physik. Z.*, **30**, 467 (1929).

[14] Linus Pauling, This Journal, **51**, 1010 (1929).

evidence from crystal structure data for $[\mathrm{OHO}]^{=}$ groups. In many crystals containing H and O, including topaz,[15] $\mathrm{Al_2SiO_4(F,OH)_2}$; diaspore,[16] $\mathrm{AlHO_2}$; goethite,[16] $\mathrm{FeHO_2}$; chondrodite,[17] $\mathrm{Mg_5Si_2O_8(F,OH)_2}$; etc., the sum of the strengths of the electrostatic bonds from all cations (except hydrogen) to an anion is either 2 or 1, indicating, according to the electrostatic valence rule,[14] the presence of $\mathrm{O^{=}}$ and of $\mathrm{F^{-}}$ or $\mathrm{(OH)^{-}}$, respectively. But in some crystals, including[18] $\mathrm{KH_2PO_4}$; staurolite,[19] $\mathrm{H_2FeAl_4Si_2O_{12}}$; and lepidocrocite,[16] $\mathrm{FeHO_2}$, the sum of bond strengths is 2 or $^3/_2$, the latter value occurring twice for each H; the electrostatic valence rule in these cases supports the assumption of $[\mathrm{O^{=}H^{+}O^{=}}]^{=}$ groups, the hydrogen ion contributing a bond of strength $^1/_2$ to each of two oxygen ions.

In other cases, discussed below, the lowest electron-pair-bond structure and the lowest ionic-bond structure do not have the same multiplicity, so that (when the interaction of electron spin and orbital motion is neglected) these two states cannot be combined, and a knowledge of the multiplicity of the normal state of the molecule or complex ion permits a definite statement as to the bond type to be made.

Change in Quantization of Bond Eigenfunctions.—A normal carbon atom, in the state $2s^22p^2\ {}^3P$, contains only two unpaired electrons, and can hence form no more than two single bonds or one double bond (as in CO, formed from a normal carbon atom and a normal oxygen atom). But only about 1.6 v. e. of energy is needed to excite a carbon atom to the state $2s2p^3\ {}^5S$, with four unpaired electrons, and in this state the atom can form four bonds. We might then describe the formation of a substituted methane CRR′R″R‴ in the following way. The radicals R, R′, and R″, each with an unpaired electron, form electron-pair bonds with the three p electrons of the carbon atom, the bond directions making angles of 90° with one another. The fourth radical R‴ then forms a weaker bond with the s electron, probably at an angle of 125° with each of the other bonds. This would give an unsymmetrical structure, with non-equivalent bonds, and considerable discussion has been given by various authors to the difference in the carbon bonds due to s and p electrons. Actually the foregoing treatment is fallacious, for the phenomenon of change in quantization of the bond eigenfunctions, first discussed in the note referred to before,[1] leads simply and directly to the conclusion that *the four bonds formed by a carbon atom are equivalent and are directed toward tetrahedron corners.*

The importance of s, p, d, and f eigenfunctions for single atoms and ions

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[15] Linus Pauling, *Proc. Nat. Acad. Sci.*, **14**, 603 (1928); N. A. Alston and J. West, *Z. Krist.*, **69**, 149 (1928).

[16] Unpublished investigation in this Laboratory.

[17] W. L. Bragg and J. West, *Proc. Roy. Soc.* (London), **A114**, 450 (1927); W. H. Taylor and J. West, *ibid.*, **A117**, 517 (1928).

[18] J. West, *Z. Krist.*, **74**, 306 (1930).

[19] St. Naray-Szabo, *ibid.*, **71**, 103 (1929).

results from the fact that the interaction of one electron with the nucleus and other electrons can be represented approximately by a non-Coulombian central field, so that the wave equation can be separated in polar coördinates r, θ, and φ, giving rise to eigenfunctions involving tesseral harmonics such as those in Equation 1. The deeper penetration of s electrons within inner shells causes them to be more tightly bound than p electrons with the same total quantum number. If an atom approaches a given atom, forming a bond with it, the interaction between the two can be considered as a perturbation, and the first step in applying the perturbation theory for a degenerate system consists in finding the correct zeroth-order eigenfunctions for the perturbation, one of which is the eigenfunction which will lead to the largest negative perturbation energy. This will be the one with the largest values along the bond direction. The correct zeroth-order eigenfunctions must be certain normalized and mutually orthogonal linear aggregates of the original eigenfunctions. If the perturbation is small, the s eigenfunction cannot be changed, and the only combinations which can be made with the p eigenfunctions are equivalent merely to a rotation of axes. But in case the energy of interaction of the two atoms is greater than the difference in energy of an s electron and a p electron (or, if there are originally two s electrons present, as in a normal carbon atom, of twice this difference), hydrogen-like s and p eigenfunctions must be grouped together to form the original degenerate state, and the interaction of the two atoms together with the deviation of the atomic field from a Coulombian one must be considered as the perturbation, with the former predominating. The correct zeroth-order bond eigenfunctions will then be those orthogonal and normalized linear aggregates of both the s and p eigenfunctions which would give the strongest bonds according to Rule 5.

A rough criterion as to whether the quantization is changed from that in polar coördinates to a type giving stronger bond eigenfunctions is thus that the possible bond energy be greater than the s–p (or, if d eigenfunctions are also involved, s–d or p–d) separation.[20]

This criterion is satisfied for quadrivalent carbon. The energy difference of the states[21] $2s^22p^2\ {}^3P$ and $2s2p^3\ {}^3P$ of carbon is 9.3 v. e., and a similar value of about 200,000 cal. per mole is found for other atoms in the first row of the periodic system. The energy of a single bond is of the order of 100,000 cal. per mole. Hence a carbon atom forming four bonds would certainly have changed quantization, and even when the bond energy must be divided between two atoms, as in a diamond crystal, the criterion is sufficiently well satisfied. The same results hold for quadrivalent

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[20] This criterion was expressed in Ref. 1.

[21] States with the same multiplicity should be compared, for increase in multiplicity decreases the term value, the difference between $2s^22p^2\ {}^3P$ and $2s2p^3\ {}^5S$ being only about 1.6 v. e., as mentioned above.

nitrogen, a nitrogen *ion* in the state N^+ $2s2p^3$ ^5S forming four bonds, as in $(NH_4)^+$, $N(CH_3)_4^+$, etc. But for bivalent oxygen there is available only about 200,000 cal. per mole bond energy, and the s–p separation for two s electrons corresponds to about 400,000 cal. per mole, so that it is very probable that the oxygen bond eigenfunctions in H_2O, for example, are p eigenfunctions, as assumed in a previous section. Trivalent nitrogen is a border-line case; the bond energy of about 300,000 cal. per mole is sufficiently close to the s–p energy of 400,000 cal. per mole to permit the eigenfunctions to be changed somewhat, but not to the extent that they are in quadrivalent carbon and nitrogen.

It may be pointed out that the s–p separation for atoms in the same column of the periodic table is nearly constant, about 200,000 cal. per mole for one s electron. The bond energy decreases somewhat with increasing atomic number. Thus the energies of a bond in the compounds H_2O, H_2S, H_2Se, and H_2Te, calculated from thermochemical and band spectral data, are 110,000, 90,000, 73,000, and 60,000 cal. per mole, respectively. Hence we conclude that if quantization in polar coördinates is not broken for a light atom on formation of a compound, it will not be broken for heavier atoms in the same column of the periodic system. The molecules H_2S, H_2Se, and H_2Te must accordingly also have a non-linear structure, with bond angles of 90° or slightly greater.

Let us now determine the zero$^{\text{th}}$-order eigenfunctions which will form the strongest bonds for the case when the s–p quantization is broken. The dependence on r of s and p hydrogen-like eigenfunctions is not greatly different,[22] and it seems probable that the effect of the non-Coulombian field would decrease the difference for actual atoms. We may accordingly assume that $R_{n0}(r)$ and $\mathrm{R}_{n1}(r)$ are effectively the same as far as bond formation is concerned, so that the problem of determining the bond eigenfunctions reduces to a discussion of the θ, φ eigenfunctions of Equation 1. Arbitrary sets of θ, φ eigenfunctions formed from s, p_x, p_y, and p_z are given by the expressions

$$\left.\begin{aligned} \psi_1 &= a_1s + b_1p_x + c_1p_y + d_1p_z \\ \psi_2 &= a_2s + b_2p_x + c_2p_y + d_2p_z \\ \psi_3 &= a_3s + b_3p_x + c_3p_y + d_3p_z \\ \psi_4 &= a_4s + b_4p_x + c_4p_y + d_4p_z \end{aligned}\right\} \qquad (6)$$

in which the coefficients a_1, etc., are restricted only by the orthogonality and normalization requirements

$$\int \psi_i^2 d\tau = 1 \quad \text{or } a_i^2 + b_i^2 + c_i^2 + d_i^2 = 1 \qquad i = 1,2,3,4 \qquad (7a)$$

and

$$\int \psi_i\psi_k d\tau = 0 \quad \text{or } a_ia_k + b_ib_k + c_ic_k + d_id_k = 0 \quad i,k = 1,2,3,4 \quad i \neq k \quad (7b)$$

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[22] See the curves given by Linus Pauling, *Proc. Roy. Soc.* (London), **A114**, 181 (1927), or A. Sommerfeld, "Wellenmechanischer Ergänzungsband," p. 88.

From Rule 5 the best bond eigenfunction will be that which has the largest value in the bond direction. This direction can be chosen arbitrarily for a single bond. Taking it along the x axis, it is found that the best single bond eigenfunction is[23]

$$\psi_1 = \frac{1}{2}s + \frac{\sqrt{3}}{2}p_x \tag{8a}$$

with a maximum value of 2, considerably larger than that 1.732 for a p eigenfunction. A graph of this function in the xz plane is shown in Fig. 3.

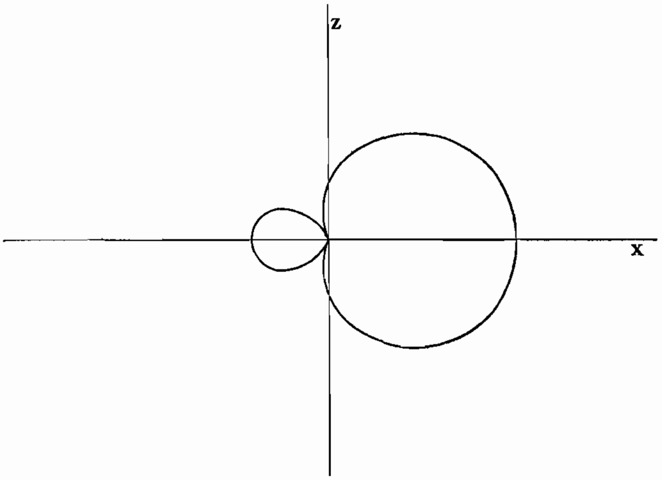

Fig. 3.—Polar graph of $\left| {}^1/_2 + {}^3/_2 \sin\theta \right|$ in the xz plane, representing a tetrahedral eigenfunction, the best bond eigenfunction which can be formed from s and p eigenfunctions.

A second bond can be introduced in the xz plane. The best eigenfunction for this bond is found to be

$$\psi_2 = \frac{1}{2}s - \frac{1}{2\sqrt{3}}p_x + \frac{\sqrt{2}}{\sqrt{3}}p_z \tag{8b}$$

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[23] It is easily shown with the use of the method of undetermined multipliers that the eigenfunction with the maximum value in the direction defined by the polar angles θ_0, φ_0 has as coefficients of the initial eigenfunctions quantities proportional to $\psi_k(\theta_0,\varphi_0)$, and that the maximum value is itself equal to $\{\Sigma_k[\psi_k(\theta_0,\varphi_0)]^2\}^{1/2}$. For let $\psi(\theta,\varphi) = \Sigma_{k=1}^{n} a_k\psi_k(\theta,\varphi)$, with $\Sigma a_k^2 = 1$. We want $\psi(\theta_0,\varphi_0) = \Sigma a_k\psi_k(\theta_0,\varphi_0)$ to be a maximum with respect to variation in the a_k 's. Consider the expression

$$\Lambda = \psi(\theta_0,\varphi_0) - \frac{\lambda}{2}\{\Sigma a_k^2 - 1\} = \Sigma\left\{a_k\psi_k(\theta_0,\varphi_0) - \frac{\lambda}{2}a_k^2\right\} + \frac{\lambda}{2}$$

in which λ is an undetermined multiplier. Then we put

$$\frac{\partial\Lambda}{\partial a_k} = \psi_k(\theta_0,\varphi_0) - \lambda a_k = 0 \text{ or } a_k = \frac{\psi_k(\theta_0,\varphi_0)}{\lambda}, \; k = 1,2\ldots n$$

in which λ has such a value that $\Sigma a_k^2 = 1$; *i. e.*, $\lambda = \{\Sigma[\psi_k(\theta_0,\varphi_0)]^2\}^{1/2}$. $\psi(\theta_0,\varphi_0)$ is itself then equal to $\Sigma[\psi_k(\theta_0,\varphi_0)]^2/\lambda$ or $\{\Sigma[\psi_k(\theta_0,\varphi_0)]^2\}^{1/2}$.

This eigenfunction is equivalent to and orthogonal to ψ_1, and has its maximum value of 2 at $\theta = 19°28'$, $\varphi = 180°$, that is, at an angle of 109°28′ with the first bond, *which is just the angle between the lines drawn from the center to two corners of a regular tetrahedron.* The third and fourth best bond eigenfunctions

$$\psi_3 = \frac{1}{2}s - \frac{1}{2\sqrt{3}}p_z - \frac{1}{\sqrt{6}}p_x + \frac{1}{\sqrt{2}}p_y \tag{8c}$$

and

$$\psi_4 = \frac{1}{2}s - \frac{1}{2\sqrt{3}}p_z - \frac{1}{\sqrt{6}}p_x - \frac{1}{\sqrt{2}}p_y \tag{8d}$$

are also equivalent to the others, and have their maximum values of 2 along the lines toward the other two corners of a regular tetrahedron.

An equivalent set of four tetrahedral eigenfunctions is[24]

$$\left.\begin{aligned}
\psi_{111} &= \frac{1}{2}(s + p_x + p_y + p_z) \\
\psi_{1\bar{1}\bar{1}} &= \frac{1}{2}(s + p_x - p_y - p_z) \\
\psi_{\bar{1}1\bar{1}} &= \frac{1}{2}(s - p_x + p_y - p_z) \\
\psi_{\bar{1}\bar{1}1} &= \frac{1}{2}(s - p_x - p_y + p_z)
\end{aligned}\right\} \tag{9}$$

These differ from the others only by a rotation of the atom as a whole.

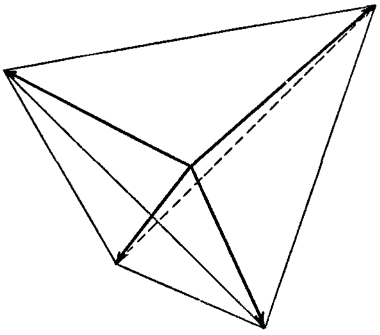

Fig. 4.—Diagram showing relative orientation in space of the directions of the maxima of four tetrahedral eigenfunctions.

The Tetrahedral Carbon Atom.—We have thus derived the result that *an atom in which only s and p eigenfunctions contribute to bond formation and in which the quantization in polar coördinates is broken can form one, two, three, or four equivalent bonds, which are directed toward the corners of a regular tetrahedron* (Fig. 4). This calculation provides the quantum mechanical justification of the chemist's tetrahedral carbon atom, present in diamond and all aliphatic carbon compounds, and for the tetrahedral quadrivalent nitrogen atom, the tetrahedral phosphorus atom, as in phosphonium compounds, the tetrahedral boron atom in B_2H_6 (involving single-electron bonds), and many other such atoms.

Free or Restricted Rotation.—Each of these tetrahedral bond eigen-

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[24] It should be borne in mind that the bond eigenfunctions actually are obtained from the expressions given in this paper by substituting for s the complete eigenfunction $\Psi_{n00}(r,\theta,\varphi)$, etc. It is not necessary that the r part of the eigenfunctions be identical; the assumption made in the above treatment is that they do not affect the evaluation of the coefficients in the bond eigenfunctions.

functions is cylindrically symmetrical about its bond direction. Hence the bond energy is independent of orientation about this direction, so that there will be *free rotation about a single bond*, except in so far as rotation is hindered by steric effects, arising from interactions of the substituent atoms or groups.

A double bond behaves differently, however. Let us introduce two substituents in the octants xyz and $\bar{x}\bar{y}z$ of an atom, a carbon atom, say, using the bond eigenfunctions ψ_{111} and $\psi_{\bar{1}\bar{1}1}$. The two eigenfunctions $\psi_{1\bar{1}\bar{1}}$ and $\psi_{\bar{1}1\bar{1}}$ are then left to form a double bond with another such group. Now $\psi_{1\bar{1}\bar{1}}$ and $\psi_{\bar{1}1\bar{1}}$ (or any two eigenfunctions formed from them) are not cylindrically symmetrical about the z axis or any direction, nor are the two eigenfunctions on the other group. Hence the energy of the double bond will depend on the relative orientation of the two tetrahedral carbon atoms, and will be a maximum when the two sets of eigenfunctions show the maximum overlapping. This will occur when the two tetrahedral atoms share an edge (Fig. 5). Thus we derive the result, found long ago by chemists, that there are two stable states for a simple compound involving a double bond, a *cis* and a *trans* state, differing in orientation by 180°. *There is no free rotation about a double bond.*[25]

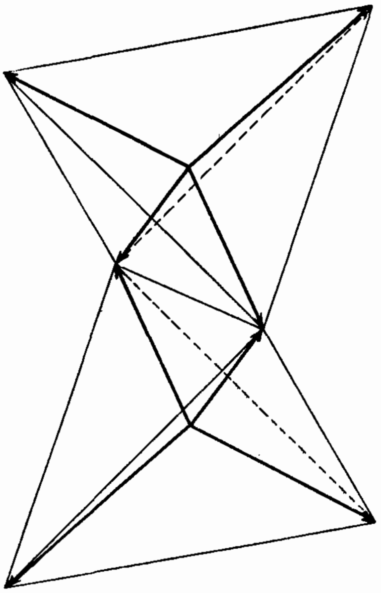

Fig. 5.—Directions of maxima of tetrahedral eigenfunctions in two atoms connected by a double bond.

The three eigenfunctions which would take part in the formation of a triple bond can be made symmetrical about the bond direction, for an atom of the type considered above, with only four eigenfunctions in the outer shell; but since the group attached by the fourth valence lies on the axis of the triple bond, there is no way of verifying the resulting free rotation about the triple bond.

The Angles between Bonds.—The above calculation of tetrahedral angles between bonds when the quantization is changed sets an upper limit on bond angles in doubtful cases, when the criterion is only approximately satisfied. For we can now state that the bond angles in H_2O and NH_3

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[25] A discussion of rotation about a double bond on the basis of the quantum mechanics has been published by E. Hückel, *Z. Physik*, **60**, 423 (1930), which is, I feel, neither so straightforward nor so convincing as the above treatment, inasmuch as neither the phenomenon of concentration of the bond eigenfunctions nor that of change in quantization is taken into account.

should lie between 90 and 109°28′, closer to 90° for the first and to 109°28′ for the second compound. The same limits should apply to other atoms with an outer 8-shell (counting both shared and unshared electron pairs). Direct evidence on this point is provided by crystal structure data for non-ionic crystals, given in Table I. Every one of the angles given in this table depends on one or more parameters, which have been determined experimentally from observed intensities of x-ray reflections. The probable error in most cases is less than 5°, and in many is only about ±1°. It will be observed that quadrivalent carbon and nitrogen and trivalent nitrogen form bonds at tetrahedral angles, whereas heavier atoms forming only two or three bonds prefer smaller bond angles. The series As, Sb, Bi is particularly interesting. We expect, from an argument given earlier,

TABLE I

ANGLES BETWEEN BONDS, FROM CRYSTAL STRUCTURE DATA[a]

Compound	Atom	Number of bonds	Angles between bonds
$C_6N_4H_{12}$	C	2 C—N, 2 C—H	112° between C—N bonds
$C_6N_4H_{12}$	N	3 N—C	108°
$(NH_2)_2CO$[b]	C	2 single C—N 1 double C=O	115° between single bonds
As	As	3	97°
Sb	Sb	3	96°
Bi	Bi	3	94°
Se	Se	2	105°
Te	Te	2	102°
FeS_2[d] MnS_2 CoS_2 NiS_2	S^{++}	1 S—S 3 S—M	103° between S—S and S—M bonds 115° between two M—S bonds
MoS_2[e]	S^+	3 S—Mo	82°
$Co_4(As_4)_3$	As^-	2 As—As	90°
$CaSi_2$	Si	3 Si—Si	103° between Si—Si bonds
HgI_2	I^+	2 Hg—I	103°
GeI_4	Ge	4 Ge—I	109.5°
SnI_4	Sn	4 Sn—I	109.5°
As_4O_6	As	3 As—O	109.5°
	O	2 O—As	109.5°
Sb_4O_6	Sb	3 Sb—O	109.5°
	O	2 O—Sb	109.5°
$NaClO_3$[c]	Cl^{++}	3 Cl—O	109.5°
$KClO_3$	Cl^{++}	3 Cl—O	109.5°
$KBrO_3$	Br^{++}	3 Br—O	109.5°

[a] Data for which no reference is given are from the *Strukturbericht* of P. P. Ewald and C. Hermann. [b] R. W. G. Wyckoff, *Z. Krist.*, 75, 529 (1930). [c] W. H. Zachariasen, *ibid.*, 71, 501, 517 (1929). [d] The very small paramagnetic susceptibility of pyrite requires the presence of electron-pair bonds, eliminating an ionic structure $Fe^{++}S_2^{=}$. Angles are calculated for FeS_2, for which the parameters have been most accurately determined. [e] The parameter value (correct value $u = 0.371$) and interatomic distances for molybdenite are incorrectly given in the *Strukturbericht*.

that the bond eigenfunctions will deviate less and less from pure *p* eigenfunctions in this order, and this evidences itself in a closer approach of the bond angle to 90° in the series. Geometrical effects sometimes affect the bond angles, as in As_4O_6 and Sb_4O_6, where a decrease in the oxygen bond angle would necessarily be accompanied by an increase in that for the other atom, and in molybdenite and pyrite.

Many compounds with tetrahedral structures (diamond, sphalerite, wurzite, carborundum, etc.) are known, in which the four bonds have tetrahedral angles. Tetrahedral atoms in such crystals include C (diamond, SiC), Si, Ge, Sn, Cl^{3+} (in CuCl), Br^{3+}, I^{3+}, O^{++} (in Cu_2O and ZnO), S^{++}, Se^{++}, Te^{++}, N^+ (in AlN), P^+, As^+, Sb^+, Bi^+, $Cu^{\equiv}$, $Zn^{=}$, $Cd^{=}$, $Hg^{=}$, Al^-, Ga^- and In^-.

The Valence of Atoms.—In the last paragraph and in Table I the atoms are represented with electrical charges which are not those usually seen. These charges are obtained by the application of Rule 1, according to which an electron-pair bond is formed by one electron from each of the two atoms (even though as the atoms separate the type of bonding may change in such a way that both electrons go over to one atom). Accordingly in determining the state of ionization of the atoms in a molecule or crystal containing electron-pair bonds each shared electron-pair is to be split between the two atoms. In this way every atom is assigned an electrovalence obtained by the above procedure and a covalence equal to the number of its shared electron-pair bonds.

It is of interest to note that a quantity closely related to the "valence" of the old valence theory is obtained for an atom by taking the algebraic sum of the electrovalence and of the covalence, the latter being given the positive sign for metals and the negative sign for non-metals. For example, oxygen in OH^- is O^- with a covalence of 1, in H_2O it is O with a covalence of 2, in H_3O^+ it is O^+ with a covalence of 3, and in crystalline ZnO it is O^{++} with a covalence of 4; in each case the above rule gives -2 for its valence.

Trigonal Quantization.—We have seen that an atom with *s-p* quantization unchanged will form three equivalent bonds at 90° to one another. If quantization is changed, the three strongest bonds will lie at tetrahedral angles. But increase in the bond angle beyond the tetrahedral angle is not accompanied by a very pronounced decrease in bond strength. Thus three equivalent bond eigenfunctions in a plane, with maxima 120° apart, can be formed

$$\left.\begin{aligned}\psi_1 &= \frac{1}{\sqrt{3}}s + \sqrt{\frac{2}{3}}\,p_x\\ \psi_2 &= \frac{1}{\sqrt{3}}s - \frac{1}{\sqrt{6}}p_x + \frac{1}{\sqrt{2}}p_y\\ \psi_3 &= \frac{1}{\sqrt{3}}s - \frac{1}{\sqrt{6}}p_x - \frac{1}{\sqrt{2}}p_y\end{aligned}\right\} \qquad (10)$$

and these have a strength of 1.991, only a little less than that 2.000 of tetrahedral bonds (Fig. 6). As a result, we may anticipate that in some cases the bond angles will be larger than 109°28′. The carbonate ion in calcite and the nitrate ion in sodium nitrate are assigned a plane configuration from the results of x-ray investigations. In these ions the oxygen atoms are only 2.25 Å. from one another, so that their characteristic repulsive forces must be large, resisting decrease in the bond angle (the smallest distance observed between oxygen ions in ionic crystals is 2.5 Å.). But repulsion of the oxygen atoms would not be very effective in increasing the bond angle in the neighborhood of 120°, so that we might expect equilibrium to be achieved at a somewhat smaller angle, such as 118°. This would give $CO_3^=$ and NO_3^- a pyramidal structure, like that of NH_3. There would be two configurations possible for a given orientation of the O_3 plane, one in which the carbon (or nitrogen) atom was a short distance above this plane (taken as horizontal) and one with it below the plane. If there is appreciable interaction between these two, as there will be in case the pyramid is flat, the symmetric and antisymmetric combinations of the two will be the correct eigenfunctions, corresponding to the rapid inversion of the pyramid, with a frequency of the order of magnitude of the vibrational frequency of the complex ion along its symmetry axis. This inversion would introduce an effective symmetry plane normal to the three-fold axis, so that a pyramidal structure with rapid inversion is compatible with the x-ray observations.[26]

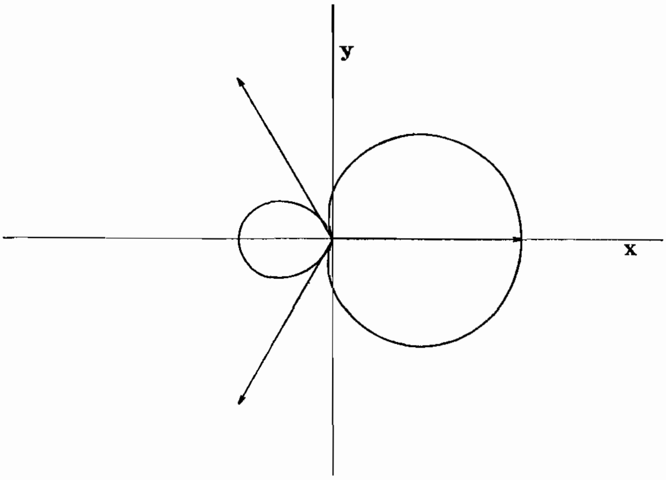

Fig. 6.—Polar graph of $\left|\frac{1}{\sqrt{3}} + \sqrt{2}\cos\varphi\right|$ in the xy plane, representing a trigonal eigenfunction. The maximum directions of the other two equivalent eigenfunctions are also shown.

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[26] Simulation of symmetry by molecules or complex ions in crystals has been discussed by Linus Pauling, *Phys. Rev.*, **36**, 430 (1930).

Thus the x-ray data do not decide between this structure and a truly plane structure. Evidence from another source is at hand, however. A plane $CO_3^=$ or NO_3^- ion should show three characteristic fundamental vibrational frequencies. These have been observed as reflection maxima in the infra-red region. But two of the maxima, at 7μ and 14μ, are double,[27] and this doubling, which is not explicable with a plane configuration, is just that required by a pyramidal structure, the separation of the components giving the frequency of inversion of the pyramid.[28]

In graphite each carbon atom is bound to three others in the same plane; and here the assumption of inversion of a puckered layer is improbable, because of the number of atoms involved. A probable structure is one in which each carbon atom forms two single bonds and one double bond with other atoms. These three bonds should lie in a plane, with angles 109°28′ and 125°16′, which are not far from 120°. Two single bonds and a double bond should be nearly as stable as four single bonds (in diamond), and the stability would be increased by the resonance terms arising from the shift of the double bond from one atom to another. But this problem and the closely related problem of the structure of aromatic nuclei demand a detailed discussion, perhaps along the lines indicated, before they can be considered to be solved.

The Structures of Simple Molecules.—The foregoing considerations throw some light on the structure of very simple molecules in the normal and lower excited states, but they do not permit such a complete and accurate discussion of these questions as for more complicated molecules, because of the difficulty of taking into consideration the effect of several unshared and sometimes unpaired electrons. Often the bond energy is not great enough to destroy s–p quantization, and the interaction between a bond and unshared electrons is more important than between a bond and other shared electrons because of the absence of the effect of concentration of the eigenfunctions.

Let us consider an atom forming a bond with another atom in the direction of the z axis. Then p_z and s form two eigenfunctions designated σ, p_x and p_y two designated π (one with a resultant moment of $+1$ along the z axis, one with -1). If s–p quantization is not broken, the strongest bond will be formed by p_z, and weaker ones by π. If s–p quantization is broken, new eigenfunctions σ_b and σ_o will be formed from s and p_z. In this case the strongest bond is formed by the σ_b eigenfunction, which extends out toward the other atom, weaker ones are formed by $\pi+$ and $\pi-$, and an extremely weak one, if any, by σ_o. We can also predict the stability of

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[27] C. Schaefer, F. Matossi and F. Dane, *Z. Physik*, **45**, 493 (1927).

[28] The normal states of these ions are similar to certain excited states of ammonia, which also show doubling. The frequency of inversion of the normal ammonia molecule is negligibly small.

unshared electrons; σ_o, involving s with its greater penetration of the atom core, will be more stable than π.

As examples we may discuss CO, CN, N_2 and NO. CO might be composed of normal or excited atoms, or even of ions. A neutral oxygen atom can form only two bonds. Hence a normal carbon atom, ^3P, which can also form two bonds, is at no disadvantage. We can write the following reaction, using symbols similar to those of Lennard-Jones[29] and Dunkel,[30] whose treatments of the electronic structure of simple molecules have several points of similarity with ours

$$\mathrm{C}\ 2s^22p2p\ {}^3P + \mathrm{O}\ 2s^22p^22p2p\ {}^3P \longrightarrow \mathrm{CO}\ (2\sigma_o{}^2)(2\sigma_o{}^22\pi^2)\{2\sigma_b2\pi + 2\sigma_b2\pi\}{}^1\Sigma$$

$$:\underset{\cdot}{\mathrm{C}}\cdot + \cdot\underset{\cdot}{\ddot{\mathrm{O}}}: \longrightarrow :\mathrm{C}::\ddot{\mathrm{O}}: \qquad \text{Normal state}$$

Here symbols in parentheses represent unshared electrons attached to C and O, respectively, and those in braces represent shared electrons. An excited carbon atom ^5S lies about 1.6 v. e. above the normal state, but can still form only a double bond with oxygen, so that the resultant molecule should be excited. We write

$$\mathrm{C}^*\ 2s2p2p2p\ {}^5S + \mathrm{O}\ 2s^22p^22p2p\ {}^3P \longrightarrow \mathrm{CO}^*\ (2\sigma_o2\pi)(2\sigma_o{}^22\pi^2)\{2\sigma_b2\pi + 2\sigma_b2\pi\}{}^3\Pi \text{ or } {}^1\Pi$$

The resultant states are necessarily Π, for σ_b and one π are used for the bond, leaving on C σ_o and π. These two electrons may or may not pair with one another, giving $^1\Pi$ and $^3\Pi$, respectively. Of these $^3\Pi$ should be the more stable, for the two electrons are attached essentially to one atom, and the rules for atomic spectra should be valid. This is substantiated; the observed excited states $^3\Pi$ and $^1\Pi$ lie at 5.98 and 7.99 v. e., respectively. Another way of considering these three states is the following: to go from $:\mathrm{C}::\ddot{\mathrm{O}}:$ to $\cdot\underset{\cdot}{\mathrm{C}}::\ddot{\mathrm{O}}:$ we lift an electron from the more deeply penetrating σ_o orbit to π; about 6–8 v. e. is needed for this, and the resultant state is either $^3\Pi$ or $^1\Pi$. This viewpoint does not necessitate the discussion of products of dissociation.

CN is closely similar. The normal nitrogen atom, $2s^22p2p2p\ {}^4S$, can form three bonds, and more cannot be formed by an excited neutral atom (with five L electrons), so that there is no reason to expect excitation. But a normal carbon atom can form only a double bond, and an excited carbon atom, only 1.6 v. e. higher, can form a triple bond, which contributes about 3 v. e. more than a double bond to the bond energy. Hence we write

$$\mathrm{C}^*\ 2s2p2p2p\ {}^5S + \mathrm{N}\ 2s^22p2p2p\ {}^4S \longrightarrow \mathrm{CN}\ (2\sigma_o)(2\sigma_o{}^2)\{2\sigma_b2\pi2\pi + 2\sigma_b2\pi2\pi\}{}^2\Sigma$$

$$\cdot\underset{\cdot}{\dot{\mathrm{C}}}\cdot + \cdot\underset{\cdot}{\dot{\mathrm{N}}}: \longrightarrow \cdot\mathrm{C}:::\mathrm{N}: \qquad \text{Normal state}$$

The first excited state of the molecule, $:\mathrm{C}::\underset{\cdot}{\mathrm{N}}:$, is built from normal atoms, and has the term symbol $^2\Pi$. It lies 1.78 v. e. above the normal state.

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[29] J. E. Lennard-Jones, *Trans. Faraday Soc.*, **25**, 668 (1929).

[30] M. Dunkel, *Z. physik. Chem.*, **B7**, 81 (1930).

Two normal nitrogen atoms form a normal molecule with a triple bond.

$$2\mathrm{N}\ 2s^2 2p2p2p\ {}^4S \longrightarrow \mathrm{N}_2(2\sigma_o{}^2)(2\sigma_o{}^2)\{2\sigma_b 2\pi 2\pi + 2\sigma_b 2\pi 2\pi\}\,{}^1\Sigma$$

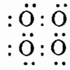
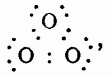
$$:\underset{\cdot}{\dot{\mathrm{N}}}\cdot + \cdot\underset{\cdot}{\dot{\mathrm{N}}}: \longrightarrow :\mathrm{N}:::\mathrm{N}: \qquad \text{Normal state}$$

All other states lie much higher.

A normal oxygen atom and a normal nitrogen atom form a normal NO molecule with a double bond.

$$\mathrm{N}\ 2s^2 2p2p2p\ {}^4S + \mathrm{O}\ 2s^2 2p^2 2p2p\ {}^3P \longrightarrow \mathrm{NO}(2\sigma_o{}^2 2\pi)(2\sigma_o{}^2 2\pi^2)\{2\sigma_b 2\pi + 2\sigma_b 2\pi\}\,{}^2\Pi$$

$$:\underset{\cdot}{\dot{\mathrm{N}}}\cdot + \cdot\underset{\cdot}{\ddot{\mathrm{O}}}: \longrightarrow :\underset{\cdot}{\mathrm{N}}::\underset{\cdot\cdot}{\mathrm{O}}: \qquad \text{Normal state}$$

This treatment sometimes fails for symmetrical molecules. Thus $:\ddot{\mathrm{O}}::\ddot{\mathrm{O}}:$ ${}^1\Sigma$ would be predicted for the normal state of O_2, whereas the observed normal state, ${}^3\Sigma$, lies 1.62 v. e. below this. It seems probable that the additional degeneracy arising from the identity of the two atoms gives rise to a new type of bond, the *three-electron bond*, and that in normal O_2 there are one single bond and two three-electron bonds, $:\mathrm{O}\overset{\cdots}{\underset{\cdots}{:}}\mathrm{O}:$, ${}^3\Sigma$; a definite decision regarding this question must await a detailed quantum-mechanical treatment. Evidence regarding the oxygen–oxygen single bond is provided by O_4, with the square structure  $\begin{array}{c}:\ddot{\mathrm{O}}:\ddot{\mathrm{O}}:\\ :\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:\end{array}$. The 90° bond angles are expected, since quantization in *s* and *p* eigenfunctions is not changed. The equality in energy of O_4 and $2O_2$ leads to an energy of 58,000 cal. per mole per single bond in O_4; the difference between this value and that for a carbon–carbon single bond (100,000 cal.) shows the greater bond-forming power of tetrahedral eigenfunctions over *p* eigenfunctions. Ozone, which very probably has the symmetrical arrangement , has 60° bond angles, and this distortion from the most favorable bond angle of 90° shows up in the bond energy, for the heat of formation of −34,000 cal. per mole leads to 47,000 cal. per mole per single bond, a decrease of 11,000 cal. over the favored O_4 bonds.

For some polyatomic molecules predictions can be made regarding the atomic arrangement from a knowledge of the electronic structure or *vice versa*. Thus $\cdot\mathrm{C}:::\mathrm{N}:$ ${}^2\Sigma$ can form a bond through the unpaired σ_o electron of carbon, and this bond will extend along the CN axis. Hence the molecules $\mathrm{H}:\mathrm{C}:::\mathrm{N}:$, $:\mathrm{N}:::\mathrm{C}:\mathrm{C}:::\mathrm{N}:$ and $:\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}:\mathrm{C}:::\mathrm{N}:$ should be linear. This is verified by band spectral data.[31] The isocyanides, RNC, such as H_3CNC, may be given either a triple or a double bond structure: $\mathrm{R}:\mathrm{N}:::\mathrm{C}:$ or $\mathrm{R}:\underset{\cdot\cdot}{\mathrm{N}}::\mathrm{C}:$. The first of these is built of the ions N^+ ${}^5S$ and C^- ${}^4S$, which may be an argument in favor of the second structure, built of normal

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[31] Private communication from Professor Richard M. Badger of this Laboratory, who has kindly provided me with much information concerning the results of band spectroscopy.

atoms.[32] A decision between the two alternatives could be made by determining the atomic arrangement of an isocyanide, for the triple bond gives a linear molecule, bond angle 180°, and the double bond a kinked molecule, bond angle between 90 and 109°28′.

The molecules and complex ions containing three kernels and sixteen L electrons form an interesting group. Of these CO_2, formed from excited carbon ${}^5S$ and normal oxygen atoms, would have the structure $:\ddot{\mathrm{O}}::\mathrm{C}::\ddot{\mathrm{O}}:$. The two double bonds make the molecule linear, which is verified by both crystal structure and band spectral data. Crystal structure data also show N_2O to be linear, although it is not known whether or not the molecule has oxygen in the middle or at one end, as first suggested by Langmuir[33] and supported by the kernel-repulsion rule.[34] The known linear arrangement eliminates structures built of neutral atoms, $:\underset{\cdot}{\dot{\mathrm{N}}}:\mathrm{O}:\underset{\cdot}{\dot{\mathrm{N}}}:$ and $:\underset{\cdot}{\dot{\mathrm{N}}}::\underset{\cdot\cdot}{\mathrm{N}}:\underset{\cdot}{\ddot{\mathrm{O}}}:$, for these have bond angles between 90 and 125°. The structures $:\underset{\cdot\cdot}{\mathrm{N}}::\mathrm{N}::\underset{\cdot\cdot}{\mathrm{O}}:$ and $:\underset{\cdot\cdot}{\mathrm{N}}::\mathrm{O}::\underset{\cdot\cdot}{\mathrm{N}}:$, built from $N\ N^+\ O^-$ and $N^-\ O^{++}\ N^-$, respectively, would both be linear, and so compatible with the known arrangement. An *a priori* decision between them is difficult, although previously advanced arguments favor the unsymmetrical structure. Band spectra should soon decide the question.

The trinitride, cyanate, and isocyanate ions, the first two of which are known[35] to be linear, no doubt have identical electronic structures.

$$:\underset{\cdot}{\ddot{\mathrm{N}}}\cdot^{-}\ {}^3P + \cdot\underset{\cdot}{\dot{\mathrm{N}}}\cdot^{+}\ {}^5S + \cdot\underset{\cdot}{\ddot{\mathrm{N}}}:^{-} \longrightarrow\ :\ddot{\mathrm{N}}::\mathrm{N}::\ddot{\mathrm{N}}:^{-}$$

or

$$N^- + N^+ + N^- \longrightarrow N_3^-\ \text{Trinitride ion}$$
$$N^- + C + O \longrightarrow NCO^-\ \text{Cyanate ion}$$

The fulminate ion, CNO^-, probably has a structure intermediate between $:\ddot{\mathrm{C}}::\mathrm{N}::\ddot{\mathrm{O}}:^{-}$ and $:\mathrm{C}:::\mathrm{N}:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:^{-}$; for since these two bond types have the same bond angles and term symbols (${}^1\Sigma$), they can form intermediate structures lying anywhere between the two extremes. Which extreme is the more closely approached could be determined from a study of the bond angles in un-ionized fulminate molecules, such as AgCNO or ONCHgCNO, for the first structure would lead to an angle of 125° between the CNO axis and the metal–carbon bond, the second to an angle of 180°.

Bonds Involving *d*-Eigenfunctions.—When d eigenfunctions as well as s and p can take part in bond formation, the number and variety of bonds which can be formed are increased. Thus with an s, a p and a d subgroup as many as nine bonds can be formed by an atom. It is found from a

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[32] Thus W. Heitler and G. Rumer, *Nachr. Ges. Wiss. Göttingen, Math. physik. Klasse*, **7**, 277 (1930), in a paper on the quantum mechanics of polyatomic molecules, discuss only the second structure.

[33] I. Langmuir, THIS JOURNAL, **41**, 1543 (1919).

[34] Linus Pauling and S. B. Hendricks, *ibid.*, **48**, 641 (1926).

[35] S. B. Hendricks and Linus Pauling, THIS JOURNAL, **47**, 2904 (1925).

consideration of the eigenfunctions that all cannot be equivalent, but six equivalent bonds extending toward the corners of either a regular octahedron or a trigonal pyramid, four extending toward the corners of a tetrahedron or a square, etc., can be formed; and the strength and mutual orientation of the bonds are determined by the number of d eigenfunctions involved in their formation.

There are five d eigenfunctions in a subgroup with $l = 2$ and with given n. They are

$$\left.\begin{aligned} d_z &= \sqrt{5/4}\,(3\cos^2\theta - 1) \\ d_{y+z} &= \sqrt{15}\sin\theta\cos\theta\cos\varphi \\ d_{x+z} &= \sqrt{15}\sin\theta\cos\theta\sin\varphi \\ d_{x+y} &= \sqrt{15/4}\sin^2\theta\sin 2\varphi \\ d_x &= \sqrt{15/4}\sin^2\theta\cos 2\varphi \end{aligned}\right\} \quad (11)$$

or any set of five orthogonal functions formed by linear combination of these. These functions are not well suited to bond formation. d_{y+z}, d_{x+z} and d_{x+y}, which are similarly related to the x, y and z axes, respectively, have the form shown in Fig. 7. Each eigenfunction has maxima in four directions. d_x is similar in shape, differing from d_{x+y} only in a rotation of 45° about the z axis. d_z, shown in Fig. 8, has two maxima along the z axis, and a girdle about its waist.

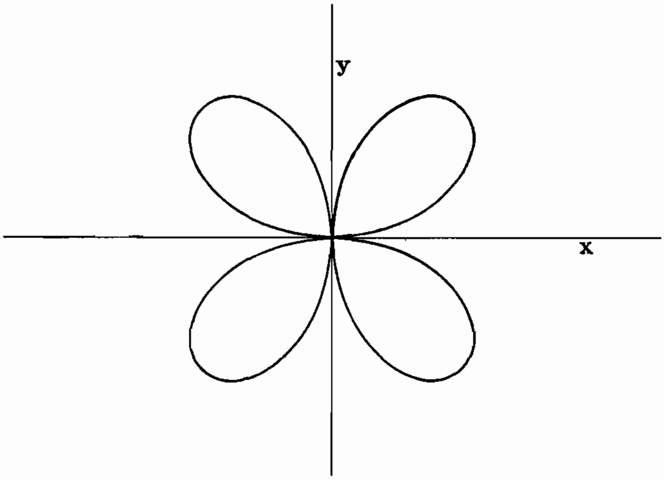

Fig. 7.—Polar graph of $\left|\frac{\sqrt{15}}{2}\sin^2\theta\sin 2\varphi\right|$ in the xy plane, representing the $d_x +$ eigenfunction.

Assuming as before that the dependence on r of the s, p and d eigenfunctions under discussion is not greatly different, the best bond eigenfunctions can be determined by the application of the treatment already applied to s and p alone, with the following results.

The best bond eigenfunction which can be obtained from s, p and d is

$$\frac{1}{3}s + \frac{1}{\sqrt{3}}p_z + \frac{\sqrt{5}}{3}d_z$$

and has a strength of 3. The best two equivalent bond eigenfunctions involving one d eigenfunction

$$\frac{1}{2\sqrt{3}}s + \frac{1}{\sqrt{2}}p_z + \frac{\sqrt{5}}{2\sqrt{3}}d_z \quad \text{and}$$

$$\frac{1}{2\sqrt{3}}s - \frac{1}{\sqrt{2}}p_z + \frac{\sqrt{5}}{2\sqrt{3}}d_z$$

are oppositely directed and have a strength of 2.96.

The atoms of the transition elements, for which d eigenfunctions need to be considered, are of such a size as usually to have a coördination number of 4 or 6, so that four or six equivalent bond eigenfunctions are here of especial interest. If there is available only one d eigenfunction to be combined with an s and three p eigenfunctions, then no more than five bond eigenfunctions can be formed. One may have the maximum strength 3, in which case the others are weak; or two may be strong and three weak; but *with a single d eigenfunction no more than four strong bonds can be formed, and these lie in a plane.* The fifth bond is necessarily weak. The four equivalent bond eigenfunctions formed from s, p and one d eigenfunction are

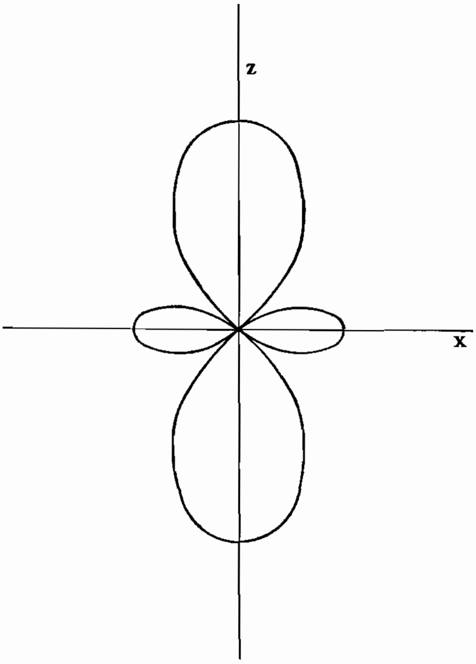

Fig. 8.—Polar graph of $\left|\frac{\sqrt{5}}{2}(3\cos^2\theta - 1)\right|$ in the xz plane, representing the d_z eigenfunction.

$$\left.\begin{aligned}
\psi_1 &= \frac{1}{2}s + \frac{1}{2}d_z + \frac{1}{\sqrt{2}}p_x \\
\psi_2 &= \frac{1}{2}s + \frac{1}{2}d_z - \frac{1}{\sqrt{2}}p_x \\
\psi_3 &= \frac{1}{2}s - \frac{1}{2}d_z + \frac{1}{\sqrt{2}}p_y \\
\psi_4 &= \frac{1}{2}s - \frac{1}{2}d_z - \frac{1}{\sqrt{2}}p_y
\end{aligned}\right\} \qquad (12)$$

One of these is shown in Fig. 9. These all have their maxima in the *xy* plane, directed toward the corners of a square. The strength of these bond eigenfunctions, 2.694, is much greater than that of the four tetrahedral eigenfunctions formed from *s* and *p* alone (2.00). But if three *d* eigenfunctions are available, stronger bonds directed toward tetrahedron corners can be formed. The equivalent tetrahedral bond eigenfunctions

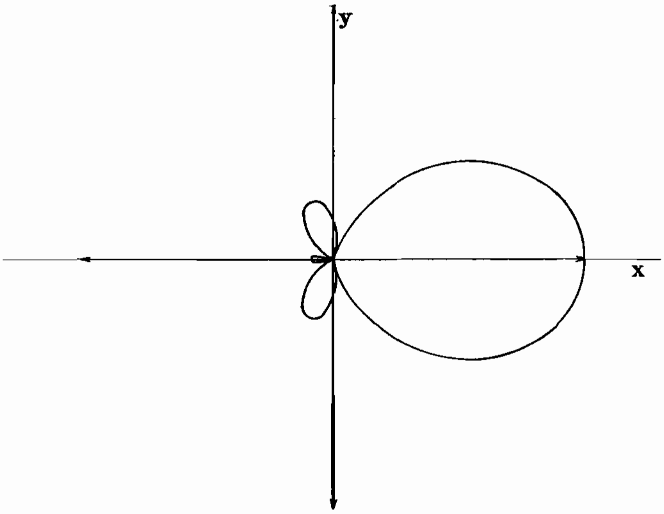

Fig. 9.—Polar graph of $\left| {}^1/_2 + \sqrt{{}^3/_2}\cos\varphi + \frac{\sqrt{15}}{4}\cos 2\varphi \right|$ in the *xy* plane, representing one of the four equivalent dsp^2 bond eigenfunctions. The directions of the maxima of the four are represented by arrows.

$$\psi_{111} = \frac{1}{2}s + \frac{\sqrt{3}}{4\sqrt{2}}(p_x + p_y + p_z) + \frac{\sqrt{5}}{4\sqrt{2}}(d_{y+z} + d_{x+z} + d_{x+y})$$

$$\psi_{1\bar{1}\bar{1}} = \frac{1}{2}s + \frac{\sqrt{3}}{4\sqrt{2}}(p_x - p_y - p_z) + \frac{\sqrt{5}}{4\sqrt{2}}(d_{y+z} - d_{x+z} - d_{x+y})$$

$$\psi_{\bar{1}1\bar{1}} = \frac{1}{2}s + \frac{\sqrt{3}}{4\sqrt{2}}(-p_x + p_y - p_z) + \frac{\sqrt{5}}{4\sqrt{2}}(-d_{y+z} + d_{x+z} - d_{x+y})$$

$$\psi_{\bar{1}\bar{1}1} = \frac{1}{2}s + \frac{\sqrt{3}}{4\sqrt{2}}(-p_x - p_y + p_z) + \frac{\sqrt{5}}{4\sqrt{2}}(-d_{y+z} - d_{x+z} + d_{x+y})$$

have a strength of 2.950, nearly equal to the maximum 3. These leave only two pure *d* eigenfunctions behind, however, the others being part *d* and part *p*. Thus we conclude that if there are three *d* eigenfunctions available, a transition group element forming four electron-pair bonds will direct them toward tetrahedron corners. Examples of such bonds are provided by $CrO_4^=$, $MoO_4^=$, etc. Only when one *d* eigenfunction alone is available will the four bonds lie in a plane. In compounds of bivalent nickel, palladium, and platinum, such as $K_2Ni(CN)_4$, $K_2Pd(CN)_4$, K_2PdCl_4, K_2PtCl_4, etc., there are eight unshared *d* electrons on each metal atom, which occupy four of the five *d* eigenfunctions. Hence the four added atoms or groups lie in a plane at the corners of a square about the metal atom. Such a configuration was assigned to palladous and platinous compounds by Werner because of the existence of apparent *cis* and *trans* compounds, and has been completely substantiated by the x-ray investigation of the chloropalladites and chloroplatinites.[36] The square configuration has not before been attributed to $K_2Ni(CN)_4$; it is supported by the observed isomorphism of the monoclinic crystals $K_2Pd(CN)_4 \cdot H_2O$ and $K_2Ni(CN)_4 \cdot H_2O$, and it will be shown in a following section that it is compatible with the magnetic data.

The non-existence of compounds K_3PtCl_5, etc., is explained by the weak bond-forming power (1.732) of the remaining eigenfunction p_z.

Now if two *d* eigenfunctions are available, six equivalent eigenfunctions

$$\left.\begin{aligned}
\psi_1 &= \frac{1}{\sqrt{6}}\,s + \frac{1}{\sqrt{2}}\,p_z + \frac{1}{\sqrt{3}}\,d_z \\
\psi_2 &= \frac{1}{\sqrt{6}}\,s - \frac{1}{\sqrt{2}}\,p_z + \frac{1}{\sqrt{3}}\,d_z \\
\psi_3 &= \frac{1}{\sqrt{6}}\,s + \frac{1}{\sqrt{12}}\,d_z + \frac{1}{2}\,d_x + \frac{1}{\sqrt{2}}\,p_x \\
\psi_4 &= \frac{1}{\sqrt{6}}\,s + \frac{1}{\sqrt{12}}\,d_z + \frac{1}{2}\,d_x - \frac{1}{\sqrt{2}}\,p_x \\
\psi_5 &= \frac{1}{\sqrt{6}}\,s + \frac{1}{\sqrt{12}}\,d_z - \frac{1}{2}\,d_x + \frac{1}{\sqrt{2}}\,p_y \\
\psi_6 &= \frac{1}{\sqrt{6}}\,s + \frac{1}{\sqrt{12}}\,d_z - \frac{1}{2}\,d_x - \frac{1}{\sqrt{2}}\,p_y
\end{aligned}\right\} \qquad (13)$$

can be formed. These form strong bonds, of strength 2.923, directed toward the corners of a regular octahedron; and no stronger octahedral bonds can be formed even though more *d* eigenfunctions be available (Figs. 10 and 11). Hence we expect transition group atoms with six or less unshared electrons to form six electron-pair bonds. Examples of such compounds are numerous: $PtCl_6^{=}$, $Fe(CN)_6^{=}$, etc., although the definite assignment of an electron-pair bond structure rather than an ionic structure (as in $FeF_6^{\equiv}$, formed of Fe^{+++} and 6 F^-) can be made only after the discussion of paramagnetic susceptibility.

I have not succeeded in determining whether or not these octahedral eigenfunctions are the strongest six equivalent bond eigenfunctions which can be formed when more than two *d*'s are available. The known structure of molybdenite, MoS_2, suggests that six bonds directed toward the corners of a trigonal prism are stable; but only a small increase in bond strength can possibly be obtained (from 2.923 to not over 3), and the mutual re-

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[36] R. G. Dickinson, This Journal, 44, 2404 (1922).

pulsion of the six atoms or groups will in most cases overcome this, if it does exist, and leave the octahedral configuration the stable one.

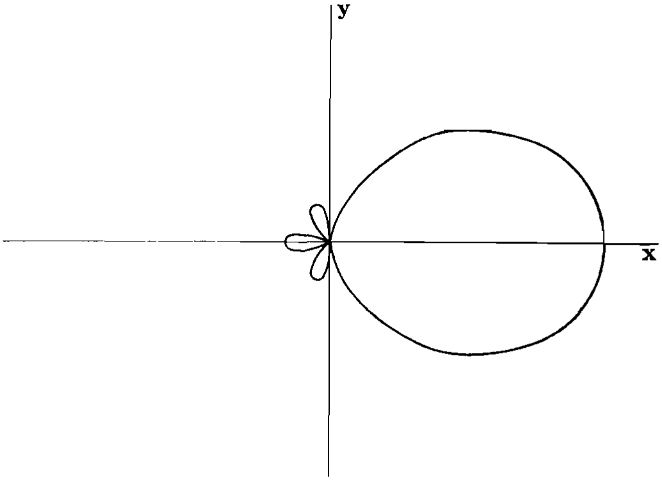

Fig. 10.—Polar graph of $|\psi_3|$ of Equation 13, in the *xy* plane, representing one of the six equivalent d^2sp^3 bond eigenfunctions (octahedral eigenfunctions).

II. The Magnetic Moments of Molecules and Complex Ions

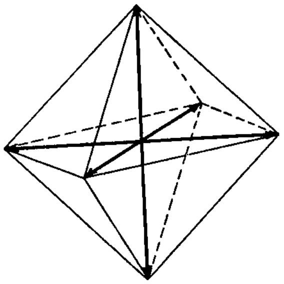

Fig. 11.—Diagram showing relative orientation in space of the directions of the maxima of the octahedral eigenfunctions.

The theory of the paramagnetic susceptibility of substances has been developed gradually over a long period of years through the efforts of a number of investigators. The theoretical calculation of the magnetic moments of complex molecules and ions has in particular attracted much attention recently, and both theoretical and empirical considerations have been used in developing rules applicable in various cases. The work reported in this paper provides little more than the justification and unification of previously developed rules. This finishing touch is, however, of much significance for the problem of the nature of the chemical bond; for it, in conjunction with the quantum mechanical discussion of the previous sections, permits definite conclusions to be drawn regarding type of bond in many molecules and complex ions from a knowledge of their magnetic moments, and conversely provides the basis for the definite prediction of magnetic moments from a knowledge of the type of bonds and the atomic arrangement.

The calculation of the magnetic moments of the rare-earth ions by

Hund[37] in 1926 and of oxygen and nitric oxide by Van Vleck[38] in 1928 were triumphs of the theory of spectra. The magnetic moment of an atom or monatomic ion with Russell–Saunders coupling of the quantum vectors is

$$\mu_J = g\sqrt{J(J+1)}$$

in which g, the Landé splitting factor, is given by

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

Here L, S, and J are the quantum numbers corresponding to the total orbital angular momentum of the electrons, the total spin angular momentum, and the resultant of these two. Hund predicted values of L, S, and J for the normal states of the rare-earth ions from spectroscopic rules, and calculated μ-values for them which are in generally excellent agreement with the experimental data for both aqueous solutions and solid salts.[39] In case that the interaction between L and S is small, so that the multiplet separation corresponding to various values of J is small compared with kT, Van Vleck's formula[38]

$$\mu_{LS} = \sqrt{4S(S+1) + J(J+1)}$$

is to be used.

But similar calculations for the iron-group ions show marked disagreement with experiment, and many attempts were made to explain the discrepancies. The explanation is simple: *in many condensed systems the perturbing effect of the atoms or molecules surrounding a magnetic atom destroys the contribution of the orbital momentum to the magnetic moment, which is produced entirely by the spin moments of unpaired electrons.*[40]

This conclusion is easily deduced from the consideration of the nature of eigenfunctions giving rise to magnetic moments. In an atom containing unpaired p electrons, say, a component of orbital magnetic moment of $\pm(h/2\pi)\cdot(e/2mc)$ is obtained when an unpaired electron is in a state given by the eigenfunction $p_x \pm i\,p_y$. Now if the perturbing influence of surrounding atoms or molecules is such as to make the perturbation energy for the eigenfunction p_x or p_y or any combination of them other than $p_x \pm i\,p_y$ greater than the field energy, this will be the correct zero$^{\text{th}}$ order eigenfunction, and the atom will show no orbital magnetic moment. In an atom with Russell–Saunders coupling the interaction energy of L and S takes the place of the field energy, so that the criterion to be satisfied in order that the magnetic moment due to L be destroyed is that the perturbation energy due to surrounding atoms and ions be greater than the multiplet separation, which for the iron-group ions is of the order of magnitude of 1 v. e.[41]

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[37] F. Hund, *Z. Physik*, **33**, 345 (1925).

[38] J. H. Van Vleck, *Phys. Rev.*, **31**, 587 (1928).

[39] The few discrepancies have been accounted for by S. Freed [This Journal, **52**, 2702 (1930)] and J. H. Van Vleck and A. Frank [*Phys. Rev.*, **34**, 1494 (1929), and a paper delivered at the Cleveland meeting of the American Physical Society, December 31, 1930].

[40] This assumption was first made by E. C. Stoner, *Phil. Mag.*, **8**, 250 (1929), in order to account for the observed moments of iron-group ions.

[41] Essentially the same conclusion has been announced by J. H. Van Vleck at the Cleveland meeting of the American Physical Society, December 31, 1930.

If the perturbation function shows cubic symmetry, and in certain other special cases, the first-order perturbation energy is not effective in destroying the orbital magnetic moment, for the eigenfunction $p_x \pm i\, p_y$ leads to the same first-order perturbation terms as p_x or p_y or any other combinations of them. In such cases the higher order perturbation energies are to be compared with the multiplet separation in the above criterion.

In linear molecules only the component of orbital momentum normal to the figure axis is destroyed, that along the figure axis being retained. In non-linear molecules with strong interatomic interactions the concept of orbital angular momentum loses its significance.

The rare-earth ions owe their magnetic moments to an incompleted $4f$ subshell, which lies within an outer shell of $5s$ and $5p$ electrons, and is thus protected from strong perturbations by surrounding atoms. As a consequence the orbital magnetic moment is not destroyed, and the ion is not affected by its environment. But in the iron-group ions and other transition-group ions the incompleted subshell is the outermost one. Hence it is not surprising that the solvent molecules or the surrounding atoms or ions in a complex ion or a crystal interact sufficiently strongly with these atoms or ions to destroy, in whole, or in part, the orbital magnetic moment, leaving the spin moment, with perhaps a small contribution from the orbital moment in border-line cases. We can state with certainty that the formation of electron-pair bonds will destroy the orbital moment.

This greatly simplifies the theory of the magnetic moments of molecules and complex ions. *The magnetic moment of a molecule or complex ion is determined entirely by the number of unpaired electrons, being equal to*

$$\mu_S = 2\sqrt{S(S+1)}$$

in which S is one-half that number. The factor 2 is the g-factor for electron spin.

As a matter of fact, Sommerfeld[42] in 1924, a year before Hund's treatment of the rare-earth ions, noticed that the observed magnetic moments of K^+ and Ca^{++}, Ca^+ (spectroscopic), Ca (spectroscopic), Cr^{3+}, Cr^{++}, Mn^{++}, Fe^{++}, Co^{++}, Ni^{++}, Cu^{++} and Cu^+ are approximately reproduced by the above equation with $S = 0, {}^1/_2, 1, {}^3/_2, 2, {}^5/_2, 2, {}^3/_2, 1, {}^1/_2$ and 0, respectively. But with the development of spectral theory he apparently gave up this simple formula because of lack of a theoretical derivation of it, and it remained for Bose[43] in 1927 to state explicitly the assumption that only S contributes to the moment in these cases, without, however, explaining why L gives no contribution, and for Stoner[40] in 1929 to supply the explanation. The comparison of calculated and observed values is given in Table I. It may be pointed out that S increases to a maximum value of ${}^5/_2$ when the $3d$ subgroup is half filled; Pauli's principle requires that succeeding electrons decrease the spin, so that μ_S is symmetrical about

[42] A. Sommerfeld, "Atombau," 4th ed., p. 639.

[43] D. M. Bose, *Z. Physik*, **43**, 864 (1927).

this point. The agreement with experiment, while much better than for μ_J, is not perfect; ions with more than five 3*d* electrons are found to have moments larger than μ_S, while V^{3+} deviates in the other direction. Bose suggested that perhaps *S* could in some cases exceed the maximum value allowed by Pauli's principle, but the obviously correct explanation is that the perturbing effect of surrounding atoms is not sufficient completely to destroy the *L* moment. Hence the observed moment should lie between μ_S and μ_J, which it does in every case.

Since the interaction is not strong enough to destroy the *L* moment, we conclude that in aqueous solution and in some crystalline salts the atoms[44] Fe^{II}, Co^{III}, Co^{II}, Ni^{II} and Cu^{II} do not form strong electron-pair bonds with H_2O, Cl, or certain other atoms, the bonds instead being ion-dipole or ionic bonds.

The formation of a stable coördination compound involving the four tetrahedral sp^3 eigenfunctions might decrease the *L* contribution appreciably. It was indeed pointed out by Bose that in the compounds listed in the last column of Table II the observed moments approach more closely the theoretical values μ_S.

The Magnetic Moments of Complexes with Electron-Pair Bonds.—The peculiar magnetic behavior of some complex ions has attracted much attention. $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$, for example, have $\mu = 2.0$ and 0.00, respectively, instead of the values 5.9 and 4.9 for Fe^{3+} and Fe^{++}. Welo and Baudisch[45] and later Sidgwick and Bose expressed essentially the following rule: the magnetic moment of a complex is the same as that of the atom with the same number of electrons as the central atom of the complex, counting two for each electron-pair bond. Fe^{++} has 24 electrons; adding 12 for the six bonds gives 36, the electron number of krypton, so that the diamagnetism of the ferrocyanide ion is explained. This rule is satisfactory in many cases, but there are also many exceptions. Thus $[Ni(CN)_4]^{=}$ is diamagnetic, although the above rule would make it as paramagnetic as $[Ni(NH_3)_4]^{++}$.

The whole question is clarified when considered in relation to the foregoing quantum mechanical treatment of the electron-pair bond. For the iron-group elements the following rules follow directly from that treatment and from the rules of line spectroscopy.

1. *Bond eigenfunctions for iron-group atoms are formed from the nine eigenfunctions* $3d^5$, *4s and* $4p^3$, *as described in preceding sections. One bond eigenfunction is needed for each electron-pair bond.*

2. *The remaining (unshared) electrons are to be introduced into the 3d eigenfunctions not involved in bond formation.*

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[44] The symbol Fe^{II} is used for bivalent iron, etc., when the type of bond is undetermined.

[45] L. A. Welo and O. Baudisch, *Nature*, **116**, 606 (1925).

TABLE II

MAGNETIC MOMENTS OF IRON-GROUP IONS[a]

Ion	Normal state	μ_J	μ_S	Obs. moment in aqueous soln.	Solid salts, probable coördination number 6		Solid salts, coördination number	
K^+, Ca^{++}, Sc^{3+}, Ti^{4+}	$^1S_0$	0.00	0.00	0.00				
V^{4+}	$^2D_{3/2}$	1.55	1.73	1.7				
V^{3+}	$^3F_2$	1.63	2.83	2.4				
V^{++}, Cr^{3+}	$^4F_{3/2}$	0.78	3.88	3.8–3.9	$Cr_2O_3 \cdot 7H_2O$	3.85		
					$CrCl_3$	3.81		
Cr^{++}, Mn^{3+}	$^5D_0$	0.00	4.90	4.8–4.9				
Mn^{++}, Fe^{3+}	$^6S_{5/2}$	5.91	5.91	5.8	$MnCl_2$	5.75		
					$MnSO_4$	5.87		
					$MnSO_4 \cdot 4H_2O$	5.87		
					$Fe_2(SO_4)_3$	5.86		
					$(NH_4)_2Fe_2(SO_4)_4$	5.86		
Fe^{++}, Co^{3+}	$^5D_4$	6.76	4.90	5.3	$FeCl_2$	5.23	$Fe(N_2H_4)_2Cl_2$	4.87
					$FeCl_2 \cdot 4H_2O$	5.25		
					$FeSO_4$	5.26		
					$FeSO_4 \cdot 7H_2O$	5.25		
					$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$	5.25		
Co^{++}	$^4F_{9/2}$	6.68	3.88	5.0–5.2	$CoCl_2$	5.04	$Co(N_2H_4)_2SO_3 \cdot H_2O$	4.31
					$CoSO_4$	5.04–5.25	$Co(N_2H_4)_2(CH_3COO)_2$	4.56
					$CoSO_4 . 7H_2O$	5.06	$Co(N_2H_4)_2Cl_2$	4.93
					$(NH_4)_2Co(SO_4)_2 \cdot 6H_2O$	5.00		
Ni^{++}	$^3F_4$	5.64	2.83	3.2	$NiCl_2$	3.24–3.42	$Ni(N_2H_4)_2SO_3$	3.20
					$NiSO_4$	3.42	$Ni(N_2H_4)_2(NO_2)_2$	2.80
							$Ni(NH_3)_4SO_4$	2.63
							$Ni(C_2H_4(NH_2)_2)_2(SCN)_2H_2O$	2.63
Cu^{++}	$^2D_{5/2}$	3.56	1.73	1.9–2.0	$CuCl_2$	2.02	$Cu(NH_3)_4(NO_3)_2$	1.82
					$CuSO_4$	2.01	$Cu(NH_3)_4SO_4 \cdot H_2O$	1.81
Cu^+, Zn^{++}	$^1S_0$	0.00	0.00	0.00				

[a] Observed magnetic moments, other than those in the last column, are from "International Critical Tables."

3. *The normal state is the state with the maximum resultant spin S allowed by Pauli's principle.*

These rules apply also to the palladium and platinum groups, the eigenfunctions involved being $4d^5 5s5p^3$ and $5d^5 6s6p^3$, respectively.

There are several important types of molecules and complexes to be given separate discussion.

If the bonds are ionic or ion-dipole bonds, the magnetic moments are those of the isolated central ions, given in the first column of moments in Table III. If the complex involves electron-pair bonds formed from sp^3 alone, such as four tetrahedral sp^3 bonds, the magnetic moments are the same, for the five d eigenfunctions are still available for the remaining electrons. The hydrazine and ammonia complexes mentioned above come in this class.

If four strong bonds involving a d eigenfunction are formed (giving a square configuration), only four d eigenfunctions are available for the additional electrons. The magnetic moments are then those given in the second column of the table. Examples of such compounds are $K_2Ni(CN)_4$, $K_2Pd(CN)_4 \cdot H_2O$, K_2PdCl_4, K_2PtCl_4, $K_2Pt(C_2O_4)_2 \cdot 2H_2O$ and $Pt(NH_3)_4SO_4$. With eight unshared d electrons, these should all be diamagnetic. This has been experimentally verified for the first and the last three compounds; data for the others are not available. The square configuration has been experimentally verified for the chloropalladites and chloroplatinites, as mentioned before. It can be predicted that in the $[Pt(C_2O_4)_2 \cdot 2H_2O]^=$ complex the two oxalate groups lie in a plane, each attached to the platinum atom by two electron-pair bonds of the type dsp^2. The two water molecules, if attached to the complex, are held by ion-dipole bonds.

In complexes in which the central atom forms a coördinated octahedron of six atoms or groups, the bonds may be any of several types. If they are all ionic or ion-dipole bonds, the moments are those in the first column. If four electron-pair bonds are formed, these must be dsp^2 and lie in a plane (sp^3 gives tetrahedral bonds); the $[Pt(C_2O_4)_2 \cdot 2H_2O]^=$ ion is of this type, assuming that the water molecules are part of the complex. The moments are then those of the second column. If six electron-pair bonds are formed, only three d eigenfunctions are left for the additional electrons, giving the magnetic moments of the third column. It is seen that in atoms with three or fewer unshared electrons magnetic data provide no information as to bond type with coördination number six, but that in other cases a definite statement can be made as to the type of bond when magnetic data are available. The observed magnetic moments are collected in Table IV. From them we deduce that trivalent and bivalent manganese, chromium, iron, and cobalt form six strong electron-pair bonds with cyanide groups, and in some cases with other groups, including NH_3, Cl and NO_2.[46] Tri-

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[46] An electron-pair bond with a water molecule may perhaps be formed when induced by other strong bond-forming groups in the complex.

TABLE III

PREDICTED MAGNETIC MOMENTS OF COMPLEXES CONTAINING TRANSITION ELEMENTS

			For ion or $4sp^3$ bonds	For 4 dsp^2 bonds	For 6 d^2sp^3 bonds	For 8 d^4sp^3 bonds
$\mathrm{K^{I}}$ $\mathrm{Ca^{II}}$ $\mathrm{Sc^{III}}$ $\mathrm{Ti^{IV}}$, etc.	$\mathrm{Rb^{I}}$ $\mathrm{Sr^{II}}$ $\mathrm{Y^{III}}$ $\mathrm{Zr^{IV}}$ $\mathrm{Nb^{V}}$ $\mathrm{Mo^{VI}}$	$\mathrm{Cs^{I}}$ $\mathrm{Ba^{II}}$—$\mathrm{Hf^{IV}}$$\mathrm{Ta^{V}}$ $\mathrm{W^{VI}}$	0.00	0.00	0.00	0.00
$\mathrm{V^{IV}}$	$\mathrm{Nb^{IV}}$$\mathrm{Mo^{V}}$	$\mathrm{W^{V}}$	1.73	1.73	1.73	1.73
$\mathrm{V^{III}}$ $\mathrm{Cr^{IV}}$	$\mathrm{Mo^{IV}}$ $\mathrm{Ru^{VI}}$	$\mathrm{W^{IV}}$ $\mathrm{Os^{VI}}$	2.83	2.83	2.83	0.00
$\mathrm{V^{II}}$ $\mathrm{Cr^{III}}$ $\mathrm{Mn^{IV}}$	$\mathrm{Mo^{III}}$		3.88	3.88	3.88	
$\mathrm{Cr^{II}}$ $\mathrm{Mn^{III}}$ $\mathrm{Fe^{IV}}$	$\mathrm{Mo^{II}}$ $\mathrm{Ru^{IV}}$	$\mathrm{Os^{IV}}$	4.90	4.90	2.83	
$\mathrm{Mn^{II}}$ $\mathrm{Fe^{III}}$ $\mathrm{Co^{IV}}$	$\mathrm{Ru^{III}}$	$\mathrm{Os^{III}}$ $\mathrm{Ir^{IV}}$	5.91	3.88	1.73	
$\mathrm{Fe^{II}}$ $\mathrm{Co^{III}}$	$\mathrm{Ru^{II}}$$\mathrm{Rh^{III}}$$\mathrm{Pd^{IV}}$	$\mathrm{Ir^{III}}$ $\mathrm{Pt^{IV}}$	4.90	2.83	0.00	
$\mathrm{Co^{II}}$ $\mathrm{Ni^{III}}$	$\mathrm{Rh^{II}}$		3.88	1.73		
$\mathrm{Ni^{II}}$	$\mathrm{Rh^{I}}$ $\mathrm{Pd^{II}}$ $\mathrm{Ag^{III}}$	$\mathrm{Pt^{II}}$ $\mathrm{Au^{III}}$	2.83	0.00		
$\mathrm{Cu^{II}}$			1.73			
$\mathrm{Cu^{I}}$ $\mathrm{Zn^{II}}$ $\mathrm{Ca^{III}}$ $\mathrm{Ge^{IV}}$, etc.	$\mathrm{Ag^{I}}$ $\mathrm{Cd^{II}}$ $\mathrm{In^{III}}$ $\mathrm{Sn^{IV}}$ $\mathrm{Sb^{V}}$ $\mathrm{Te^{VI}}$	$\mathrm{Au^{I}}$ $\mathrm{Hg^{II}}$ $\mathrm{Tl^{III}}$ $\mathrm{Pb^{IV}}$ $\mathrm{Bi^{V}}$ $\mathrm{Po^{VI}}$	0.00			

valent iron apparently does not form electron-pair bonds with fluorine (in $[FeF_5{\cdot}H_2O]^-$); although investigation of $(NH_4)_3FeF_6$ is to be desired in order to be sure of this conclusion. Ir^{III} and Pt^{IV} form six electron-pair bonds with Cl, NO_2 or NH_3.

TABLE IV

OBSERVED MAGNETIC MOMENTS OF COMPLEXES CONTAINING TRANSITION ELEMENTS[a]

	μ		μ
$K_3[Mn(CN)_6]$	3.01	$[Co(NH_3)_6]Cl_3$	0.00
$K_4[Cr(CN)_6]$	3.3	$[Co(NH_3)_5Cl]Cl_2$	.00
$K_3[Fe(CN)_6]$	2.0	$[Co(NH_3)_4Cl_2]Cl$	.00
$K_4[Mn(CN)_6]$	2.0	$[Co(NH_3)_3(NO_2)_3]$	.00
$K_4[Fe(CN)_6]{\cdot}3H_2O$	0.00	$[Co(NH_3)_5H_2O]_2(C_2O_4)_3$	.00
$Na_3[Fe(CN)_5NH_3]$	.00		
$K_3[Co(CN)_6]$	.00	$K_2Ni(CN)_4$	0.00
$(NH_4)_2[FeF_5{\cdot}H_2O]$	5.97	$K_2Ni(CN)_4{\cdot}H_2O$	.00
$K_4[Mo(CN)_8]$	0.00	K_2PtCl_4	.00
$K_4[W(CN)_8]{\cdot}2H_2O$	.00	$K_2Pt(C_2O_4)_2{\cdot}2H_2O$	.00
$Na_3[IrCl_2(NO_2)_4]$	.00	$Pt(NH_3)_4SO_4$	.00
$[Ir(NH_3)_5NO_2]Cl_2$	.00		
$[Ir(NH_3)_4(NO_2)_2]Cl$	.00	$Na_2[Fe(CN)_5NO]{\cdot}2H_2O$	.00
$[Ir(NH_3)_3(NO_2)_3]$	.00	$[Ru(NH_3)_4{\cdot}NO{\cdot}H_2O]Cl_3$	.00
$K_2[PtCl_6]$	.00	$[Ru(NH_3)_4{\cdot}NO{\cdot}Cl]Br_2$	.00
$[Pt(NH_3)_6]Cl_4$	.00	$[Co(NH_3)_5NO]Cl_2$	2.81
$[Pt(NH_3)_5Cl]Cl_3$	.00		
$[Pt(NH_3)_4Cl_2]Cl_2$	.00	$Ni(CO)_4$	0.00
$[Pt(NH_3)_3Cl_3]Cl$	.00	$Fe(CO)_5$	.00
$[Pt(NH_3)_2Cl_4]$	.00	$Cr(CO)_5$	.00

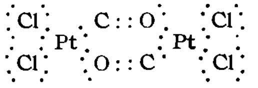
[a] Values quoted are from "International Critical Tables" or from W. Biltz, *Z. anorg. Chem.*, **170**, 161 (1928), and D. M. Bose, *Z. Physik*, **65**, 677 (1930). I am indebted to Mr. P. D. Brass for collecting from the literature some of the data in this table.

The moments of complexes containing NO offer a puzzling problem. The diamagnetism of compounds of iron and ruthenium suggests that Fe^{IV} and Ru^{IV} form a double bond with NO, making seven bonds in all, which woud lead to $\mu = 0$. But this structure cannot be applied to $[Co(NH_3)_5NO]Cl_2$, which has a moment corresponding to a triplet state. Further study of such complexes is needed.

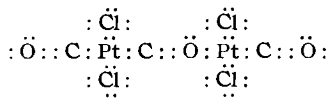
The observed diamagnetism of the ions $[Mo(CN)_8]^{4-}$ and $[W(CN)_8]^{4-}$ shows that the central atom forms eight electron-pair bonds, involving the eigenfunctions d^4sp^3 (fourth column of Table III).

The metal carbonyls $Ni(CO)_4$, $Fe(CO)_5$, and $Cr(CO)_6$ are observed to be diamagnetic. This follows from the theoretical discussion if it is assumed that an electron-pair bond is formed with each carbonyl; for the nine eigenfunctions available ($3d^54s4p^3$) are completely filled by the n bonds and $2(9-n)$ additional electrons attached to the metal atom ($n = 4, 5, 6$). The theory also explains the observed composition of these unusual substances; for the formulas $M(CO)_n$, with $n = 4, 5$, and 6, respectively, follow at once from the assumption that CO molecules add on as long as bond eigenfunctions are available. Since a single unshared electron can occupy an eigenfunction, this assumption leads to the formula $Co(CO)_4$, which is known to be correct. This substance should have $\mu = 1.73$. The compounds $Mn(CO)_5$ and $V(CO)_6$ should also exist, and have $\mu = 1.73$. $Co(CO)_4$ and $Mn(CO)_5$ should form un-ionized diamagnetic cyanides, $[Co(CO)_4CN]$ and $[Mn(CO)_5CN]$, while $V(CO)_6$ would not form a stable cyanide, since steric effects would prevent the cyanide group from forming an electron-pair bond with the vanadium atom, and ionic cyanides are formed only by strong metals. It is interesting to note the effect of the four strong bond eigenfunctions and one weak one formed from dsp^3; whereas nickel forms no lower carbonyl than $Ni(CO)_4$, iron forms $Fe(CO)_4$ and $Fe_2(CO)_9$ in addition to $Fe(CO)_5$.

The palladium and platinum metals also form carbonyl compounds. Of the expected compounds $Pd(CO)_4$, $Pt(CO)_4$, $Ru(CO)_5$, $Os(CO)_5$, $Mo(CO)_6$, and $W(CO)_6$ only $Mo(CO)_6$ has been prepared, although some unsaturated ruthenium carbonyls have been prepared. The compounds $Pd(CO)_2Cl_2$, $Pt(CO)_2Cl_2$, $K[PtCOCl_3]$, etc., show the stability of the four dsp^2 bonds. It would be interesting to determine whether or not each CO is bonded to two metal atoms in compounds such as $[Pt(CO)Cl_2]_2$, whose structure is predicted to be



with the whole molecule in one plane. The compounds $2PdCl_2{\cdot}3CO$ and $2PtCl_2{\cdot}3CO$ probably have the structure



$$\begin{array}{ccccccccccc} & & & :\ddot{Cl}: & & & & :\ddot{Cl}: & & & \\ :\ddot{O}:: & C & : & \ddot{Pt} & :C:: & \ddot{O} & : & \ddot{Pt} & :C:: & \ddot{O}: & \\ & & & :\underset{..}{\ddot{Cl}}: & & & & :\underset{..}{\ddot{Cl}}: & & & \end{array}$$

or one of the structures isomeric with this.

This by no means exhaustive discussion may serve to indicate the value of the information provided by magnetic data relative to the nature of the chemical bond. The quantum-mechanical rules for electron-pair bonds are essential to the treatment. Much further information is provided when these methods of attack are combined with crystal structure data, a topic which has been almost completely neglected in this paper. It has been found that the rules for electron-pair bonds permit the formulation of a set of structural principles for non-ionic inorganic crystals similar to that for complex ionic crystals; the statement of these principles and applications illustrating their use will be the subject of an article to be published in the *Zeitschrift für Kristallographie.*

Summary

With the aid of the quantum mechanics there is formulated a set of rules regarding electron-pair bonds, dealing particularly with the strength of bonds in relation to the nature of the single-electron eigenfunctions involved. It is shown that one single-electron eigenfunction on each of two atoms determines essentially the nature of the electron-pair bond formed between them; this effect is accentuated by the phenomenon of concentration of the bond eigenfunctions.

The type of bond formed by an atom is dependent on the ratio of bond energy to energy of penetration of the core (*s–p* separation). When this ratio is small, the bond eigenfunctions are *p* eigenfunctions, giving rise to bonds at right angles to one another; but when it is large, new eigenfunctions especially adapted to bond formation can be constructed. From *s* and *p* eigenfunctions the best bond eigenfunctions which can be made are four equivalent tetrahedral eigenfunctions, giving bonds directed toward the corners of a regular tetrahedron. These account for the chemist's tetrahedral atom, and lead directly to free rotation about a single bond but not about a double bond and to other tetrahedral properties. A single *d* eigenfunction with *s* and *p* gives rise to four strong bonds lying in a plane and directed toward the corners of a square. These are formed by bivalent nickel, palladium, and platinum. Two *d* eigenfunctions with *s* and *p* give six octahedral eigenfunctions, occurring in many complexes formed by transition-group elements.

It is then shown that (excepting the rare-earth ions) the magnetic moment of a non-linear molecule or complex ion is determined by the number of unpaired electrons, being equal to $\mu_S = 2\sqrt{S(S+1)}$, in which S is half that number. This makes it possible to determine from magnetic data which eigenfunctions are involved in bond formation, and so to decide between electron-pair bonds and ionic or ion-dipole bonds for various complexes. It is found that the transition-group elements almost without exception form electron-pair bonds with CN, ionic bonds with F, and ion-dipole bonds with H_2O; with other groups the bond type varies.

Examples of deductions regarding atomic arrangement, bond angles and other properties of molecules and complex ions from magnetic data, with the aid of calculations involving bond eigenfunctions, are given.

Pasadena, California

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THE NATURE OF THE CHEMICAL BOND. II. THE ONE-ELECTRON BOND AND THE THREE-ELECTRON BOND

By Linus Pauling

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The work of Heitler and London and its recent extensions[1] have shown that the Lewis electron-pair bond between two atoms involves essentially a pair of electrons and two eigenfunctions,[2] one for each atom. It will be shown in the following paragraphs that under certain conditions bonds can be formed between two atoms involving one electron or three electrons, in each case one eigenfunction for each atom being concerned. The conditions under which the one-electron bond and the three-electron bond can be formed will be stated, and their properties will be discussed. These bonds have not the importance of the electron-pair bond, for they occur in only a few compounds, which, however, are of especial interest on account of their unusual and previously puzzling properties.

The One-electron Bond.—The resonance phenomenon of the quantum mechanics, which provides the energy of the shared-electron chemical bond, occurs even between two unlike atoms when an electron-pair bond is formed, on account of the identity of the two electrons. But if only one electron is available, resonance is not expected in general. The application[3] of the first-order perturbation theory of the quantum mechanics to a system of two nuclei and one electron, although not leading to accurate numerical results, is illuminating. It is found that with two nuclei of different charges there occur in most cases only repulsive states, so that $Li + H^+$ or $Li^+ + H$ would not form a stable molecule LiH^+. Only when the unperturbed system is degenerate or nearly degenerate, as in H_2^+ where the two nuclei have the same charge, does there exist a resonance energy leading to molecule formation. The criterion for the stabilization of a single-electron bond by resonance energy is the following: *A stable one-electron bond can be formed only when there are two conceivable electronic states of the system with essentially the same energy, the states differing in that for one there is an unpaired electron attached to one atom, and for the other the same unpaired electron is attached to the second atom.*

By "essentially the same energy" it is meant that the energies of the states of the unperturbed system differ by an amount less than the possible

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[1] Linus Pauling, This Journal, 53, 1367 (1931).

[2] Throughout this paper the word eigenfunction will be used to denote a single-electron eigenfunction, such as one of the four tetrahedral bond eigenfunctions of a carbon atom.

[3] Linus Pauling, *Chem. Rev.*, **5**, **173** (1928).

resonance energy. (In H_2^+ the resonance energy in the normal state is about 60,000 cal. per mole.) The criterion is of course satisfied in H_2^+, where the two nuclei are identical, and in H_3^+. We may write for these molecule-ions the electronic formulas

$$H\cdot H^+ \text{ and } H\cdot H\cdot H^+$$

This discussion may be given the following somewhat more precise form. Let us consider various functions of the coördinates of the electrons relative to those of the nuclei, which, as usual in molecular problems, are assumed to retain fixed positions.

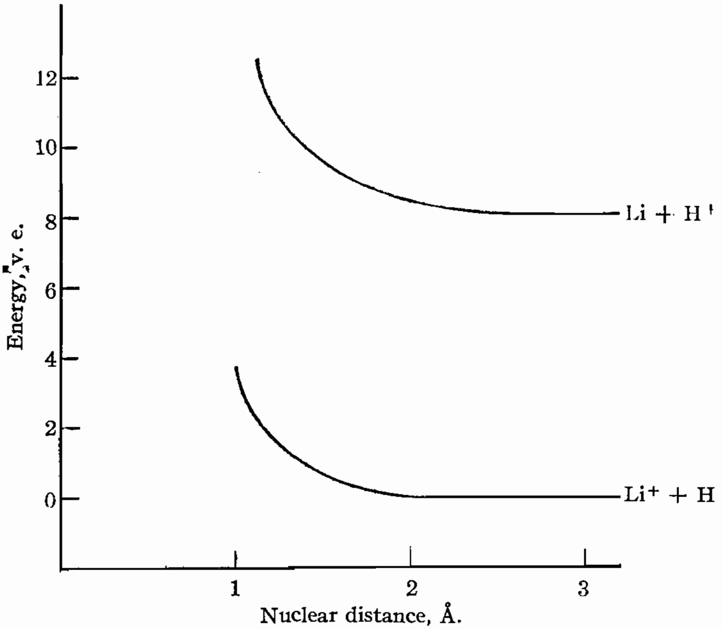


Fig. 1.—Potential curves for $Li^+ + H$ and $Li + H^+$ as functions of the nuclear separation.

Let Ψ_A and Ψ_B be functions which minimize the variational integral $E = \int \Psi^* H \Psi d\tau$ when the nuclei of the two atoms A and B (or two groups of atoms) are far apart, Ψ_A corresponding to the configuration A· B and Ψ_B to the configuration A ·B. Other electrons in the atoms or groups are of course also included in the eigenfunctions. The coördinates of each electron are taken relative to axes fixed by the nucleus to which the electron is attached. Thus if we neglect the K electrons in Li, the functions of interest for the system $Li^+ + H^+ + E^-$ would be a 2s eigenfunction for Li as Ψ_A, corresponding to $Li\cdot + H^+$, and a 1s eigenfunction for H as Ψ_B, corresponding to $Li^+ + \cdot H$. The values of the variational integral for Ψ_A and Ψ_B

$$E_A = \int \Psi_A^* H \Psi_A d\tau$$

and

$$E_B = \int \Psi_B^* H \Psi_B d\tau$$

are then to be calculated as functions of the distance between the two nuclei. If E_A and E_B differ considerably for all values of this distance D, then resonance will not occur; if they approach one another closely resonance is expected. Then a new function formed from Ψ_A and Ψ_B, corresponding to the structure A · B, will give a curve lying lower than either E_A or E_B. Three cases are shown in Figs. 1, 2 and 3. In Fig. 1, E_A and E_B are separated by about 8 v. e. throughout their course, so that resonance is not expected, and E_A and E_B themselves represent two repulsive states of the system.[4] In Fig. 2, E_A and E_B coincide, because of the identity of the two nuclei involved, so that resonance is of importance at all internuclear distances. In Fig. 3 the functions Ψ_A and Ψ_B correspond to $A\cdot^- + B^+$ and $A + \cdot B$, respectively. E_A and E_B are widely separated for large internuclear distances, but because of the Coulomb attraction of the ions $A\cdot^-$ and B^+, E_B rapidly approaches E_A as D decreases. Resonance then occurs only at small internuclear distances. The normal state would have the structure A·B, which goes over to A ·B as the nuclei are separated.

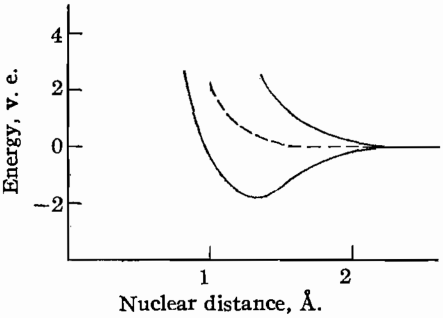
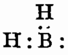
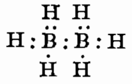
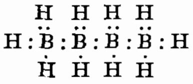


Fig. 2.—Potential curve for $H + H^+$ or $H^+ + H$ (dashed line) and for $H{\cdot}H^+$ (lower full line). The upper full line corresponds to the nuclear-antisymmetric repulsive state.

The boron hydrides offer an interesting problem. With boron trivalent, we should expect compounds such as BF_3, BH_3, etc. Actually the halides all do have the formula BX_3, and show no tendency to associate, while the simplest hydride, B_2H_6, has not begun to dissociate into $2BH_3$ at a temperature at which it begins to lose hydrogen. If BH_3 were given an electronic formula with an electron-pair bond between boron and each hydrogen,  $\overset{\mathrm{H}}{\mathrm{H}:\ddot{\mathrm{B}}:\mathrm{H}}$ the only electrons left to form a bond between the two boron atoms in B_2H_6 would be the K electrons, which are so tightly bound that there is no possibility that they take part in bond formation. Sidgwick suggested[5] that there are one-electron bonds in B_2H_6 and the higher hydrides, B_4H_{10}, etc. with the formulas

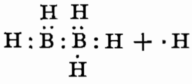


$$\begin{array}{c}\mathrm{H}\ \ \mathrm{H}\\ \mathrm{H}:\ddot{\mathrm{B}}:\ddot{\mathrm{B}}:\mathrm{H}\\ \dot{\mathrm{H}}\ \ \dot{\mathrm{H}}\end{array}$$



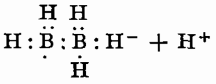
$$\begin{array}{c}\mathrm{H}\ \ \mathrm{H}\ \ \mathrm{H}\ \ \mathrm{H}\\ \mathrm{H}:\ddot{\mathrm{B}}:\ddot{\mathrm{B}}:\ddot{\mathrm{B}}:\ddot{\mathrm{B}}:\mathrm{H}\\ \dot{\mathrm{H}}\ \ \dot{\mathrm{H}}\ \ \dot{\mathrm{H}}\ \ \dot{\mathrm{H}}\end{array}$$

pointing out that these structures agree with the unusual properties of the compounds, which are decomposed by water, give off hydrogen easily, and are immensely powerful reducing agents. In view of the quantum mechanical discussion of the one-electron bond, this suggestion is to be accepted. We write as the two structures to be discussed for B_2H_6



$$\begin{array}{c}\mathrm{H}\ \ \mathrm{H}\\ \mathrm{H}:\ddot{\mathrm{B}}:\ddot{\mathrm{B}}:\mathrm{H} + \cdot\mathrm{H}\\ \qquad\dot{\mathrm{H}}\end{array}$$

and



$$\begin{array}{c}\mathrm{H}\ \ \mathrm{H}\\ \mathrm{H}:\ddot{\mathrm{B}}:\ddot{\mathrm{B}}:\mathrm{H}^- + \mathrm{H}^+\\ \cdot\ \ \dot{\mathrm{H}}\end{array}$$

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[4] The effect of polarization has been neglected. This is usually permissible, since polarization energies rarely amount to more than one or two volt-electrons.

[5] N. V. Sidgwick, "Electronic Theory of Valency," London, 1929, p. 103.

The first of these consists of a B_2H_5 group and an H atom, the second of a $B_2H_5^-$ ion and a proton. If the values of *E* for these two structures differ by only one or two volt-electrons for small internuclear distances, our criterion for the formation of a one-electron bond is satisfied. The energy of formation of $B_2H_5 + H$ from $B_2H_5 + E^- + H^+$ is 13.53 v. e., and the interaction energy of B_2H_5 and H is small. The electron affinity of B_2H_5 may be estimated as 3 v. e. and the Coulomb attraction of $B_2H_5^-$ and H^+ may well contribute 10 or 11 v. e. to the energy of the second configuration, as shown in Fig. 3, so that it is not at all improbable that the two curves approach each other in the region of interest. We accordingly conclude, in default of another structure, that the one-electron bond is to be accepted for the boron hydrides, whose existence provides the strongest evidence that the condition for the formation of this bond is satisfied.

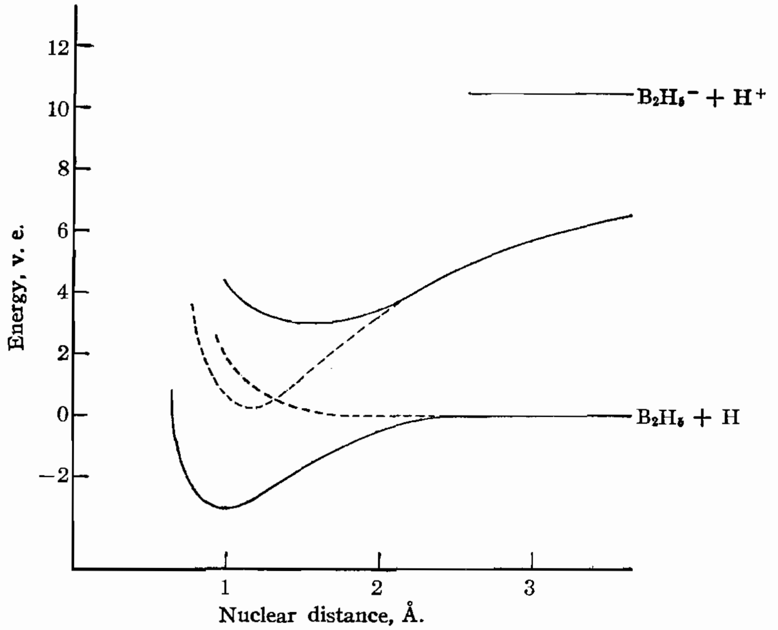

Fig. 3.—Potential curves for B_2H_6. The two dashed lines are potential curves for the structures $B_2H_5 + H$ and $B_2H_5^- + H^+$, the lower full line that for the normal B_2H_6 molecule and the upper one that for an excited state of the molecule.

The electronic formulas written above are not to be interpreted as indicating that two of the six hydrogen atoms in B_2H_6 are singled out for the one-electron bonds. Instead the various configurations with different pairs of hydrogen atoms attached in this way are all included in the final structure, since they correspond to the same energy, and this additional degeneracy provides further resonance energy, increasing the stability of the molecule.

Sidgwick decided from consideration of the compounds containing them that one-electron bonds are stable only when one of the atoms so linked is hydrogen. From the foregoing theoretical considerations this is to be rejected. It would be surprising if Li_2^+, Na_2^+, etc., were not stable, with dissociation energies about two-thirds as great as those of Li_2, Na_2, etc., and it is possible that other compounds involving one-electron bonds between two unlike atoms will be discovered.[6]

The Three-electron Bond.—The approximate solution of the wave equation for a system composed of a pair of electrons attached to one nucleus and a single electron attached to another nucleus has shown that the resonance forces corresponding to interchange of the three electrons are in the main repulsive. Thus normal He and H have no tendency whatever to molecule formation.[7] But if the two nuclei are identical or nearly so, an additional degeneracy is introduced, for the two configurations A: ·B and A· :B, in one of which atom A contains an electron pair and B an unpaired electron, and in the other A contains an unpaired electron and B an electron pair, then have nearly the same energy. The interactions of the two atoms will then cause the eigenfunction for the normal state of the system to be the stable nuclear-symmetric combination of the eigenfunctions corresponding to these two configurations; and the accompanying resonance energy will lead to the formation of a stable molecule containing a three-electron bond.

A three-electron bond, involving one eigenfunction for each of two atoms and three electrons, can be formed in case the two configurations A: ·B *and* A· :B *correspond to essentially the same energy.* As in the case of the one-electron bond, "essentially the same energy" means that the energies of the two unperturbed configurations differ by an amount less than the possible resonance energy.

Another way of looking at the problem is to neglect the mutual repulsion of the electrons. Then the eigenfunction for one electron in the field of two essentially identical nuclei is either the nuclear-symmetric one, which gives rise to the stable one-electron bond, or the nuclear-antisymmetric one, which corresponds to a repulsive potential function. Two electrons with opposed spins can be introduced into the nuclear-symmetric eigenfunction, producing an electron-pair bond with about double the energy of a one-electron bond (neglecting the mutual repulsion of the electrons). This eigenfunction is then completely occupied, according to Pauli's principle, and a third electron must be introduced into the nuclear-antisymmetric eigenfunction, whose repulsive potential neutralizes the attraction of one of the nuclear-symmetric electrons, producing a three-electron

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[6] The lavish use made of one-electron bonds by some English authors is without justification.

[7] G. Gentile, *Z. Physik*, **63**, 795 (1930).

bond with about the same energy as a one-electron bond. With four electrons, two are necessarily nuclear-symmetric and two nuclear-antisymmetric, so that there is no tendency to form a strong bond.

The Helium Molecule and Molecule-ion.—The simplest example of a molecule containing a three-electron bond is the helium molecule-ion, in which a 1s eigenfunction for each of two identical atoms is involved. The two unperturbed states of equal energy are $\mathrm{He}:\cdot\mathrm{He}^+$ and $\mathrm{He}\cdot^+:\mathrm{He}$. The formation of this molecule might be represented by the equation

$$\mathrm{He}\ 1s^2\ {}^1S + \mathrm{He}^+\ 1s\ {}^2S \longrightarrow \mathrm{He}_2^+(1s + 1s)^3\ {}^2\Sigma$$

Three dots in a horizontal line placed between the two atomic symbols may be used to designate a three-electron bond: $\mathrm{He}\cdots\mathrm{He}^+$.

Evidence has been advanced[8] that the neutral helium molecule which gives rise to the helium bands is formed from one normal and one excited helium atom. Excitation of one atom leaves an unpaired 1s electron which can then interact with the pair of 1s electrons of the other atom to form a three-electron bond. The outer electron will not contribute very much to the bond forces, and will occupy any one of a large number of approximately hydrogen-like states, giving rise to a roughly hydrogen-like spectrum. The small influence of the outer electron is shown by the variation of the equilibrium internuclear distance within only the narrow limits 1.05–1.13 Å. for all of the more than 25 known states of the helium molecule.

Oxides of Nitrogen.—Nitric oxide and nitrogen dioxide are very unusual substances in that they are stable odd molecules with no steric excuse such as triphenylmethyl has. Thus if we give NO the double-bonded structure $:\dot{\mathrm{N}}::\ddot{\mathrm{O}}:$, we would expect two such molecules to combine to N_2O_2 by pairing their unshared electrons with an energy of reaction of about 3 v. e. But the substance does not show this behavior. G. N. Lewis wrote[9] of nitric oxide, "Of all the substances which have odd molecules it exhibits the least degree of unsaturation. It is colorless, and at ordinary temperatures does not associate into double molecules, although this process seems to occur at low temperatures. By some method which is not yet understood, the odd electron is obviously much more firmly held in the molecule, and the molecule itself is more nearly saturated, than in the case of any other odd molecule."

I believe that the explanation of these facts is provided by the three-

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[8] W. Weizel, *Z. Physik*, **59**, 320 (1929). Weizel and F. Hund [*ibid.*, **63**, 719 (1930)] have discussed the possible electronic states of the helium molecule. Neither one, however, explains why He $1s^2$ + He^+ 1s form a stable molecule-ion, nor gives the necessary condition for the formation of a three-electron bond. In earlier papers they assumed that both atoms had to be excited in order to form a stable molecule [W. Weizel, *ibid.*, **51**, 328 (1928); F. Hund, *ibid.*, **51**, 759 (1928)].

[9] G. N. Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., Inc., New York, **1923**, p. 128.

electron bond. Nitrogen and oxygen have nearly the same effective nuclear charges, so that we might expect the two states $:\dot{N}::\ddot{O}:$ and $:\ddot{N}::\dot{O}:$ to have nearly the same energy, in which case resonance between them would lead to a more stable combined state involving a double bond and a three-electron bond $:N\overset{\cdot\cdot\cdot}{::}O:$. This, the normal state of NO, would lie about 1.5 v. e. below the energy level expected for $:\dot{N}::\ddot{O}:$, and so would not tend to polymerize.

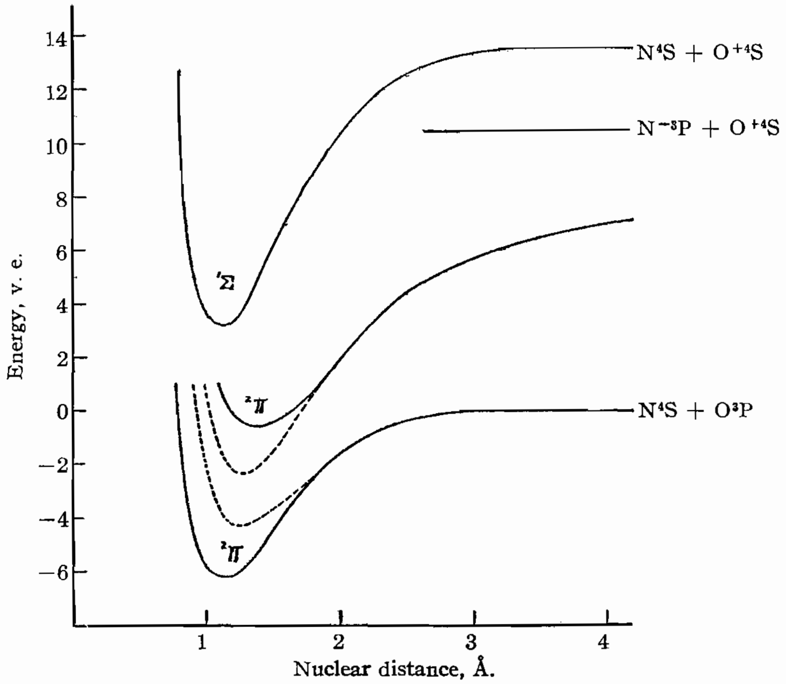

Fig. 4.—Potential curves for nitric oxide. The two dashed lines are potential curves for the structures $:\dot{N}::\ddot{O}:$ and $:\ddot{N}::\dot{O}:$, the lowest full line that for the normal molecule $:N\overset{\cdot\cdot\cdot}{::}O:$, the next for the excited $^2\Pi$ state, and the uppermost that for the normal ion $:N:::O:^+$.

This argument may be repeated in greater detail. Each atom in the molecule contains four L eigenfunctions, σ_b, $\pi+$, $\pi-$, and σ_0, of which the last is not important for bond formation. A normal nitrogen and a normal oxygen atom can combine to form a double-bonded Π^2 molecule.

$$N\ 2s^2 2p2p2p\ {}^4S + O\ 2s^2 2p^2 2p2p\ {}^3P \longrightarrow NO\ (2\sigma_0{}^2 2\pi)(2\sigma_0{}^2 2\pi^2)\{2\sigma_b 2\pi + 2\sigma_b 2\pi\}\,{}^2\Pi$$

or

$$:\underset{\cdot}{\dot{N}}\cdot + \cdot\underset{\cdot}{\ddot{O}}: \longrightarrow :\dot{N}::\ddot{O}:$$

An assumed potential function for this state is drawn in Fig. 4. The dissociation energy is taken to be about 4.5 v. e., rather than the usual value of about 6 v. e. for double bonds with carbon, for the reason that the small bond energy is not enough to change the *s–p* quantization with the formation of more suitable bond eigenfunctions, the bond instead being formed by *p*-eigenfunctions for each atom. A similar double-bonded ${}^2\Pi$ state can also be formed from nitrogen and oxygen ions

$$N^{-}\ 2s^2 2p^2 2p 2p\ {}^3P + \mathrm{O}^{+}\ 2s^2 2p 2p 2p\ {}^4S \longrightarrow \mathrm{NO}\ (2\sigma_0{}^2 2\pi^2)(2\sigma_0{}^2 2\pi)\{2\sigma_b 2\pi + 2\sigma_b 2\pi\}\,{}^2\Pi$$

$$:\underset{\cdot}{\ddot{\mathrm{N}}}\cdot^{-} + \cdot\underset{\cdot}{\dot{\mathrm{O}}}:^{+} \ldots :\ddot{\mathrm{N}}::\dot{\mathrm{O}}:$$

A potential function for this state is also shown in Fig. 4. In drawing this the electron affinity of nitrogen was taken to be 3 v. e., and a Morse curve for small values of *r* was combined smoothly with a Coulomb curve for large values in such a way that the Coulomb interaction of the two ions contributed 8.5 v. e. to the energy of formation of the molecule. (I have found this rather arbitrary procedure satisfactory for ionic states of other molecules.) It is seen that these two ${}^2\Pi$ states approach to within 2 v. e. of one another, so that resonance is to be expected, on account of the rather large overlapping of the 2π eigenfunctions of the two atoms. Assuming the resonance energy to be of the order of magnitude of 2–3 v. e., the normal state $:\mathrm{N}\overset{\cdot\cdot\cdot}{::}\mathrm{O}:$, obtained by combining these two ${}^2\Pi$ states, has the potential function shown. The eigenfunction orthogonal to that of the normal state, also a combination of the two ${}^2\Pi$ states, leads to a potential function lying above the upper original one; it is the excited ${}^2\Pi$ state of NO, 5.6 v. e. above the normal state, and with the large equilibrium internuclear distance of 1.42 Å.

The potential function for normal NO^{+}, with a structure like that of the nitrogen molecule

$$\mathrm{N}\ 2s^2 2p 2p 2p\ {}^4S + \mathrm{O}^{+}\ 2s^2 2p 2p 2p\ {}^4S \longrightarrow \mathrm{NO}^{+}(2\sigma_0{}^2)(2\sigma_0{}^2)\{2\sigma_b 2\pi 2\pi + 2\sigma_b 2\pi 2\pi\}\,{}^1\Sigma$$

$$:\underset{\cdot}{\dot{\mathrm{N}}}\cdot + \cdot\underset{\cdot}{\dot{\mathrm{O}}}:^{+} \longrightarrow :\mathrm{N}:::\mathrm{O}:^{+}$$

is also shown in Fig. 4. The unusually large dissociation energy for a triple bond, 10.3 v. e., is to be attributed to the effect of polarization of the nitrogen atom by the oxygen ion.

There are two electronic configurations which might be written[10] for NO_2

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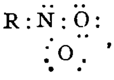
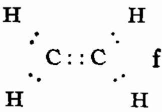
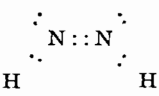
[10] This structure rather than a ring structure is supported by two pieces of evidence relative to nitro compounds and the nitrite ion. It was kindly pointed out to me by Dr. H. A. Stuart of Koenigsberg that *p*-dinitrobenzene has no electric moment, in contrast to *p*-diaminobenzene. The moment of the latter compound does not vanish because the three bonds formed by the amino nitrogen are directed toward tetrahedron corners, causing the moment of the amino group to be non-collinear with the nitrogen–carbon bond; in consequence the two amino moment vectors are not opposed. (The observed moment is the root mean square of the instantaneous resultant moment, which varies as the amino groups rotate about the single bonds, vanishing only when the two moment vectors are opposed.) With a ring structure,  $\begin{matrix}\mathrm{R}:\ddot{\mathrm{N}}:\ddot{\mathrm{O}}: \\ \dot{}\,\mathrm{O}\,\ddot{} \end{matrix}$, the nitro group would

$:\underset{\cdot\cdot}{\ddot{O}}:\dot{N}::\ddot{O}:$ and $:\underset{\cdot\cdot}{\dot{O}}:\ddot{N}::\ddot{O}:$. As in the case of NO, these should have nearly the same energy, and so should interact to give a structure with a three-electron bond, $:\underset{\cdot\cdot}{O}\overset{\cdot\cdot\cdot}{:}N::\ddot{O}:$ (The oxygen atoms are not non-equivalent, for the double bond changes places regularly with the single and three-electron bond.) This stabilizes the odd electron, as in NO, and in consequence NO_2 shows only a small tendency to polymerize to N_2O_4 or to combine with NO to N_2O_3.

The Oxygen Molecule.—There are two reasonable alternative structures for the normal oxygen molecule, the double-bonded $^1\Sigma$ structure $:\ddot{O}::\ddot{O}:$ and the $^3\Sigma$ structure $:\underset{\cdot\cdot\cdot}{\overset{\cdot\cdot\cdot}{O\,:\,O}}:$ involving one electron-pair bond and two three-electron bonds. Both are formed from normal atoms. It is difficult to decide from *a priori* arguments which is the more stable. With *s–p* quantization retained, the double bond, formed with *p*-eigenfunctions, is expected to be weaker than a carbon–carbon double bond, and to have a bond energy of 4–4.5 v. e.; but no sound estimate of the dissociation energy for the second structure can be made. It is actually found that the normal state is a $^3\Sigma$ state, with a $^1\Sigma$ state lying 1.64 v. e. higher. Hence the normal oxygen molecule contains one electron-pair bond and two three-electron bonds. Despite the triplet state (two unpaired electrons), the molecule is not highly unsaturated, because of the stabilizing influence of the three-electron bonds; on the other hand, no electronic activation of the molecule is necessary before polymerization or other chemical reaction.

Ethylene must have the double-bonded $^1\Sigma$ structure  $\begin{matrix} H & & H \\ & C::C & \\ H & & H \end{matrix}$ for there are not enough unshared electrons available for the O_2-like $^3\Sigma$ structure. It is known to be diamagnetic.

N_2H_2 should have two low-lying states,



$\begin{matrix} & N::N & \\ H & & H \end{matrix}$ $^1\Sigma$ and $H:N\underset{\cdot\cdot\cdot}{\overset{\cdot\cdot\cdot}{:}}N:H$ $^3\Sigma$

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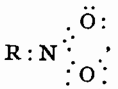
behave similarly, in disagreement with experiment. But with the structure  $R:N\begin{matrix}\ddot{O}: \\ \\ \vdots O \vdots\end{matrix}$ the atoms are coplanar, and the moment vector and the R–N bond are collinear, causing the moments of two para nitro groups to cancel each other.

The structure $:\underset{\cdot\cdot}{\ddot{O}}:\ddot{N}::\ddot{O}:^-$ for the nitrate ion (with the double and single bonds changing places) leads to an angle of 125°16′ between the two N–O bond directions, which might be increased somewhat through repulsion of the two oxygen atoms. This is supported by the value 130° found recently through the x-ray investigation of the crystal structure of sodium nitrite. (G. E. Ziegler, paper given at the meeting of the American Physical Society, Washington, D. C., May 1, 1931.)

The fact that aromatic azo compounds are all diamagnetic shows that their normal state is the $^1\Sigma$ state. The difference between O_2 and RN_2R is probably connected with the greater bond energy of the latter, and the resultant changing of *s–p* quantization for the nitrogen atoms.

The Compounds of Nitric Oxide.—It might be expected that combination of NO with an alkyl radical would result in a double-bonded $^1\Sigma$ molecule, containing no unpaired electrons.

$$\mathrm{R}\,.\;+\;:\mathrm{N}\overset{\cdot\cdot\cdot}{::}\mathrm{O}:\;=\;\mathrm{R}:\ddot{\mathrm{N}}::\ddot{\mathrm{O}}:$$

This structure, however, does not account for the observed properties of the nitroso compounds, as mentioned by Lewis, from whom we continue to quote. "Professor Branch has pointed out to me that this behavior of nitric oxide is very closely related to the anomalous properties of the nitroso compounds. When NO combines with another free radical (odd molecule) such as an alkyl group, we should expect this union of two odd molecules to produce a fully saturated compound. But this is not the case. Not only does NO in the free state behave nearly like a saturated substance, but when combined with an odd molecule like methyl it does not appear to conjugate with the odd electron of the latter. So the resulting compound, although possessing an even number of electrons, has the properties of odd molecules. The nitroso compounds in general are highly colored and they almost invariably tend to form double molecules, as though each single molecule had an odd electron." In a discussion of the unusual magnetic behavior of complex ions containing nitric oxide, Professor Lewis suggested to me that a $^3\Sigma$ structure as in the O_2 molecule might be stable rather than the $^1\Sigma$ double-bonded structure. This is evidently the explanation of the properties of organic nitroso compounds; the similarity of the N and O atoms permits the formation of an electron-pair bond and two three-electron bonds, giving the O_2-like $^3\Sigma$ structure.

$$\mathrm{R}\,.\;+\;:\mathrm{N}\overset{\cdot\cdot\cdot}{::}\mathrm{O}:\;=\;\mathrm{R}:\mathrm{N}\underset{\cdot\cdot\cdot}{\overset{\cdot\cdot\cdot}{:}}\mathrm{O}:$$

Two such $^3\Sigma$ molecules could then combine without preliminary electronic excitation, perhaps to form the compound

$$\begin{array}{l} \mathrm{R}:\ddot{\mathrm{N}}:\ddot{\mathrm{O}}: \\ \quad\;\, :\ddot{\underset{\cdot\cdot}{\mathrm{O}}}:\ddot{\underset{\cdot\cdot}{\mathrm{N}}}:\mathrm{R} \end{array}$$

or (as suggested to me by Professor T. D. Stewart of the University of California on the basis of chemical evidence) a similar compound in which nitrogen atoms are bonded together.

Compounds of several different types might be formed by introduction of nitric oxide into complex ions. If the metal atom provides one of the electrons of the electron-pair bond, NO should assume the O_2-like $^3\Sigma$ structure. If both bond electrons come originally from NO (which then behaves like NH_3, CO, etc. in complexes), a $^2\Pi$ structure as in NO itself would be retained, except that the interaction with the other atoms in the complex would probably destroy the orbital moment, so that this structure would more correctly then be given the symbol $^2\Sigma$. A third possibility is that the NO molecule not only contributes both bond electrons but also lose an additional electron to the complex, and so acquire a triple-bonded structure like that of the nitrogen molecule.

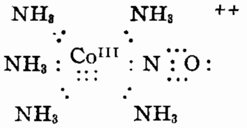
$$\mathrm{M} + :\overset{\cdots}{\mathrm{N}::\mathrm{O}}: = \cdot\mathrm{M}:\mathrm{N}:::\mathrm{O}:$$

Further variety is also possible through attachment of NO by the oxygen atom rather than the nitrogen atom.

In the preceding paper[1] it was mentioned that the known magnetic moments of nitroso complexes

$Na_2[Fe(CN)_5NO] \cdot 2H_2O$	$\mu = 0.00$
$[Ru(NH_3)_4 \cdot NO \cdot H_2O]Cl_3$	0.00
$[Ru(NH_3)_4 \cdot NO \cdot Cl]Br_2$	0.00
$[Co(NH_3)_5NO]Cl_2$	2.81

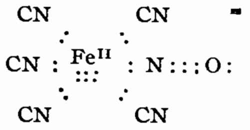
offered a puzzling problem, which has now been solved. Let us discuss the cobalt complex first. Here there are six groups attached to the cobalt atom by electron-pair bonds, which make use of the six d^2sp^3 octahedral eigenfunctions of cobalt, leaving three $3d$ eigenfunctions available for additional unshared electrons. Now we expect either cobaltous or cobaltic cobalt with 7 or 6 additional electrons, respectively. There is room for only six $3d$ electrons, however; the seventh electron in a cobaltous complex would necessarily occupy a level such as $4d$ lying several volt-electrons higher, and would make the compound unstable. Accordingly this is a cobaltic compound, the cobalt atom having given up one electron to NO, which then assumes the O_2-like $^3\Sigma$ structure.



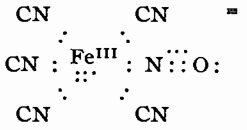
$$\begin{array}{ccccc} NH_3 & & NH_3 & & ^{++} \\ & \cdot\!\cdot & \cdot\!\cdot & & \\ NH_3 : & \underset{:::}{Co^{III}} & : N & \overset{\cdots}{\underset{\cdots}{:}} & O : \\ & \cdot\!\cdot & \cdot\!\cdot & & \\ NH_3 & & NH_3 & & \end{array}$$

(Here NO plays a role similar to that of Cl or CN in complexes, and may appropriately be called electronegative.) This $^3\Sigma$ complex should have a magnetic moment of 2.83 Bohr magnetons, a value in excellent agreement with the observed 2.81.

A similar structure for the iron compound would involve quadrivalent iron, which is very improbable, either bivalent or trivalent iron being expected. If NO loses an electron to iron, assuming the triple-bonded $^1\Sigma$ structure, the resulting bivalent iron atom, with six d^2sp^3 bonds and six unshared $3d$ electrons, will also be in a $^1\Sigma$ state, making the compound as a whole diamagnetic.



Another conceivable $^1\Sigma$ state for the complex results from pairing the odd electron of trivalent iron with that of neutral NO.

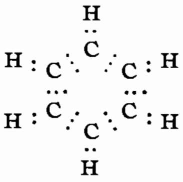


This is probably also involved to some extent in the normal state of this complex, which can then not be said to contain either bivalent or trivalent iron alone.

The ruthenium compounds are entirely analogous to the iron compound.

A profitable discussion of more of the numerous complexes containing NO can be given only after further experimental data, especially relative to magnetic moments, have been collected.

It may be mentioned that the three-electron bond developed above is *not* present in the benzene molecule, for which certain investigators have suggested the structure

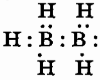


We have seen that a three-electron bond is less stable than an electron-pair bond, so that this structure would provide a very unstable rather than a very stable benzene ring.

I am grateful to Professor G. N. Lewis for his valuable suggestion relative to the structure of the nitroso compounds and for his stimulating interest in the work as a whole.

Summary

It is shown that a stable shared-electron bond involving one eigenfunction for each of two atoms can be formed under certain circumstances with either one, two, or three electrons. An electron-pair bond can be formed by two arbitrary atoms. A one-electron bond and a three-electron bond, however, can be formed only when a certain criterion involving the nature of the atoms concerned is satisfied. Of these bonds the electron-pair bond is the most stable, with a dissociation energy of 2–4 v. e. The one-electron bond and the three-electron bond have a dissociation energy

roughly half as great, about 1–3 v. e. The hydrogen molecule-ion, $\mathrm{H{\cdot}H^+}$, triatomic hydrogen ion, $\mathrm{H{\cdot}H{\cdot}H^+}$, boron hydrides  $\mathrm{H}:\overset{\mathrm{H}}{\underset{\dot{\mathrm{H}}}{\ddot{\mathrm{B}}}}:\overset{\mathrm{H}}{\underset{\dot{\mathrm{H}}}{\ddot{\mathrm{B}}}}:\mathrm{H}$, etc., lithium molecule-ion, $\mathrm{Li{\cdot}Li^+}$, etc., contain one-electron bonds. The helium molecule and molecule-ion, $\mathrm{He}\cdot\dot{:}\cdot\mathrm{He}$ and $\mathrm{He}\cdot\dot{:}\cdot\mathrm{He^+}$, nitric oxide, $:\mathrm{N}\overset{\cdot\cdot\cdot}{::}\mathrm{O}:$, nitrogen dioxide, $:\underset{\cdot\cdot}{\mathrm{O}}\overset{\cdot\cdot\cdot}{:}\mathrm{N}::\mathrm{O}:$, and oxygen molecule, $:\mathrm{O}\overset{\cdot\cdot\cdot}{\underset{\cdot\cdot\cdot}{:}}\mathrm{O}:$, contain three-electron bonds. A discussion of nitroso compounds, in particular dealing with their magnetic moments, is also given.

Pasadena, California

APRIL, 1933 JOURNAL OF CHEMICAL PHYSICS VOLUME 1

The Calculation of Matrix Elements for Lewis Electronic Structures of Molecules

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(Received February 14, 1933)

Starting from the discovery by Rumer that the eigenfunctions corresponding to different distributions of valence bonds in a molecule can be represented by plane diagrams which provide information regarding their mutual linear independence, a very simple graphical method is developed for calculating the coefficients of the integrals occurring in the matrix elements involved in Slater's treatment of the electronic structure of molecules.

In his valuable paper[1] on *Molecular Energy Levels and Valence Bonds* Slater developed a method for formulating approximate eigenfunctions for molecules and for constructing the corresponding secular equation. This method has been successfully applied by a number of investigators in the discussion of general valence theory and of the structure of individual simple molecules, its application to more complex molecules having been retarded in part by the laborious nature of the calculation of the coefficients of the various exchange integrals in the matrix elements. It is shown in the following paragraphs that these coefficients can be easily calculated by a simple procedure involving the use of plane diagrams similar to those introduced by Rumer[2] in his recent discussion of the linear independence of electronic structures.

Singlet States with Spin Degeneracy Only

For a system involving N electrons, Slater constructed the function

$$\Psi=\frac{1}{(N!)^{\frac{1}{2}}}\sum\nolimits_{P''}(-1)^{P''}P''A(1)B(2)\cdots E(N),$$

which is completely antisymmetric in the electrons (satisfying Pauli's principle). Here A, $B\cdots E$ are one-electron spin-orbit functions, and the symbol P'' represents the $N!$ permutations of the functions $A\cdots E$ among the electrons, the coefficient being -1 for odd, $+1$ for even permutations. For two such functions Ψ and Ψ' the matrix element corresponding to a dynamical quantity F is

$$(1/N!)\int\{\sum\nolimits_{P''}(-1)^{P''}P''A(1)\cdots E(N)\}F\{\sum\nolimits_{P'}(-1)^{P'}P'A'(1)\cdots E'(N)\}dv,$$

which reduces to

$$\int A(1)\cdots E(N)F\{\sum\nolimits_{P}(-1)^{P}PA'(1)\cdots E'(N)\}dv,$$

with $P'=P''P$, in case that F is completely symmetric in the electrons. This may be written as

$$\sum\nolimits_{P}(-1)^{P}(AB\cdots E/F/PA'B'\cdots E'),$$

in which each parenthesis $(A\cdots E/F/PA'\cdots E')$ represents one integral in the above sum. If F does not involve spin interactions, the integral $(A\cdots E/F/A'\cdots E')$ vanishes unless the spin of A is the same as that of A', B as B', and so on, in which case it reduces to $(ab\cdots e/F/a'b'\cdots e')$, with $a\cdots e'$ the orbital parts of $A\cdots E'$.

For four electrons, for example, with only spin degeneracy (the number of occupied orbits equalling the number of electrons), Slater gave the function $\frac{1}{2}(\Psi_{I}-\Psi_{II}-\Psi_{III}+\Psi_{IV})$ as representing the structure in which orbits a and b are bonded together, and also c and d. Here $\Psi_{I}\cdots\Psi_{IV}$

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[1] J. C. Slater, Phys. Rev. **38**, 1109 (1931).

[2] G. Rumer, Nachr. d. Ges. d. Wiss. zu Göttingen, M. P. Klasse, p. 337 (1932).

are functions of the type given above with the following distributions of spins among the orbits:

	a	b	c	d
I	$-$	$+$	$-$	$+$
II	$+$	$-$	$-$	$+$
III	$-$	$+$	$+$	$-$
IV	$+$	$-$	$+$	$-$

The energy matrix element for this function is

$$(abcd/H/abcd)+(abcd/H/bacd)+(abcd/H/abdc) \\ -\tfrac{1}{2}(abcd/H/cbad)-\tfrac{1}{2}(abcd/H/dbca) \\ -\tfrac{1}{2}(abcd/H/acbd)-\tfrac{1}{2}(abcd/H/adcb)+\text{higher exchange integrals.}$$

With the single exchange integrals negative, as they usually are for orbits on separate atoms, this leads to attraction between a and b and between c and d, and repulsion between other pairs.

Similarly a function can be formulated representing $a-d$ and $b-c$ bonds, and one representing $a-c$ and $b-d$ bonds. These three functions, corresponding to three separate electronic structures of the Lewis type, are, however, not linearly independent; any one can be represented as a combination (sum or difference) of the other two. This linear dependence of structures continues as the number of bonds increases; for n single bonds between $2n$ atoms $(2n)!/2^n n!$ structures can be drawn, of which only $(2n)!/n!(n+1)!$ are independent. In the paper mentioned above, Rumer made the very interesting and important observation that if the orbits are formally arranged in a ring or other concave curve, and straight lines are drawn between orbits bonded together, the structures represented by diagrams in which no lines intersect are independent. This observation forms the starting point for the following treatment.

Let us arrange the orbits in a ring, and then draw arrows between pairs of orbits bonded together, the head of each arrow representing positive spin and the tail negative spin. The wave function for the corresponding structure is then given, except for a normalizing factor $2^{-n/2}$, by the sum of the functions corresponding to this distribution of spins and to those obtained by reversing the arrows, each function having the coefficient $(-1)^R$, in which R is the number of reversals. Thus the $\begin{matrix} a-b \\ c-d \end{matrix}$ structure would be represented by the vector-bond diagram $\rightleftarrows$, corresponding to the function

$$\frac{1}{2}\left\{\begin{pmatrix} -+ \\ +- \end{pmatrix}-\begin{pmatrix} +- \\ +- \end{pmatrix}-\begin{pmatrix} -+ \\ -+ \end{pmatrix}+\begin{pmatrix} +- \\ -+ \end{pmatrix}\right\}.$$

It is verified at once that

$$\times = \downarrow\uparrow - \rightleftarrows,$$

so that an intersecting pair of arrows can be replaced by the difference of two non-intersecting pairs, the pair connecting head with head and tail with tail having the positive sign. By successive applications of this treatment any structure can be resolved into structures involving no intersecting bonds.

Canonical sets of independent structures

Of the various complete sets of independent structures which may be formulated, certain ones may be called "canonical" because of the relative simplicity of the calculation of matrix elements based on them. For a given order of the orbits in a ring, the canonical set of independent structures comprises those with no intersecting bonds; moreover, numbering the orbits in order about the ring, the canonical vector-bond structures for singlet states with spin degeneracy only have arrows drawn from odd to even orbits (the functions for the corresponding distributions of positive and negative spins thus occurring with the positive sign). The eigenfunction for a structure represented by a vector-bond diagram $a\rightarrow b$ $c\rightarrow d$, etc., may be written

$$\frac{1}{2^{n/2}}\sum_R(-1)^R R\left\{\frac{1}{((2n)!)^{\frac{1}{2}}}\sum_P(-1)^P Pa(1)\beta(1)b(2)\alpha(2)c(3)\beta(3)d(4)\alpha(4)\cdots\right\},$$

in which α represents positive spin and β negative spin, P represents the $(2n)!$ permutations of the orbits and their associated spins among the electrons, and R the 2^n operations of interchanging the spin functions α and β for orbits (such as a and b) which are bonded together, that is, of reversing the arrows in the vector-bond diagram. The factor $(-1)^R$ equals $+1$ for an even number of reversals, -1 for an odd number.

The Coulomb coefficient

To find the coefficient of the Coulomb integral for two structures, superimpose their vector-bond patterns to form the superposition pattern (Fig. 1). The Coulomb coefficient is 2^{-n} times the sum $(-1)^R$ for the different patterns in which each orbit serves either as the head or as the tail of two arrows which can be made by reversing the arrows, R being the number of reversals. The superposition pattern consists of "islands," or closed polygons formed by an even number of arrows. For each island there are only two satisfactory orientations of the arrows, so that the Coulomb coefficient may be written as $(-1)^r 2^{-(n-i)}$, in which i is the number of islands and r the number of reversals required for an initial satisfactory orientation.

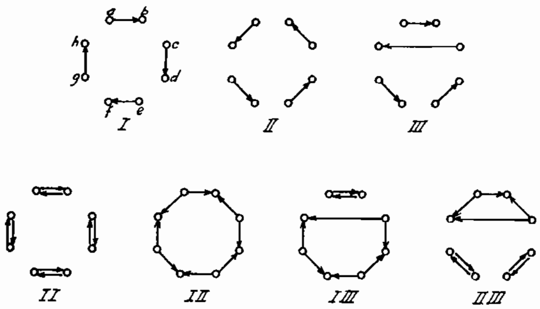

FIG. 1. The vector-bond diagrams for three structures of the canonical set of fourteen for $n=4$, and some of their superposition patterns.

For canonical structures the sign is positive, the Coulomb coefficient being $1/2^{n-i}$. In drawing the superposition pattern for canonical structures the arrows may be replaced by lines.

Coefficients of exchange integrals

Each of the $N!$ permutations may be represented by a permutation diagram, made by drawing an arrow from each orbit in $Pab\cdots e$ to the orbit whose place in $ab\cdots e$ it occupies. Thus if $Pab\cdots e = bd\cdots e$, an arrow is drawn from b to a, from d to b, etc. A closed polygon of arrows is called a cycle of the permutation.[3] A cycle may be called odd if it involves an even number of arrows, otherwise even. The permutation is odd if it contains an odd number of odd cycles; otherwise it is even. The possible permutations are obtained by drawing polygons of arrows in all possible ways such that each orbit is reached by no arrow or by the head of one and the tail of another. The permutation arrows may intersect.

To find the coefficient of a given exchange integral in a matrix element, $(\mathrm{I}/F/P\mathrm{II})$, draw the vector-bond diagram for structure II, change it as indicated by the permutation diagram for P, and form the superposition pattern of I and PII. The coefficient is then given, except for the factor $(-1)^P$, by the above rules for the Coulomb coefficient; that is, it is $(-1)^P(-1)^r 2^{-(n-i)}$.

This procedure may be simplified considerably for single exchange integrals in matrix elements between structures of a canonical set. We first form the superposition pattern of the two structures. If the permutation involves the interchange of orbits in different islands, the number of islands is decreased by one; if the orbits are an odd number of bonds apart in the same island, it is unchanged; if they are an even number apart, it is increased by one. Hence (taking into consideration the factors $(-1)^P$ and $(-1)^r$) it is seen that the coefficient of a single exchange integral for two canonical structures is $2^{-(n-i)}f(p)$, where n is the number of bonds, i is the number of islands in the superposition pattern of the two structures, p the number of bonds in the superposition pattern along the path between the two orbits which are interchanged, and $f(p)$ a factor with the values $-\frac{1}{2}$ for $p=0$, $+1$ for $p=1, 3, 5\cdots$, and -2 for $p=2, 4, 6\cdots$. It is not necessary to use arrows in forming the superposition pattern for canonical structures.

Similar rules may be formulated for more complex permutations.

An example: Six electrons with only spin degeneracy. Placing the six orbits in a ring in the order *abcdef*, the five structures forming a canonical set are those given in Fig. 2. It is seen that

$$\int \mathrm{I} F \mathrm{I} dv = Q + ab + cd + ef - \tfrac{1}{2}ac - \tfrac{1}{2}ad - \tfrac{1}{2}ae - \tfrac{1}{2}af - \tfrac{1}{2}bc - \tfrac{1}{2}bd - \tfrac{1}{2}be - \tfrac{1}{2}bf - \tfrac{1}{2}ce - \tfrac{1}{2}cf - \tfrac{1}{2}de - \tfrac{1}{2}df + \cdots,$$

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[3] The theory of permutation groups is discussed in standard treatises such as W. Burnside, *The Theory of Groups*, Second Edition, Cambridge University Press, 1911.

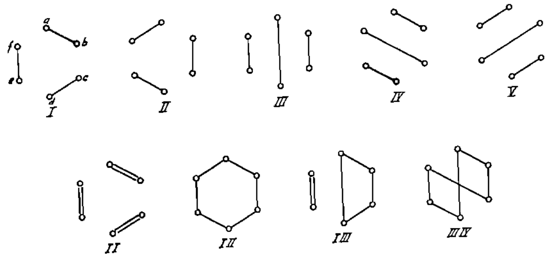

FIG. 2. The five canonical structures for $n=3$, and some of their superposition patterns.

in which Q is the Coulomb integral $(ab\cdots f/F/ab\cdots f)$, ab the single exchange integral $(ab\cdots f/F/ba\cdots f)$, etc. As in this case, it is true in general that in diagonal matrix elements the coefficient of bonding single exchange integrals is $+1$, of nonbonding $-\frac{1}{2}$. From the superposition pattern of I and II we obtain

$$\int \mathrm{I}F\mathrm{II}dv=\tfrac{1}{4}(Q+ab+bc+cd+de+ef+fa+ad+be+cf-2ac-2bd-2ce-2df-2ea-2fb+\cdots),$$

and similar expressions for the other matrix elements can be quickly written.[4] The determination of the coefficients of each of the 720 integrals would be, of course, quite a task, even by this simple method, but any one of them is easily found. Thus from Fig. 3 it is seen that in $\int \mathrm{I}F\mathrm{II}dv$ the coefficient of $(abcdef/F/bcfdae)$ is $-\frac{1}{4}$. The complete matrix for the forty-two independent structures given by ten electrons with only spin degeneracy, retaining only Coulomb and single exchange integrals, can be set up in a few hours.

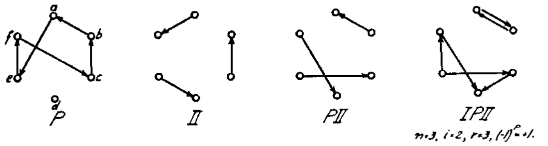

FIG. 3. The permutation diagram for $P\ abcdef=bcfdae$, and the superposition pattern for I PII.

EXTENSION TO MORE GENERAL SYSTEMS

The foregoing treatment can be extended to states of arbitrary multiplicity by the artifice of including in the system additional electrons and phantom orbits. To represent N electrons and N orbits in states with resultant spin S (multiplicity $2S+1$), form a ring of the real and phantom orbits; a canonical set of electronic structures is then obtained by drawing in all possible ways such that no bonds intersect a phantom bond between each of $2S$ phantom orbits and a real orbit and a real bond between each pair of remaining real orbits. Rules regarding reversal of bond arrows (different numbers of arrow heads on phantom orbits correspond to different M_S values) and the calculation of exchange integral coefficients are easily formulated.

A canonical set of structures for a system with more orbits than electrons is obtained by arranging all the orbits (including phantom orbits for $S>0$) in a ring and then drawing non-intersecting bonds to a number determined by the number of electrons and the multiplicity. If two electrons occupy the same orbit, forming an unshared pair, a loop is drawn with its ends at the orbit.

The bond diagrams provide an obvious simple method of determining the allowed spectral terms for equivalent electrons with Russell-Saunders coupling, which may be convenient for the reason that it separates states of different multiplicity at the start.

The methods developed in this paper have been applied in a discussion of the structure of aromatic substances, free radicals, etc., to be published soon.

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[4] A. Sherman and H. Eyring (J. Am. Chem. Soc. **54**, 2661 (1932)) have published matrix elements for this six-electron system, giving the Coulomb and single exchange integrals. Their coefficients do not show the regularities which our treatment leads to, since their five functions do not form a canonical set.

JUNE, 1933 JOURNAL OF CHEMICAL PHYSICS VOLUME 1

The Nature of the Chemical Bond. V. The Quantum-Mechanical Calculation of the Resonance Energy of Benzene and Naphthalene and the Hydrocarbon Free Radicals[1]

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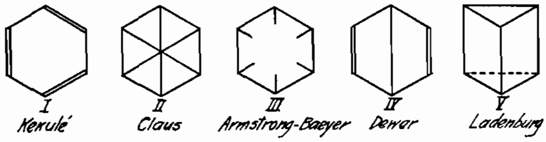
The secular equations corresponding to the five canonical structures for benzene and the forty-two for naphthalene, considered as six and ten-electron systems, respectively, are set up and solved with certain simplifying assumptions, leading to energy values differing by 1.1055α and 2.0153α, respectively, from those corresponding to unexcited (Kekulé-type) structures, α being a single exchange integral involving neighboring carbon atoms. Equating these values to the empirical values of the resonance energy, α is found to be about -1.5 v.e.

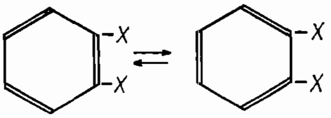
It is pointed out that the dissociation of certain substituted ethanes into free radicals is due not to weakness of the carbon-carbon bond in the ethane but to the stabilization of the free radicals resulting from resonance among the structures in which the unpaired electron is located on the methyl carbon and those in which it is on other atoms (ortho, para, etc., to the methyl carbon). The secular equations for a number of such radicals have been solved, neglecting excited structures. The experimentally determined heat of formation of hexaphenylethane from triphenylmethyl, 0.5 v.e., when equated to the calculated value $C-C+2.2156\alpha$, with $C-C=3.65$ v.e., leads to $\alpha=-1.4$ v.e. The calculated tendencies towards dissociation are in satisfactory agreement with observation, such features as the smaller dissociating power of β-naphthyl than of α-naphthyl and of biphenylene than of diphenyl being accounted for, so that resonance among the structures considered may be accepted as the principal effect causing the stability of the hydrocarbon free radicals.

THE STRUCTURE OF BENZENE AND NAPHTHALENE

A NUMBER of structural formulae have been proposed for benzene, but none of them is free from very serious objections.



The oldest and best known structure is that proposed by Kekulé (I). The objections to it are twofold. First, it suggests that ortho-disubstituted derivatives should exist in two isomeric forms—a phenomenon which has never been observed. Kekulé avoided this difficulty, however, by assuming that the double bonds were in a state of constant oscillation such that any two adjacent carbon atoms were connected part of the time by a single bond and part of the time by a double bond. For example:



Second, the Kekulé structure suggests that benzene should be a highly unsaturated and comparatively unstable compound, in complete contradiction to the observed facts. Since this point has been discussed in considerable detail in various places, we shall not go into it here. The two centric structures (II and III) were proposed to avoid both of the above difficulties. They are indeed successful in eliminating the necessity for the oscillation hypothesis, but they can hardly account for the stability of the molecule. In the Claus structure the diagonal bonds would be very weak, as a result of the large distance between the atoms in the para positions, and the structure would probably represent a molecule less stable even than the Kekulé structure. In the Armstrong-Baeyer structure the meaning of the six lines pointing toward the center is not at all clear. If these

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[1] The fourth paper of this series appeared in the J. Am. Chem. Soc. **54**, 3570 (1932).

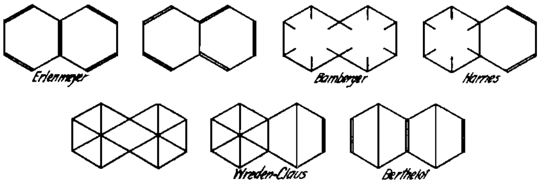
"central bonds" are left undefined, the structure is essentially meaningless; if they are considered to represent free valences, the molecule should be highly unsaturated.

The Dewar structure (IV) has never been seriously considered since it suffers from the same defects, in an accentuated form, as the Kekulé structure. Its advantage over the other structures is largely that it explains the intimate relationship that usually obtains between the para positions in the benzene ring.

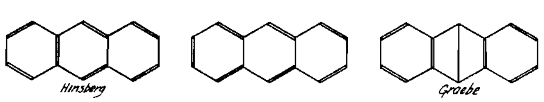
The Ladenburg prism structure (V) can be definitely ruled out, since we know that the benzene ring lies in a plane, or very nearly in a plane. The chemical evidence is also unfavorable in this case.

This by no means exhausts the list of structures proposed for benzene. The remainder, however, such as the structure of Thiele based upon his theory of partial valence and that of Collie based upon a dynamic model, are usually complicated and cannot be represented in any simple valence scheme.

In the case of the aromatic hydrocarbons with condensed ring systems the state of affairs is quite similar. Thus the following structures have been proposed for naphthalene:



for anthracene:



and so on for the other aromatic hydrocarbons. As in the case of benzene, however, the proposed structures are all unsatisfactory, on account both of the non-occurrence of predicted types of isomerism and of the unexpected stability of the molecules.

Apparently here we have a case where the classical ideas of structural organic chemistry are inadequate to account for the observed properties of a considerable group of compounds. With the development of the quantum mechanics and its application to problems of valence and molecular structure, it became evident to workers[2] in this field that the resonance of benzene between the two equivalent Kekulé structures was an essential feature of the structure of this molecule, accounting for the hexagonal symmetry of the ring and for its remarkable stability; and it seemed probable that the quantum mechanical treatment of aromatic molecules would lead to a completely satisfactory explanation of their existence and characteristic properties. E. Hückel[3] has made a valuable start in this direction in a series of papers on the quantum mechanics of benzene. His method of attack, however, is very cumbersome. In this paper we present a treatment of the problem which is rather closely similar to that of Hückel's and which leads to the same result in the case of benzene, but in which the calculations are simplified to such an extent that the method can be extended to the naphthalene molecule without undue labor. Furthermore, with the aid of additional simplifications and approximations we have been able to treat the problem of free radicals and to obtain results in surprisingly good qualitative agreement with experiment. We shall leave the discussion of these latter calculations to the second part of the paper.

We shall set up the problem in essentially the same way as Hückel. We assume that each of the six carbon atoms possesses two K electrons, and four L electrons, one for each of four orbital functions formed by linear combination of the $2s$ and the three $2p$ orbits. Three of these L orbits, each a combination of the $2s$ orbit and the two $2p$ orbits in the plane of the ring, form single bonds to the attached hydrogen atom and the two adjacent carbon atoms. The fourth orbit for each atom remains a pure p-orbit, projecting at right angles to the ring. We neglect the energy of the electrons forming the system of single bonds in the plane and of their interaction with the electrons occupying the pure p-orbits (these energy quantities occurring in the same way for all the structures considered, and hence leading to only a change in the arbitrarily-chosen zero of

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[2] As, for example, J. C. Slater, Phys. Rev. **37**, 489 (1931).

[3] E. Hückel, Zeits. f. Physik **70**, 204; **72**, 310 (1931); **76**, 628 (1932).

energy), and consider only the interaction energy of the latter electrons, which may interact with one another in different ways. That is, we treat benzene simply as a six-electron system with spin degeneracy only, and naphthalene as a ten-electron system with spin degeneracy only.

Considerable justification for this choice of orbital functions and of bond distribution is provided by the fact that each of the single exchange integrals between a pure *p*-orbit and an orbit in the plane of the ring is positive (arising from the e^2/r_{ij} term in the Hamiltonian only), and the chosen distribution of bonds causes these integrals to occur with the negative sign in the expression for the energy of the molecule, while the bonding exchange integrals, which are negative, occur with the positive sign.

In carrying out the calculations we make certain further simplifying assumptions. We neglect all exchange integrals of unity, and all exchange integrals of the energy H except single exchange integrals involving two adjacent atoms. The single exchange integrals involving adjacent atoms, $(abcdef/H/bacdef)$, $(abcdef/H/acbdef)$, etc., are represented by the symbol α. These integrals are seen to be equal in benzene; in naphthalene and other aromatic molecules, in which they are not all required to be equal by the symmetry of the molecule, the reasonable assumption is made that no serious error is introduced by giving them all the same value. The Coulomb integral $(abcdef/H/abcdef)$ is represented by the symbol Q.

Benzene

The benzene molecule can now be treated very simply by the Slater method, with the help of the rules formulated by one of us[4] for finding the matrix elements occurring in the secular equation. The bonds between the six eigenfunctions can be drawn so as to give the independent canonical structures shown in Fig. 1. Any other structures that can be drawn can be represented by eigenfunctions which are linear combinations of the five above. It will be seen that structures A and B are simply the two Kekulé structures, and C, D and E are three different forms of the Dewar structure. The Claus centric structure does not belong to the canonical set, but it can be represented as a linear combination of canonical structures; and the same is true of the Ladenburg structure if it be considered spread out in a plane, as:

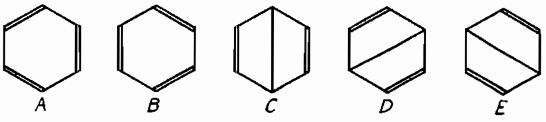
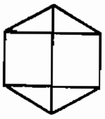


FIG. 1. The five canonical structures contributing to the normal state of the benzene molecule.



(The Claus structure $=A+B-C-D-E$; the Ladenburg structure $=A+B-D-E$.)

As can be easily verified, the secular equation is

$$\begin{vmatrix} (Q-W)+3\alpha/2 & \frac{1}{4}(Q-W)+3\alpha/2 & \frac{1}{2}(Q-W)+3\alpha/2 & \frac{1}{2}(Q-W)+3\alpha/2 & \frac{1}{2}(Q-W)+3\alpha/2 \\ \frac{1}{4}(Q-W)+3\alpha/2 & (Q-W)+3\alpha/2 & \frac{1}{2}(Q-W)+3\alpha/2 & \frac{1}{2}(Q-W)+3\alpha/2 & \frac{1}{2}(Q-W)+3\alpha/2 \\ \frac{1}{2}(Q-W)+3\alpha/2 & \frac{1}{2}(Q-W)+3\alpha/2 & (Q-W) & \frac{1}{4}(Q-W)+3\alpha/2 & \frac{1}{4}(Q-W)+3\alpha/2 \\ \frac{1}{2}(Q-W)+3\alpha/2 & \frac{1}{2}(Q-W)+3\alpha/2 & \frac{1}{4}(Q-W)+3\alpha/2 & (Q-W) & \frac{1}{4}(Q-W)+3\alpha/2 \\ \frac{1}{2}(Q-W)+3\alpha/2 & \frac{1}{2}(Q-W)+3\alpha/2 & \frac{1}{4}(Q-W)+3\alpha/2 & \frac{1}{4}(Q-W)+3\alpha/2 & (Q-W) \end{vmatrix} = 0.$$

This quintic equation is easily reduced to three linear factors and one quadratic factor, the roots being -2α, -2α, 0, $(-(13)^{\frac{1}{2}}-1)\alpha$, and $((13)^{\frac{1}{2}}-1)\alpha$. Since α is negative, the last of these roots, $((13)^{\frac{1}{2}}-1)\alpha=2.6055\alpha$, represents the normal state of the molecule. The eigenfunction corresponding to this is (before normalizing) $\psi=\psi_A+\psi_B+0.4341(\psi_C+\psi_D+\psi_E)$. If we had neglected the resonance phenomenon and calculated the energy for one of the structures A or B, we would have obtained the value $W'=Q+1.5\alpha$. Hence the extra energy of the molecule resulting from resonance among the five independent structures

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[4] L. Pauling, J. Chem. Phys. 1, 280 (1933).

is 1.1055α. It is interesting to see how much of this extra energy is due to resonance between the two Kekulé structures and how much is contributed by the excited structures *C*, *D* and *E*. A simple calculation shows that 0.9α or approximately 80 percent of the resonance energy comes from the Kekulé structures alone and only about 20 percent from the three excited structures.

In the following paper of this series[5] a value of about 1.7 v.e. has been found from thermochemical data for the resonance energy of benzene. Equating the negative of this quantity to 1.1055α, we calculate the value of α to be about -1.5 v.e. This value may not be very reliable, however, since it is based on the assumption that values of bond energies obtained from aliphatic compounds can be applied directly to aromatic compounds.

The results of the calculation for benzene are summarized in Table I. They are identical with those obtained by Hückel.

TABLE I.

	Total energy	Resonance energy	$a:b$
Single Kekulé structure	$Q+1.5\alpha$	0	
Resonance between two Kekulé structures	$Q+2.4\alpha$	0.9α	1 : 0
Resonance among all five structures	$Q+2.6055\alpha$	1.1055α	1 : 0.4341

The ratio $a:b$ is the ratio of the coefficient of structures *A* and *B* to that of the singly-excited structures *C*, *D*, and *E*.

The conclusions we draw regarding the structure of the normal benzene molecule are the following. The principal contributions to the structure are made by the two Kekulé structures, resonance between them stabilizing the molecule to the extent of 0.9α or about 1.35 v.e. over a ring with three double bonds. In addition, however, the excited structures contribute appreciably both to the energy (0.2055α) and to the eigenfunction.[6] In a sense it may be said that all structures based on a plane hexagonal arrangement of the atoms—Kekulé, Dewar, Claus, etc.—play a part, with the Kekulé structures most important. It is the resonance among these structures which imparts to the molecule its peculiar aromatic properties.

Naphthalene

With naphthalene the calculation is very much more involved. The number of canonical structures is here forty-two (Fig. 2), so that the

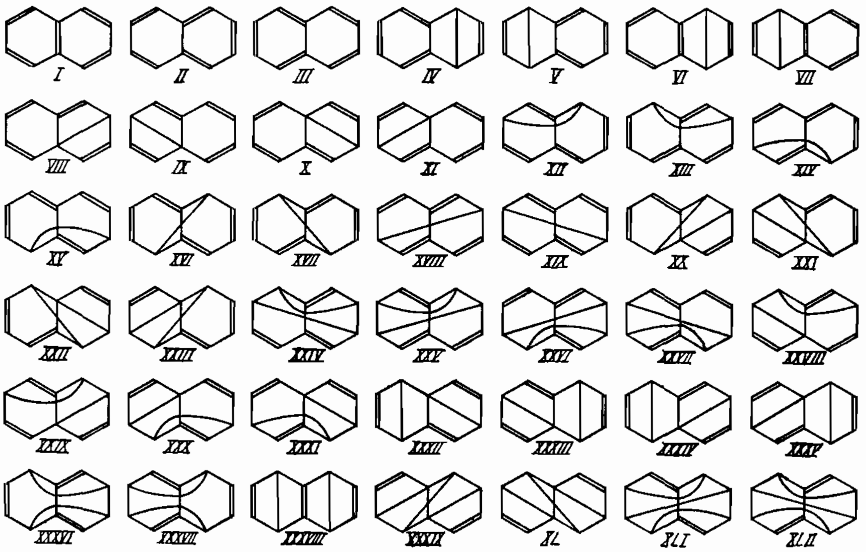

FIG. 2. The forty-two canonical structures contributing to the normal state of the naphthalene molecule.

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[5] L. Pauling and J. Sherman, J. Chem. Phys., July, 1933.

[6] The Claus centric structure, an old-quantum-theory analogue of which was suggested several years ago by one of us (L. Pauling, J. Am. Chem. Soc. **48**, 1132 (1926)), is found to make a less important contribution to the normal state of benzene than do the Kekulé structures.

secular equation is of the forty-second degree. We have evaluated the matrix elements in the secular equation by the graphical method, but do not reproduce them because of their great number. For convenience the structures with the maximum number of bonds between adjacent atoms are called unexcited structures and those with one, two, etc., fewer such bonds first excited, second excited, etc., structures. From considerations of symmetry, we can set a number of coefficients equal in the complete eigenfunction, and thereby reduce the secular equation to the fifteenth degree. To obtain an approximate solution of this we then assume that all of the first excited structures have the same coefficient, and similarly for all of the second and all of the third excited structures. The resultant secular equation, corresponding to the function

$$\psi = a\psi_{\mathrm{I}} + b(\psi_{\mathrm{II}} + \psi_{\mathrm{III}}) + c(\psi_{\mathrm{IV}} + \cdots + \psi_{\mathrm{XIX}}) + d(\psi_{\mathrm{XX}} + \cdots + \psi_{\mathrm{XXXVIII}}) + e(\psi_{\mathrm{XXXIX}} + \cdots + \psi_{\mathrm{XLII}})$$

is

$$\begin{vmatrix}
(Q-W)+2\alpha & (1/2)(Q-W)+13\alpha/4 & (35/8)(Q-W)+163\alpha/8 & (27/8)(Q-W)+165\alpha/8 & (5/8)(Q-W)+31\alpha/8 \\
(1/2)(Q-W)+13\alpha/4 & (17/8)(Q-W)+43\alpha/8 & (19/2)(Q-W)+169\alpha/4 & (21/2)(Q-W)+159\alpha/4 & 2(Q-W)+7\alpha \\
(35/8)(Q-W)+163\alpha/8 & (19/2)(Q-W)+169\alpha/4 & (557/8)(Q-W)+2035\alpha/8 & (525/8)(Q-W)+2169\alpha/8 & (95/8)(Q-W)+397\alpha/8 \\
(27/8)(Q-W)+165\alpha/8 & (21/2)(Q-W)+159\alpha/4 & (525/8)(Q-W)+2169\alpha/8 & (633/8)(Q-W)+1911\alpha/8 & (57/4)(Q-W)+189\alpha/4 \\
(5/8)(Q-W)+31\alpha/8 & 2(Q-W)+7\alpha & (95/8)(Q-W)+397\alpha/8 & (57/4)(Q-W)+189\alpha/4 & (19/4)(Q-W)-7\alpha/4
\end{vmatrix} = 0.$$

To solve this we first neglect entirely the second and third excited structures. We then solve the secular equation, which is now only a cubic, and evaluate the ratio of the coefficients, $a : b : c$. Finally, we assume that this same ratio holds in the complete eigenfunction, thus obtaining another cubic secular equation, the solution of which is an approximate solution of the original secular equation. The results are summarized in Table II.

TABLE II.

	Total energy	Resonance energy	$a : b : c : d : e$
Single unexcited structure	$Q+2\alpha$	0	1 : 0 : 0 : 0 : 0
Resonance among three unexcited structures	$Q+3.3703\alpha$	1.3703α	1 : 0.8757 : 0 : 0 : 0
Resonance among unexcited and singly excited structures	$Q+3.9760\alpha$	1.9760α	1 : 0.8513 : 0.3026 : 0 : 0
Resonance among all structures	$Q+4.01533\alpha$	2.01533α	1 : 0.8513 : 0.3026 : 0.0919 : 0.0077

It will be noticed that the singly excited structures contribute somewhat over 30 percent to the total resonance energy instead of only about 20 percent as in benzene. The doubly and triply excited structures, however, make only a very small contribution.

Pauling and Sherman have found empirically[5] that the ratio of the resonance energy of naphthalene to that of benzene is 1.90, while the present calculation gives the ratio of 1.82. The agreement is really quite satisfactory. It would have been somewhat, but probably not a great deal, better if the secular equation in the naphthalene calculation had been solved rigorously. The discrepancy must be attributed to the crudity of the method of calculation, and partly also to the fact that, as mentioned above, the resonance energy calculated by Pauling and Sherman is not strictly comparable with that found by the present method. The value of α obtained from this calculation is -1.6 v.e., in good agreement with the value of -1.5 v.e. obtained from the benzene calculation.

This treatment could be applied to anthracene and phenanthrene, with 429 linearly independent structures, and to still larger condensed systems, though not without considerable labor. It is probable that the empirical rule[5] of approximate proportionality between the resonance energy and the number of benzene rings in the molecule would be substantiated.

The Structure and Stability of Hydrocarbon Free Radicals

The dissociation of a hexaarylethane into free radicals,

$$R_3C-CR_3 \rightarrow 2R_3C-,$$

first observed by Gomberg about thirty years ago, can be considered formally to take place in two steps. First, the bond connecting the two halves of the original molecule breaks; and second, the free radicals formed thereupon stabilize themselves to a certain extent by means of a change in structure. Most theories which have been proposed to explain the existence and stability of free radicals have more or less tacitly assumed that the first of these steps is of primary importance and that the influence of the second upon the dissociation is negligible in comparison. Consequently these theories have concerned themselves very largely with attempts to explain why the ethane linkage in the undissociated molecule should be weakened by the presence of aryl groups. Of these various attempts, two stand out most prominently, one based upon the theory of "affinity-demand" (Valenzbeanspruchung), and the other upon the consideration of steric influences. According to the theory of affinity-demand, the aryl groups use up so much of the available affinity of the methyl carbon atoms that there is very little left over for the ethane linkage. This is not a very satisfactory explanation, however, for several reasons. It does not show why aryl groups should have such a great affinity-demand—as compared, for example, with alkyl groups, nitro groups, etc.—nor does it enable one to predict which aryl groups should be relatively more effective and which relatively less effective in promoting dissociation. Furthermore, it leads to definitely incorrect predictions in some cases. Thus, tetraphenylmethane would be expected to be rather unstable, while actually it is an extraordinarily stable compound, boiling at 431° without decomposition.

The steric theory of free radical dissociation is based upon the assumption that the aryl groups are so large that they prevent the two halves of the undissociated molecule from coming close enough together to permit the formation of a strong bond. There are, however, some difficulties with this explanation as well. It is roughly true, to be sure, that the effectiveness of a group in promoting free radical dissociation runs parallel to its size, but why, for example, should the linear biphenyl group have a greater steric effect than the phenyl group, and why should there be an appreciable difference between the α and the β-naphthyl groups? In addition the stability of tetraphenylmethane is about as irreconcilable with this theory as with that of affinity-demand.

We may conclude from this discussion that it is apparently impossible to base a satisfactory theory of the free radicals upon the assumption that the $C-C$ bond in the undissociated molecule is weakened by the influence of the aryl groups. We avoid the necessity of making this assumption, however, by considering that the energy necessary to carry through the first step of breaking the bond is the same in all cases, but that the subsequent stabilization of the radicals, resulting from the second step of changing the structure, may vary widely. Thus we attribute the dissociation not to the instability of the undissociated molecule but to the stability of the radicals formed in the dissociation.

This idea has been developed by Burton and Ingold,[7] but not upon a very satisfactory theoretical basis. From their work it is not clear why the postulated redistribution of charge should occur after, but not before, dissociation,

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[7] H. Burton and C. K. Ingold, Proc. Leeds Phil. Soc. **1**, 421 (1929); C. K. Ingold, Ann. Reports Chem. Soc. **25**, 154 (1928).

nor is the mechanism by which this redistribution stabilizes the radical definitely established. In the following pages we describe the extension to the free radical problem of the quantum-mechanical methods which we used with benzene and naphthalene. It is shown that a straightforward calculation of the resonance energy for the undissociated ethane and for the free radical leads to values of the dissociation energy of various substituted ethanes in excellent qualitative and semiquantitative agreement with experiment. This theory of the stability of free radicals may be considered as a refinement and extension of Burton and Ingold's general views, for which it provides a sound theoretical basis.

Before going into our methods of calculation we shall first discuss briefly the nature of the experimental results which we wish to explain. In spite of the vast amount of work which has been done on free radicals in the last thirty years, the information available regarding the degree of dissociation of most hexaarylethanes is meager, and exceedingly inaccurate. Ziegler and Ewald[8] have carried out precise photometric determinations in the cases of hexaphenylethane and tetraphenyldi-β-naphthylethane. In other cases the only data at hand are derived from determinations of the apparent molecular weights by the cryoscopic method. That this method is undependable is shown by the fact that it frequently indicates degrees of dissociation of 130 percent or even higher, and in the case of the slightly dissociated tetraphenyldi-β-naphthylethane it indicates a degree of dissociation two or three times greater than that found by Ziegler and Ewald. In some cases even this source of information is lacking, and then recourse must be had to such data as the intensity of the color of solutions, the temperature at which the color first appears, the number of times the color will reappear after having been discharged with air, the rate of absorption of oxygen, and so on. Obviously such methods can give only the crudest of results. As a further complication we have the fact that the degree of dissociation of a given ethane varies considerably with temperature, with solvent, and with concentration, and frequently the determinations have not been made under comparable conditions. In spite of all these difficulties, however, we can say with some assurance that the tendency toward dissociation increases in the following order: any ethane with less than six aryl groups $\ll$ diphenyldifluoryl $\ll$ hexaphenylethane $<$ tetraphenyldi-β-naphthylethane $<$ tetraphenyldi-α-naphthylethane $\cong$ diphenyltetrabiphenylethane $<$ hexabiphenylethane. We have intentionally omitted tetraphenyldibiphenylethane from this list since we do not consider that its degree of dissociation has been measured with sufficient accuracy to warrant its inclusion. It has been studied neither photometrically nor cryoscopically, and so the estimate of 15 percent dissociation usually given in the literature is not to be taken very seriously. In most lists like the above it occupies a position between hexaphenylethane and tetraphenyldi-β-naphthylethane.

From such crude data as are to be found in the literature we can calculate approximate values of the equilibrium constants, and hence of the free energies of dissociation for the various hexaarylethanes. From our quantum-mechanical treatment, on the other hand, we obtain only the heats of dissociation, for which, except in the single case of hexaphenylethane, we have no experimental data. Thus, in order that we may compare our results with those of experiment, we must make the plausible assumption that the entropies of dissociation vary only slightly from ethane to ethane. Then at a given temperature the heats of dissociation run parallel to the free energies and can be used instead of the latter in predicting the relative degrees of dissociation of the different molecules.

In carrying out the calculations we use essentially the same procedure as in the case of benzene and naphthalene. As an additional simplification, however, we neglect entirely all the excited states of the molecule, since their contribution to the total energy is comparatively small, and since they would complicate the calculations tremendously if retained. Another slight modification of the procedure is necessitated by the fact that a free radical possesses an odd number of electrons, one of which must remain unpaired. This is taken care of formally by introducing a "phantom orbit" X with an accompanying "phantom electron" which is paired with the odd electron.[4] In the subsequent

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[8] K. Ziegler and L. Ewald, Ann. **473**, 179 (1932).

calculations it is necessary merely to remember that all exchange integrals which involve the phantom orbit vanish. The rules for setting up the matrix elements and the secular equations are otherwise unchanged.

We shall discuss in detail only one example, and for the sake of simplicity we shall take the (actually undissociated) sym. diphenylethane. Let us first consider what happens when the ethane dissociates. In the first step, the C−C bond breaks and there are formed two phenylmethyl radicals, which however can resonate between only the structures A and B of Fig. 3.

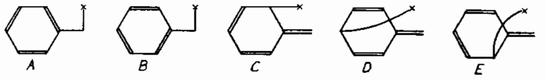


FIG. 3. The five unexcited canonical structures contributing to the normal state of the phenylmethyl radical.

ΔH for this reaction we take to be 3.65 v.e., the energy required to break a C−C bond in aliphatic compounds. The second step of the dissociation consists in a change in the structure of the radicals, involving a change in nuclear configuration from a tetrahedral arrangement of bonds about the methyl carbon to a plane arrangement of all the nuclei, and in electronic structure through the removal of the restriction of the resonance to the structures A and B, all five of the canonical structures being now allowed. ΔH for this reaction is just twice the difference between the energies of a single radical after and before the removal of the restriction. The energy change for the over-all reaction is then the algebraic sum of the energy changes of the two steps.

To evaluate ΔH for the second step we must set up and solve the secular equations corresponding to the two different states of the radical. In the case where we consider only the structures A and B the secular equation is easily shown to be:

$$\begin{vmatrix} (Q-W')+\alpha & \frac{1}{4}(Q-W')+11\alpha/8 \\ \frac{1}{4}(Q-W')+11\alpha/8 & (Q-W')+\alpha \end{vmatrix}=0.$$

On solving this we find for the energy $W'=Q+1.9\alpha$, and for the wave function $\psi'=a(\psi_A+\psi_B)$ where a is a normalization factor.

When we consider resonance between all five structures we obtain a quintic secular equation:

$$\begin{vmatrix} (Q-W)+\alpha & \frac{1}{4}(Q-W)+11\alpha/8 & \frac{1}{8}(Q-W)+7\alpha/8 & \frac{1}{4}(Q-W)+\alpha & \frac{1}{2}(Q-W)+5\alpha/4 \\ \frac{1}{4}(Q-W)+11\alpha/8 & (Q-W)+\alpha & \frac{1}{2}(Q-W)+5\alpha/4 & \frac{1}{4}(Q-W)+\alpha & \frac{1}{8}(Q-W)+7\alpha/8 \\ \frac{1}{8}(Q-W)+7\alpha/8 & \frac{1}{2}(Q-W)+5\alpha/2 & (Q-W)+\alpha & \frac{1}{2}(Q-W)+5\alpha/4 & \frac{1}{4}(Q-W)+\alpha \\ \frac{1}{4}(Q-W)+\alpha & \frac{1}{4}(Q-W)+\alpha & \frac{1}{2}(Q-W)+5\alpha/4 & (Q-W)+\alpha & \frac{1}{2}(Q-W)+5\alpha/4 \\ \frac{1}{2}(Q-W)+5\alpha/4 & \frac{1}{8}(Q-W)+7\alpha/8 & \frac{1}{4}(Q-W)+\alpha & \frac{1}{2}(Q-W)+5\alpha/4 & (Q-W)+\alpha \end{vmatrix}=0.$$

This can be simplified to a cubic equation since from considerations of symmetry it follows that the coefficients of ψ_A and of ψ_B must be the same in the complete function, and similarly for ψ_C and ψ_E. We shall however, make a further simplification by assuming that ψ_D has the same coefficient as ψ_C and ψ_E, and thereby reduce the secular equation to a quadratic:

$$\begin{vmatrix} (5/2)(Q-W)+19\alpha/4 & (7/4)(Q-W)+25\alpha/4 \\ (7/4)(Q-W)+25\alpha/4 & (11/2)(Q-W)+10\alpha \end{vmatrix}=0.$$

On solving this we find for the energy $W=Q+2.4092\alpha$, and for the wave function $\psi=a(\psi_A+\psi_B)+b(\psi_C+\psi_D+\psi_E)$ where a and b are in the ratio $a:b=1:1.0279$. The "free radical resonance energy" is thus $W-W'=0.5092\alpha$, and ΔH for the dissociation is equal to 3.65 v.e.$+2\times0.5092\alpha=3.65$ v.e.$+1.0184\alpha$. As we shall show later, the value of α is probably about −1.4 v.e., and so the heat of dissociation of sym. diphenylethane is approximately 2.2 v.e., a value in good accord with the vanishingly small degree of dissociation. In view of the uncertainty connected with the values of α and of the C−C bond energy we shall as a rule not calculate the heats of dissociation of the remaining ethanes, but instead shall use as a criterion of the tendency of a given compound to dissociate simply the coefficient of α in the expression for the free radical resonance energy. It will be noted that on account of the negative sign of α the dissociation increases as this coefficient increases.

The results obtained from this and from similar calculations for a number of other free radicals are summarized in Table III. In the first column we have listed the radical under consideration; in the second, the energy W' calculated for the radical with resonance restricted to the structures in which the unpaired electron is on the methyl carbon atom; in the third, the energy W calculated for the radical with resonance allowed among all possible states; and in the fourth, the free radical resonance energy $W-W'$.

TABLE III.

Radical	W'	W	$W-W$
Phenylmethyl	$Q+1.9000\alpha$	$Q+2.4092\alpha$	0.5092α
Biphenylmethyl	$Q+3.8000\alpha$	$Q+4.3568\alpha$	0.5568α
β-Naphthylmethyl	$Q+2.8703\alpha$	$Q+3.5012\alpha$	0.6309α
α-Naphthylmethyl	$Q+2.8703\alpha$	$Q+3.6218\alpha$	0.7515α
Fluoryl	$Q+3.3000\alpha$	$Q+4.1004\alpha$	0.8004α
Diphenylmethyl	$Q+3.8000\alpha$	$Q+4.6409\alpha$	0.8409α
Phenylfluoryl	$Q+5.2000\alpha$	$Q+6.2764\alpha$	1.0164α
Triphenylmethyl	$Q+5.7000\alpha$	$Q+6.8078\alpha$	1.1078α
Biphenyldiphenylmethyl	$Q+7.6000\alpha$	$Q+8.7310\alpha$	1.1310α
Phenyldibiphenylmethyl	$Q+9.5000\alpha$	$Q+10.6545\alpha$	1.1545α
Tribiphenylmethyl	$Q+11.4000\alpha$	$Q+12.5773\alpha$	1.1773α
β-Naphthyldiphenylmethyl	$Q+6.6636\alpha$	$Q+7.8351\alpha$	1.1715α
α-Naphthyldiphenylmethyl	$Q+6.6636\alpha$	$Q+7.9033\alpha$	1.2398α

Mention may be made of a special method developed for setting up the secular equation for free radicals. The direct calculation of matrix elements, even by the simple graphical method, would be extremely laborious for such a radical as tribiphenylmethyl, for example, for which 496 structures are taken into consideration. Let us consider three superposition patterns, each consisting of one of the substituent groups in the free radical plus the methyl carbon and the phantom orbit, the corresponding Coulomb and exchange coefficients being q_1, q_2, q_3 and a_1, a_2, a_3, respectively. It is easily proved that the Coulomb coefficient q and the exchange coefficient a for the entire superposition pattern have the values

$$q=q_1q_2q_3$$

and

$$a=a_1q_2q_3+q_1a_2q_3+q_1q_2a_3.$$

For a set of superposition patterns obtained by combining a set for each of the three groups in all possible ways, the sums of the coefficients (for equal weights of the corresponding structures) are

$$\Sigma q=\Sigma q_1\cdot\Sigma q_2\cdot\Sigma q_3$$

and

$$\Sigma a=\Sigma a_1\cdot\Sigma q_2\cdot\Sigma q_3+\Sigma q_1\cdot\Sigma a_2\cdot\Sigma q_3+\Sigma q_1\cdot\Sigma q_2\cdot\Sigma a_3.$$

As an example we may use these equations to calculate the coefficients summed over the 64 matrix elements corresponding to the eight structures of triphenylmethyl with the unpaired electron on the methyl carbon. Reference to the secular equation for phenylmethyl shows that $\Sigma q_1=\Sigma q_2=\Sigma q_3=1+1+\frac{1}{4}+\frac{1}{4}=5/2$, and $\Sigma a_1=\Sigma a_2=\Sigma a_3=11/4$, leading to the values $\Sigma q=125/8$ and $\Sigma a=1425/16$.

The secular equations which must be solved for the values of W are frequently of very high degree, even after all of the simplifications arising from considerations of symmetry have been introduced. In such cases we have reduced the equations to cubics (sometimes to quadratics) by equating coefficients in a more or less arbitrary manner. The calculated values for the free radical resonance energy are, therefore, uncertain to the extent to which they are affected by this not strictly legitimate simplification. We feel, however, that the errors introduced in this way are not very large, since we have found by actual calculation in two cases that the energies are not very sensitive to small changes in the coefficients. For example, the energy W of the triphenylmethyl radical is given in Table III as $Q+6.8078\alpha$. This was obtained by solving rigorously the secular equation, which in this case could be reduced to a cubic. If, on the other hand, we equate all coefficients and make the equation linear, we obtain for W the value $Q+6.8064\alpha$. In the case of the α-naphthyldiphenylmethyl radical the value of $Q+7.9033\alpha$ given for W in Table IV was derived from a cubic

TABLE IV.

Radical	Position of odd electron	Number of structures	Relative values of coefficients
Phenylmethyl	methyl carbon	2	1
	phenyl group	3	1.0279
Biphenylmethyl	methyl carbon	4	1
	biphenyl group	9	0.4526
β-Naphthylmethyl	methyl carbon[a]	1	1
	methyl carbon[b]	2	0.8789
	naphthyl group	6	0.5458
α-Naphthylmethyl	methyl carbon[a]	1	1
	methyl carbon[b]	2	0.8828
	naphthyl group	7	0.5916
Fluoryl	methyl carbon	4	1
	biphenylene group[c]	8	0.6768
	biphenylene group[c]	4	0.6056
Diphenylmethyl	methyl carbon	4	1
	phenyl group	12	0.7232
Phenylfluoryl	methyl carbon	8	1
	phenyl group	12	0.8983
	biphenylene group	24	0.8430
Triphenylmethyl	methyl carbon	8	1
	phenyl group (para)	12	0.8829
	phenyl group (ortho)	24	0.9896
Biphenyldiphenylmethyl	methyl carbon	16	1
	phenyl group	48	0.8546
	biphenyl group	36	0.6477
Phenyldibiphenylmethyl	methyl carbon	32	1
	phenyl group	48	0.7881
	biphenyl group	144	0.5969
Tribiphenylmethyl	methyl carbon	64	1
	biphenyl group	432	0.5535
β-Naphthyldiphenylmethyl	methyl carbon	12	1
	phenyl group	36	0.9085
	naphthyl group	24	0.8497
α-Naphthyldiphenylmethyl	methyl carbon	12	1
	phenyl group	36	0.9200
	naphthyl group	28	0.9121

[a] With the naphthyl group symmetrical as in structure I, Fig. 2.
[b] With the naphthyl group unsymmetrical as in structures II and III, Fig. 2.
[c] The distinction between these two types of structure is described below in the discussion of the fluoryl radical.

equation, obtained by equating the coefficients of all structures in which the odd electron is (1) on the methyl carbon atom, (2) on the naphthyl group, and (3) on a phenyl group. If the equation is reduced further to a quadratic by equating the coefficients of all structures of the last two types the energy W is changed only in the fifth decimal. The effect of these errors which, though small, are sometimes quite appreciable will always be to make the value of W too large (that is, the coefficient of α too small). Since the secular equations for W' can be solved rigorously in all cases, this will cause the radicals to appear less stable relative to the ethanes than they should. This effect should be particularly pronounced in the cases of the α- and the β-naphthyldiphenylmethyl radicals because of the high degree of the secular equations. Furthermore, in these radicals we have had to give the structures in which the naphthyl group has the symmetrical form (as in structure I, Fig. 2) the same coefficient as the structures in which the naphthyl group has the unsymmetrical form (as in structures II and III, Fig. 2), and this simplification seems to be particularly unjustified. At any rate it is found to be pretty far off in the cases of the simple α and β-naphthylmethyl radicals where the calculations have been carried through somewhat more rigorously. This error has been partially corrected by making the same approximation in the calculations of W'; that is, by putting all coefficients equal and solving linear instead of quadratic secular equations.

In order to make clear the manner in which we have simplified the treatment of the various radicals, we give in Table IV a statement of the value and significance of the coefficients occurring in the function ψ in the individual cases. It will not be necessary to give a similar table for the functions ψ' since, except in the cases of the α and the β-naphthyldiphenylmethyl radicals which have been discussed above, no simplifications were necessary for them, and the secular equations were solved rigorously.

Discussion of results

The principal source of inaccuracy in the treatment given the free radicals is the neglect of all excited structures. In the case of benzene the three excited structures contribute 0.2055α to the resonance energy, which is about 20 percent of the total resonance energy of the molecule. The same error is introduced in W' for the phenylmethyl radical. The change in W produced by the inclusion of the nine excited structures as well as the five unexcited structures is not so large, so that $W-W'$ is decreased from 0.5092α to 0.4455α, a decrease of 0.06α or 12 percent of $W-W'$. Similar changes in the values of $W-W'$ would result from the consideration of excited structures for other radicals. In consequence, so long as excited structures are not included in the treatment the values of $W-W'$ cannot be considered to be accurate to 10 percent. This does not prevent us from making use of the values given in Table III, however, in certain cases. Thus for each of the radicals included in the table the value of $W-W'$ can be considered to give the extra resonance energy stabilizing the radical with an accuracy of 10–20 percent. Moreover, in some cases differences in the $W-W'$ values for different radicals can be trusted to the same extent; namely, when one radical differs from another only by the addition of a group, so that all of the structures considered for the first radical are retained for the second, as well as other structures. Thus the difference of the $W-W'$ values for biphenylmethyl and phenylmethyl should give with considerable accuracy the extra stability resulting from the substitution of biphenyl for phenyl, and a similar comparison should be reliable for α-naphthyl and β-naphthyl, α or β-naphthyl and phenyl, fluoryl and diphenyl, etc., but not for α-naphthyl and biphenyl, inasmuch as in these completely different groups the effect of neglect of excited structures may well mask the small differences under consideration. When this restriction in the interpretation of the $W-W'$ values is borne in mind, it is found that the agreement between the rather rough theoretical calculations and the existent empirical information is excellent, and provides sound evidence that resonance of the type considered is the primary factor in the stabilization of the hydrocarbon free radicals. A number of details in the comparison are treated in the following paragraphs.

(a) The calculation for triphenylmethyl leads to a value of 3.65 v.e.$+2.2156\alpha$ for the heat of dissociation of hexaphenylethane. Equating this to the experimentally determined value of 0.5

v.e., we obtain as a result that $\alpha = -1.4$ v.e. This is in fair agreement with the value of -1.5 v.e. obtained from the calculation for benzene; the discrepancy may be due in part to the fact mentioned before that the evaluation of α from the benzene calculation is not strictly legitimate, and in part to the neglect of excited structures, which (from analogy with phenylmethyl) are expected to decrease the coefficient of α in $W-W'$, and so increase the absolute value of α.

(b) Except for comparisons of naphthyl and biphenyl, the amounts of dissociation indicated by the values of $W-W'$ for various radicals are in excellent qualitative agreement with experiment. It is undoubtedly significant that, as is demanded by experiment, the variations in the free radical resonance energies obtained by increasing the number of aryl groups is large compared with the variations obtained by changing the nature of the groups already present.

(c) In order to make a quantitative comparison of our results with experiment, let us calculate the ratio of the dissociation constants corresponding to a difference in the free radical resonance energies of 0.01α. If we let the subscript 1 refer to the more highly dissociated ethane and 2 to the less highly dissociated, we have the following relation:

$$RT \ln (K_2/K_1) = \Delta F_1 - \Delta F_2 \cong \Delta H_1 - \Delta H_2 = 0.02\alpha.$$

Since α is equal to -1.4 v.e. or $-32{,}000$ calories per mole, this equation becomes

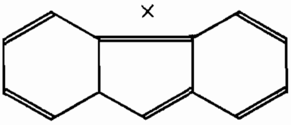
$$RT \ln (K_1/K_2) = 640 \text{ cal./mole}$$

which at 20°C leads to

$$\ln (K_1/K_2) = 1.1 \quad \text{or} \quad K_1/K_2 = 3.0.$$

From Table III we see that the difference between the free radical resonance energies of tribiphenylmethyl and triphenylmethyl is 0.07α. Hence $K_1/K_2 = 3^7 = 2.2 \times 10^3$. Ziegler and Ewald[8] found that at 20°C the value of the dissociation constant for hexaphenylethane in benzene solution is 4.1×10^{-4} and consequently we calculate for hexabiphenylethane a value of $K = 2.2 \times 10^3 \times 4.1 \times 10^{-4} = 0.90$. This value is probably too low as the compound is reported to be completely dissociated; the error may not be large, however, since a dissociation constant of 0.90 would lead to 91 percent dissociation in $0.05M$ solution. The solutions actually worked with have usually been more dilute than this, and so our calculated value may be within the experimental error.

(d) The ability of the present method to distinguish between apparently small differences in structure is brought out forcibly by a comparison of the relative effectiveness of the α- and the β-naphthyl groups on the one hand, and of the fluoryl and the diphenylmethyl groups on the other. The greater dissociating power of α-naphthyl is qualitatively correlated with the fact that for it there are seven unexcited structures with the odd electron on a naphthyl carbon, whereas there are only six for β-naphthyl. The case of fluoryl is particularly striking. For the fluoryl radical it is possible to write six more unexcited structures than for the diphenylmethyl radical. These extra structures are all of the type



That is, they all have a double bond in the ortho linkage between the phenyl groups, and they all have the odd electron on one or the other of the phenyl groups. Hence it would seem that the radical should be stabilized by these extra possibilities of resonance, while the ethane should be left practically unaltered, and that consequently the dissociation should be increased. Actually, however, the opposite is the case. On putting in the phantom orbit and drawing all the bonds it is found that no matter where the phantom orbit is put with respect to the other orbits all the possible structures cannot be made canonical simultaneously. There will always be six non-canonical structures which must be represented as linear combinations of the canonical ones, and so the structures suggesting extra resonance are eliminated. Just which six structures are non-canonical will depend upon the position given the phantom orbit. If it be put in the symmetrical position indicated above, the non-canonical structures will be those in which there is a double bond between the two phenyl groups. Two of these structures turn out to be combinations of excited structures and so are neglected. The remaining four are combinations of one unexcited and one excited structure each.

These excited structures are also neglected, and the four unexcited structures are distinguished from the remaining eight by being given a different coefficient. This is the reason for the fact noted in Table IV that for the fluoryl radical there are three instead of two coefficients. Since, however, the coefficients for the two different types of structures proved to be nearly the same here, they were put equal to each other in the calculation for the phenylfluoryl radical. This explains why the fluoryl group should not be more effective in promoting dissociation than the diphenylmethyl group, but to see why it is actually less effective we must turn our attention to the rules by which the matrix elements are calculated. Since we have shown that we can eliminate all the extra resonance structures of the fluoryl radical, the structures which we have left are exactly the same as those in the case of diphenylmethyl, except for the ortho bond between the two phenyl groups. Therefore the secular equation is the same except for the effect of the interchange integral between the atoms at either end of the bond, and this integral will always come into the matrix elements with a negative sign. Consequently the coefficient of α in any given matrix element for the fluoryl radical will be less than in the corresponding element for the diphenylmethyl radical. As a result of this, the coefficient of α will be decreased in both the energies W and W', and since this decrease is greater in the former case than in the latter, the coefficient in the extra resonance energy $W-W'$ will also be decreased.

(e) Although the theory described in this paper is able to explain qualitatively and semi-quantitatively the dissociation of a considerable number of free radicals, it proves to be definitely inadequate in some cases. For example, di-tert.-butyl-tetraphenylethane has been found to be appreciably dissociated at room temperature, although our calculation would give exactly the same value of the free radical resonance energy as in the case of the undissociated tetraphenylethane, since the presence of the tert. butyl group does not affect the number of resonating structures nor the values of the matrix elements. The same considerations also apply to decaphenylbutane, which has been found to be completely dissociated into pentaphenylethyl radicals. We consider that in these cases the steric effect may enter and be of dominating importance. There is no doubt that the tert. butyl and the triphenylmethyl groups are relatively large, and their presence in these compounds may tend to keep the radicals apart.

Furthermore, there are a number of interesting free radicals other than the hydrocarbons to which our treatment could be extended. In order to carry through similar calculations for compounds containing oxygen or nitrogen, however, we would have to introduce a number of additional parameters, corresponding to exchange integrals other than that to which we have given the value of α, which would make the calculations more difficult and the results less valuable.

Mention may be made of the interesting observation of Wieland that triphenylmethyldi-*p*-anisylamine does not dissociate appreciably except at temperatures above 140°

$$(C_6H_5)_3C-N(C_6H_4OCH_3)_2 \rightleftarrows (C_6H_5)_3C- + -N(C_6H_4OCH_3)_2$$

although the free radicals formed can exist to an appreciable extent in the monomeric form even at room temperature—a fact which has excited considerable comment. The explanation does not involve a difference in resonance in this compound and the corresponding ethane and hydrazine, but instead a difference in the energy of the carbon-nitrogen bond and the mean for the carbon-carbon and nitrogen-nitrogen bonds, resulting from additional ionic character of the unsymmetrical bond. This amounts to about 0.5 v.e.,[9] and so is large enough to prevent dissociation.

On the other hand, the stability of positive and negative triarylmethyl ions is due to the same resonance effect as that of the neutral radicals discussed in this paper.

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[9] See the preceding and the following paper of this series.

THE NATURE OF THE CHEMICAL BOND. V.

Calculation of the Resonance Energy of Benzene and Naphthalene and the Hydrocarbon Free Radicals

By Linus Pauling and G. W. Wheland
J.Chem.Phys., 1, 362 (1933)

Errata: In this paper a number of numerical errors appeared. The corrected values are given below.

Substitute the following for the corresponding lines in Table III, p. 370:

Radical	W'	W	W - W'
Biphenylmethyl	$Q+3.8000\alpha$	$Q+4.4473\alpha$	0.6473α
Phenylfluoryl	$Q+5.2000\alpha$	$Q+6.2764\alpha$	1.0764α
Biphenyldiphenylmethyl	$Q+7.6000\alpha$	$Q+8.7738\alpha$	1.1738α
Phenyldibiphenylmethyl	$Q+9.5000\alpha$	$Q+10.7347\alpha$	1.2347α
Tribiphenylmethyl	$Q+11.4000\alpha$	$Q+12.6905\alpha$	1.2905α

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And in Table IV, p. 371:

Radical	Position of odd electron	Number of structures	Relative values of coefficients
Biphenylmethyl	methyl carbon	4	1
	diphenyl group	9	0.5608
Biphenyldiphenylmethyl	methyl carbon	16	1
	phenyl group	48	0.8861
	biphenyl group	36	0.7816
Phenyldibiphenylmethyl	methyl carbon	32	1
	phenyl group	48	0.8433
	biphenyl group	144	0.7392
Tribiphenylmethyl	methyl carbon	64	1
	biphenyl group	432	0.7007

The discussion in section (c), page 373, regarding the quantitative agreement of the calculations with experiment has to be altered somewhat in accordance with the corrected values of the free radical resonance energies. The calculated dissociation constant of hexabiphenylethane now becomes $3.0^{18} \times 4.1 \times 10^{-4} = 1.6 \times 10^{5}$. This value is in good agreement with the reported complete dissociation of the molecule, but may be too high. In general, the constants found in this manner for the various hexaarylethanes seem to be uniformly too large, in comparison with that of hexaphenylethane. This discrepancy may perhaps arise from the neglect of excited structures, or may be due merely to the fact that we are comparing small differences between larger quantities. It is significant, however, that the qualitative agreement with experiment is now perfect, the empirical order given on page 368 being reproduced without error.

AUGUST, 1933 JOURNAL OF CHEMICAL PHYSICS VOLUME 1

The Nature of the Chemical Bond. VI. The Calculation from Thermochemical Data of the Energy of Resonance of Molecules Among Several Electronic Structures[1]

LINUS PAULING AND J. SHERMAN, *Gates Chemical Laboratory, California Institute of Technology*

(Received April 13, 1933)

In the first part of this paper there is given a set of bond-energy values for single, double, and triple bonds between atoms, obtained from thermochemical data, such that the total energy of formation from separate atoms of a molecule containing given bonds is equal to the sum of the energies for those bonds. In the derivation of these values data were used only for molecules for which it is probable that one electronic structure, corresponding to one distribution of valence bonds, represents the normal state to a satisfactory degree of approximation. For other molecules more than one electronic structure of this type contributes essentially to the normal state, the energy of formation of the molecule then being larger than that for any one of the contributing structures. On comparing the energies of formation given by thermochemical data with the values calculated for various structures, it is verified that this difference is always positive or zero (to within the limits of error involved). The difference in energy is interpreted as the resonance energy of the molecule among several electronic structures, and its existence in a given case provides strong evidence that more than one structure is contributing to the normal state of the molecule, the number and importance of the contributing structures being indicated by the magnitude of the resonance energy. In this way the existence of resonance is shown for many molecules, and values found for the resonance energy are tabulated. The substances discussed include carbon dioxide, carbon disulfide, alkyl isocyanates, carboxylic acids and esters, aliphatic amines, carbonic esters, urea and related substances, benzene and benzene derivatives, naphthalene and other condensed ring systems, pyridine and related heterocyclic compounds, biphenyl, fluorene, phenylethylene, dihydronaphthalene, quinone, some ureides and purines, etc.

INTRODUCTION

It has been recently recognized that molecules can be divided roughly into two classes, the first comprising those for which the normal electronic state can be reasonably well approximated by an eigenfunction corresponding to a single electronic structure of the Lewis type; that is, to a single distribution of valence bonds, and the second those for which the normal electronic state can be satisfactorily represented only by a linear combination of several such eigenfunctions. A molecule belonging to this second class is said to resonate among the corresponding electronic structures. Information as to the classification of a given molecule may be obtained from the consideration of theoretical or empirical energy curves,[2] from the comparison of observed interatomic distances with the sum of atomic radii,[3] and in other ways. In particular the comparison of the energy of the molecule with the values corresponding to various electronic structures should provide a valuable criterion, inasmuch as the energy of the normal molecule must be equal to or less than the energy for any electronic structure. If more than one of the reasonable electronic structures for a molecule correspond to nearly the same energy value, which is somewhat higher than the actual energy of the molecule, the difference in energy may be confidently interpreted as the resonance energy of the molecule among these electronic structures. Assuming that the total energy of formation of a nonresonating molecule from separated atoms may be represented as the sum of bond energies, we in this work have calculated values of the energies of various single, double, and triple bonds from thermochemical data. With the use of these we have then predicted energies for various electronic structures for other molecules, and have in this way shown the existence of resonance and have calculated values of the resonance energy for a large number of substances, including in particular carboxylic acids, amides, and other compounds with a resonating

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[1] The fifth paper of this series appeared in J. Chem. Phys. **1**, 362 (1933).

[2] L. Pauling, J. Am. Chem. Soc. **54**, 988 (1932).

[3] L. Pauling, Proc. Nat. Acad. Sci. **18**, 293, 498 (1932).

double bond, aromatic hydrocarbons and their derivatives, heterocyclic compounds, etc.

It has been pointed out[4] that bonds between non-identical atoms may be considered to resonate between a covalent and an ionic structure, the bond in this way having partially covalent and partially ionic character. The resonance energy of this effect, which is usually essentially the same for a given bond in different molecules, is included in the values given for the bond energies in the nonresonating molecules discussed.

Although much of the body of thermochemical data which we use has been available for a long time, and many attempts at interpreting it by the introduction of the concept of bond energies have been made, the derivation of a satisfactory set of essentially constant bond energies was not made earlier because the necessity of using a restricted class of molecules was not recognized. It remained for the quantum mechanics to indicate the possibility of resonance of some molecules among several structures corresponding to different distributions of valence bonds, with a consequent change in total energy, and to suggest the determination of bond energies by the consideration of only those molecules for which a single electronic structure can be written with considerable confidence.

BOND ENERGIES IN MOLECULES REPRESENTED BY A SINGLE ELECTRONIC STRUCTURE

In formulating a set of bond-energy values we first calculated the energies of formation of molecules from experimental values of the heats of combustion of the compounds[5] and thermochemical data pertaining to the products of combustion—carbon dioxide, water, nitrogen, etc. The same values for the latter quantities were used as previously.[4]

Throughout this paper the unit of energy is the volt-electron (1 v.e. = 23.054 kcal.). The symbol A—B denotes a single bond between the atoms A and B, A=B a double bond, etc. The letter E represents the heat of formation of the gaseous substance at 25°C from widely separated atoms, the energy of the substance (except for small pv terms) being equal to $-E$.

In a previous discussion[4] it was pointed out that there is some arbitrariness in the choice of bond energies, arising from uncertainty in the experimental data, lack of constancy of bond energies from compound to compound, and other causes. Because of differences in the data used and their treatment, the values given in that paper and the present one differ somewhat; the difference in no case exceeds 0.1 v.e., however, which is of the order of magnitude of the errors inherent in the data.

The bond-energy values obtained in this way[6] are given in Table I. It is noteworthy that the energy of a given bond may in some cases change somewhat from one compound to another of different type; thus the C=O bond energy is considerably changed as hydrogen attached to the carbon atom under consideration is replaced by aliphatic radicals. This effect is probably due in the main to interactions of bonds from the same atom, inasmuch as it is especially pronounced for bonds (such as C—O, C=O, C≡N) with which large electric dipole moments are associated. In default of a thorough understanding of the phenomenon, we have contented ourselves with using for each substance values of bond energies obtained from substances resembling it.

TABLE I. *Bond energies.*

Bond	Energy	Source
C—H	4.323 v.e.	Methane
N—H	3.895	Ammonia
O—H	4.747	Water
C—C	3.65	Paraffins
C=C	6.56	Olefins and Cyclic Compounds
C≡C	8.61	Acetylene Hydrocarbons
N—N	1.44	Reference 4
C—O	3.47	Aliphatic Primary Alcohols
	3.59	Aliphatic Ethers
C=O	7.20	Formaldehyde
	7.56	Other Aldehydes
	7.71	Ketones
C—N	2.95	Amines
C=N	5.75	Estimated Value
C≡N	8.75	Hydrogen Cyanide
	9.07	Aliphatic Cyanides
C—S	2.92	Mercaptans and Thio-ethers
C=S	5.60	Estimated Value

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[4] L. Pauling, J. Am. Chem. Soc. **54**, 3570 (1932).

[5] The heats of combustion used were taken from Kharasch's compilation (Bur. Standards J. Research **2**, 359 (1929)) or from Landolt-Börnstein Tables.

[6] The detailed discussion of the derivation of these values is omitted for the sake of brevity.

The surprisingly large value of the $C{=}O$ bond is no doubt associated with the possibility of writing for R_2CO the structure $R_2{=}\overset{+}{C}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:^{-}$ as well as $R_2{=}C::\overset{\cdot\cdot}{O}:$, the former "semipolar" structure contributing an appreciable resonance energy. The magnitude of this contribution might be especially easily influenced by adjacent groups, the presence of hydrogen attached to the carbon atom having a pronounced effect in inhibiting it.

Resonance Energies of Carbon Dioxide, Alkyl Isocyanates, etc.

In calculating the resonance energy of a molecule, we write for the molecule the electronic structure corresponding to the usually accepted distribution of valence bonds, and calculate the corresponding value of E' by summing the bond energies, using values from similar compounds in case more than one bond energy is given in Table I. The difference between the experimental value of E and the calculated value of E' is interpreted as resonance energy resulting from contributions of other electronic structures to the normal state of the molecule. This treatment is applicable at present only to molecules for which stable structures can be written involving neutral atoms only; compounds such as HN_3, with the structure $H:\overset{\cdot\cdot}{N}::\overset{+}{N}::\overset{\cdot\cdot}{N}:^{-}$ making the largest contribution to the normal state, cannot be discussed until methods are developed for evaluating the energies of partially ionic bonds.

Evidence from interatomic distances[3] has shown the existence of resonance in CO, CO_2, CS_2, RNCO, and many other simple molecules. This is supported by the consideration of the energy of these molecules. The value of E for CO is 11.30 v.e., 3.59 v.e. greater than the ketone value for $C{=}O$. This very large difference has already been accounted for[3] as resulting from the great stability of the structure $:\overset{-}{C}:::\overset{+}{O}:$, whose contribution to the eigenfunction for the normal state is even larger than that of $:C::\overset{\cdot\cdot}{O}:$.

Carbon dioxide, with $E=16.79$ v.e., has a resonance energy of 1.37 v.e. relative to the structure $:\overset{\cdot\cdot}{O}{=}C{=}\overset{\cdot\cdot}{O}:$, with the ketone $C{=}O$ value. This large resonance energy is due to the structures $:\overset{+}{O}:::C:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:^{-}$ and $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:^{-}C:::\overset{+}{O}:$, direct evidence for which is provided by the observed interatomic distances. The molecules SCO, with $E=14.55$ v.e., and CS_2, with $E=12.46$ v.e., have resonance energies of 0.84 v.e. and 0.46 v.e., respectively.

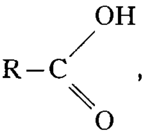
The values $E=29.64$ v.e. for methyl isocyanate and $E=41.99$ v.e. for ethyl isocyanate correspond to resonance energies of 0.26 v.e. and 0.31 v.e., respectively, relative to the structure $R:\overset{\cdot\cdot}{N}{=}C{=}\overset{\cdot\cdot}{O}:$. The other structures contributing to the normal state are no doubt the same as in CO_2. Methyl isothiocyanate, CH_3NCS, with $E=28.10$ v.e., has a resonance energy of 0.43 v.e.

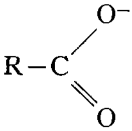
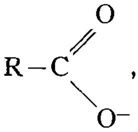
The value $E=20.01$ v.e. for cyanamide leads to a resonance energy of 0.20 v.e. relative to the structure $H_2\overset{\cdot\cdot}{N}-C\equiv N:$, which is without doubt due to resonance with $H_2\overset{+}{N}{=}C{=}\overset{\cdot\cdot}{N}:^{-}$.

It should be emphasized that the resonance energies calculated by the use of bond energies such as $C{=}O$ from ketones do not include the energy of resonance between $C::\overset{\cdot\cdot}{O}:$ and $\overset{+}{C}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:^{-}$. For example, if we were to assign to $C::\overset{\cdot\cdot}{O}:$, that is, the normal covalent carbon-oxygen double bond, the estimated bond energy 6.60 v.e., then the ketones would show a resonance energy of 1.11 v.e. arising from the $R_2{=}\overset{+}{C}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:^{-}$ structure, and carbon dioxide a total resonance energy of 3.59 v.e. The procedure of using ketone $C{=}O$, etc., bond energies rather than the normal covalent energies has been adopted for two reasons. First, there is no satisfactory way of determining the value of $C::\overset{\cdot\cdot}{O}:$, for in no molecule is resonance to $\overset{+}{C}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:^{-}$ prohibited. Second, since in every molecule containing C=O there is resonance between $\mathrm{C::\overset{\cdot\cdot}{O}:}$ and $\overset{+}{\mathrm{C}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}:^{-}$, it must always be considered in interpreting the total resonance energy, and this is most easily done by simply using a C=O bond energy which already includes this resonance energy.

Resonance Energies of Aliphatic Acids, Esters, Amides, and Related Compounds

Carboxylic acids and esters

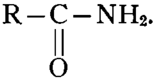
Data for acetic acid and eight other monobasic acids lead to a value of 1.20 v.e. for the resonance energy of the carboxyl group relative to the structure , with the use of the ketone value for C=O. Data for eight dibasic carboxylic acids lead to the value 1.19 v.e. per carboxyl group, in excellent agreement with the monobasic acid value.

In the carboxylic anions there is complete degeneracy between the structures  and , so that appreciable energy of resonance between these two structures may well be expected. We have not obtained any empirical data for these ions. The extent to which the resonance is inhibited by attaching hydrogen to one of the two previously equivalent oxygen atoms cannot be predicted. Our value of 1.20 v.e. for the resonance energy in the carboxylic acids is a lower limit for the resonance energy in the corresponding anions.

It is to be expected from chemical evidence that the replacement of hydrogen by an aliphatic radical would have some further inhibiting effect on the carboxyl resonance. It is found, however, that to within the experimental error of about 0.2 v.e. the resonance energy is the same for methyl and ethyl esters as for carboxylic acids.

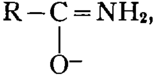
Aliphatic amides

The values $E=23.55$ v.e. for formamide, $HCONH_2$, and 35.96 v.e. for acetamide, CH_3-$CONH_2$, lead to a resonance energy of 0.93 v.e. and 0.89 v.e., respectively, calculated relative to the structure



$$\mathrm{R-\underset{\underset{O}{\|}}{C}-NH_2.}$$

The expected resonance is between this structure and the structure



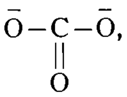
$$\mathrm{R-\underset{\underset{O^-}{|}}{C}=\overset{+}{N}H_2,}$$

and the value 0.9 v.e. obtained is not greatly different from the related value 1.20 v.e. for the carboxyl group.

Oxamide, $(CONH_2)_2$, with $E=42.60$ v.e., has a total resonance energy of 2.05 v.e., or 1.03 v.e. per amide group, in agreement with the above value. Oxamic acid, $COOH\cdot CONH_2$, with $E=40.12$ v.e., has a total resonance energy of 1.99 v.e., nearly the sum of the values for the carboxyl group in oxalic acid and for the amide group in oxamide.

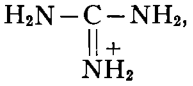
Carbonic esters, urea, etc.

In the carbonate ion,



$$\mathrm{\overset{-}{O}-\underset{\underset{O}{\|}}{C}-\overset{-}{O},}$$

guanidonium ion,



$$\mathrm{H_2N-\underset{\underset{NH_2}{\|+}}{C}-NH_2,}$$

etc., there is complete degeneracy of the three structures corresponding to the three positions of the double bond, so that a resonance energy considerably larger than that in the carboxyl group is anticipated. Data on these symmetrical ions are not available, but data for similar unsymmetrical compounds, discussed below, in which resonance is only partially inhibited by the incomplete degeneracy lead to resonance energies of about 1.8 v.e.

Dimethyl carbonate, with $E=49.81$ v.e., and diethyl carbonate, with $E=74.46$ v.e., lead to a carbonate resonance energy of 1.78 v.e. and 1.83 v.e., respectively. Urea, $CO(NH_2)_2$, with $E=30.78$ v.e., and urethane, $C_2H_5OCONH_2$, with $E=52.79$ v.e., have resonance energies of 1.59 v.e. and 1.89 v.e., respectively. No thermal data are available for guanidine.

THE AROMATIC HYDROCARBONS

Benzene

The value of E' calculated for one of the Kekulé structures for benzene, $E'=6C-H+3C-C+3C=C$, is 56.58 v.e. The data given in Table II for benzene and five other compounds lead to an average resonance energy between the two equivalent Kekulé structures, together with the additional contributions of the three excited states,[7] of 1.71 v.e.

TABLE II. *Benzene and benzene derivatives.*

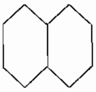
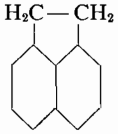
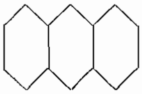
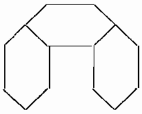
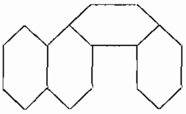
Compound	Formula	E	E'	Resonance energy
Benzene	C_6H_6	58.20	56.58	1.62 v.e.
Toluene	$C_6H_5CH_3$	70.58	68.88	1.70
Ethylbenzene	$C_6H_5C_2H_5$	82.90	81.18	1.72
Propylbenzene	$C_6H_5C_3H_7$	95.27	93.48	1.79

The values of E' and E can be estimated from their internal consistency to be accurate to about ±0.1 v.e., the value of 1.71 v.e. for the resonance energy being accurate to about ±0.15 v.e. The quantum mechanical discussion of resonance in benzene and naphthalene is given in the preceding paper.[1]

Naphthalene, anthracene, and other condensed ring systems

Data given in Table III lead to resonance energies relative to the usual structures with the maximum number of double bonds between adjacent carbon atoms of 3.24 v.e. and 3.07 v.e. for naphthalene and acenaphthene, 4.54 v.e. for anthracene, 4.78 v.e. for phenanthrene, and 6.53 v.e. for chrysene. These values are roughly equal to integral multiples of 1.71 v.e., the value found for benzene, the integral factor being in each case the number of benzene rings in the condensed ring system. The deviations are always in the direction of decreased resonance, the ratios for

TABLE III. *Condensed ring systems.*

Compound	Formula	Structure	E	E'	Resonance energy
Naphthalene	$C_{10}H_8$		92.52	89.28	3.24
Acenaphthene	$C_{12}H_{10}$		111.95	108.88	3.07
Anthracene	$C_{14}H_{10}$		126.54	122.00	4.54
Phenanthrene	$C_{14}H_{10}$		126.78	122.00	4.78
Chrysene	$C_{18}H_{12}$		161.25	154.72	6.53

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[7] See reference 1.

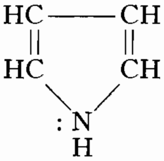
benzene and these five molecules being 1 : 1.90 : 1.80 : 2.66 : 2.80 : 3.82.

The saturated side ring in acenaphthene should not change the resonance energy from that of naphthalene, the small discrepancy observed (3.07 v.e. as against 3.24 v.e.) being attributed to experimental error. The ratio to 1.71 v.e. for acenaphthene, 1.80, is in better agreement with the quantum-mechanical ratio 1.82 than is the ratio 1.90 found for naphthalene itself, though in both the disagreement is within the experimental error.

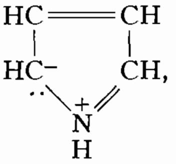
HETEROCYCLIC COMPOUNDS

Data are given in Table IV for heterocyclic compounds. For piperidine there is no difference between *E* and *E′*, showing that the bond energies used are applicable to saturated heterocyclic molecules. Pyridine and quinoline differ from benzene and naphthalene only by the presence of one N in place of CH; and, as expected, the values 1.87 v.e. and 3.01 v.e., respectively, of the resonance energy are equal to within 10 percent to the values for the corresponding hydrocarbons.

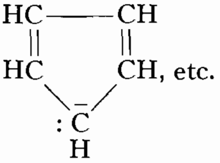
Pyrrole, C_4H_5N, is found to have a resonance energy of 0.98 v.e., despite the fact that the structure



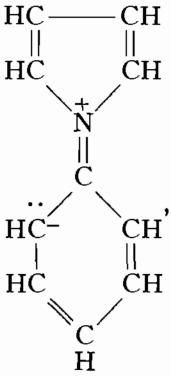
is the only structure that can be written for it in which each carbon atom forms four bonds with adjacent atoms. The large resonance energy requires that other structures contribute strongly to the normal state of this molecule. The most reasonable additional structures that can be written are the four of the type



which differ from the first in that the two double bonds are shifted and the unshared electron pair is on carbon rather than nitrogen. A negative carbon atom, with one unshared and three shared electron pairs, occurs rather often in resonating structures, as in carbon monoxide, the negative hydrocarbon free radicals, the ion $C_5H_5^-$ (in the alkali salts of pentadiene), which resonates among the five equivalent structures



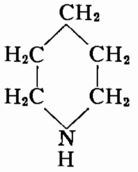
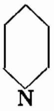
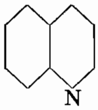
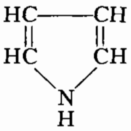
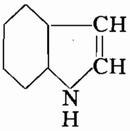
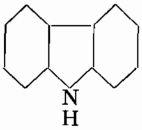
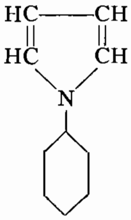
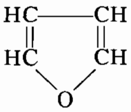
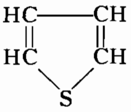
Indole, C_8H_7N, and carbazole, $C_{12}H_9N$, have resonance energies of 2.34 v.e. and 3.93 v.e., respectively, 0.63 v.e. and 0.51 v.e. greater than for the benzene rings in the indicated structures. For indole we expect the resonance energy to be somewhat smaller than the sum for benzene and pyrrole, because of the suppression of resonance from the sharing of two atoms by the two rings; in agreement with this argument, the observed value is 0.35 v.e. less than the sum $1.71+0.98=2.69$ v.e. Similarly for carbazole the observed resonance energy is 0.47 v.e. less than the sum $2\times1.71+0.98=4.40$ v.e. The resonance energy of phenylpyrrole, 3.29 v.e., is 0.60 v.e. greater than the sum of the pyrrole and benzene resonance energies; this additional stability is due to structures such as



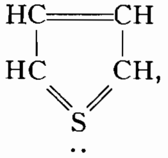
in which the unshared electron pair is on a carbon atom ortho or para to nitrogen.

The resonance energy of 0.93 v.e. for furane, C_4H_4O, arises from the same structures as for pyrrole.

TABLE IV. *Resonance energies of heterocyclic compounds.*

Compound	Formula	Structure	*E*	*E′*	Resonance energy
Piperidine	$C_5H_{11}N$		67.58	67.60	—
Pyridine	C_5H_5N		52.61	50.74	1.87
Quinoline	C_9H_7N		86.46	83.45	3.01
Pyrrole	C_4H_5N		44.84	43.86	0.98
Indole	C_8H_7N		78.91	76.57	2.34
Carbazole	$C_{12}H_9N$		113.22	109.29	3.93
Phenylpyrrole	$C_{10}H_9N$		98.45	95.16	3.29
Furane	C_4H_4O		42.18	41.25	0.93
Thiophene	C_4H_4S		41.21	39.86	1.35

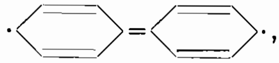
Despite its five-membered ring, thiophene, C_4H_4S, shows a remarkably close resemblance to benzene in its properties. The resonance energy found for it, 1.35 v.e., is to be mainly attributed to the same structures as for pyrrole, though the structure

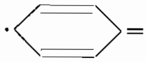


using five *M* orbits in sulfur, may make a small contribution also.

RESONANCE IN CONJUGATED SYSTEMS CONTAINING AROMATIC NUCLEI

Biphenyl and related compounds

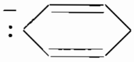
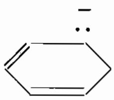
The thermochemical data for aliphatic hydrocarbons containing conjugated double bonds, such as butadiene, $CH_2=CH-CH=CH_2$, etc., are not very reliable, but suggest a value of about 0.2 v.e. for the resonance energy. The data for molecules containing aromatic rings are more reliable, and show the existence of extra resonance accompanying increase in length of a conjugated system. Thus the value 3.77 v.e. for the resonance energy of biphenyl is 0.35 v.e. larger than the resonance energy of two benzene rings, the additional resonance being attributed to the contribution of structures such as , the dots representing single electrons on ortho or para carbon atoms. (These electrons are formally to be considered paired, in order to give a singlet state.) The resonance energy of fluorene should be the same as for biphenyl; the somewhat larger value given in Table V is probably due to error in the reported heat of combustion. For 1,3,5-triphenylbenzene, for which many quinone-type structures must be considered, the additional resonance energy is found to be 1.1 v.e.

For phenylethylene, in which a double bond conjugated with a benzene ring permits structures such as  $=CH-CH_2\cdot$, the additional resonance energy is 0.29 v.e., and for stilbene, with two phenyl groups conjugated with the double bond, it is 0.67 v.e. The conjugation of a triple bond and a benzene ring in phenylacetylene provides extra resonance energy to the extent of 0.45 v.e. The extra resonance energy in 1,2-dihydronaphthalene is 0.32 v.e., in good agreement with the value for phenylethylene. The extra resonance energy in furylethylene is 0.25 v.e.

Benzene derivatives

The extra resonance energy of phenylcyanide, benzoic acid, benzaldehyde, acetophenone, and other benzene derivatives in which a double or triple bond in a side chain is conjugated with the benzene ring should be about the same as for phenylethylene. The average value for these four compounds (Table VI) is 0.21 v.e. In benzophenone the larger extra resonance energy of 0.45 v.e. results from the conjugation of $C=O$ with the two benzene rings.

For symmetrical and unsymmetrical diphenylurea we expect some extra resonance energy in addition to that for two benzene rings and urea because of conjugation of these groups; the values found are 0.55 v.e. and 0.50 v.e., respectively.

In phenol, aniline, and other compounds in which an atom with unshared electron pairs is attached directly to the benzene ring, structures such as  $=\overset{\cdot\cdot}{O}{}^{+}:H$ or especially  $=\overset{\cdot\cdot}{O}{}^{+}:H$ may contribute appreciably to the normal state of the molecule; this is presumably the cause of the extra resonance energy of about 0.25 v.e. found for such compounds (Table VI). The high value for hydroquinone may indicate some additional resonance, the cause of which is not evident.

The quinones

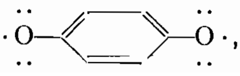
The data given in Table VII for the quinones show large extra resonance energies of 0.57 v.e. in quinone, 1.42 v.e. in anthraquinone, and 1.4 v.e. in phenanthraquinone, in addition to the resonance energy of two benzene rings in the last two compounds. These large values we attribute to structures such as ,

TABLE V. *Resonance energies of biphenyl and related compounds.*

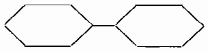
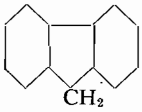
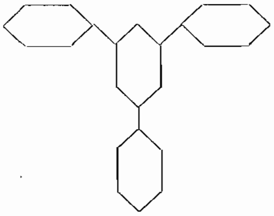
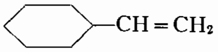
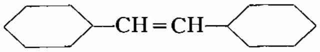
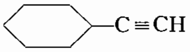
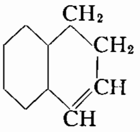
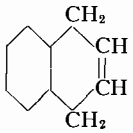
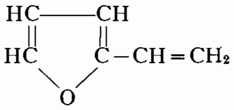
Compound	Formula	Structure	*E*	*E′*	Resonance energy	Extra resonance energy
Biphenyl	$C_{12}H_{10}$		111.91	108.14	3.77	0.35
Fluorene	$C_{13}H_{10}$		119.57	115.44	4.13	0.71
1,3,5-Triphenylbenzene	$C_{24}H_{18}$		219.2	211.3	7.9	1.1
Phenylethylene	C_8H_8		77.42	75.42	2.00	0.29
Stilbene	$C_{14}H_{12}$		131.08	126.99	4.09	0.67
Phenylacetylene	C_8H_6		70.99	68.83	2.16	0.45
1,2-Dihydronaphthalene	$C_{10}H_{10}$		97.05	95.02	2.03	0.32
1,4-Dihydronaphthalene	$C_{10}H_{10}$		96.73	95.02	1.71	0.00
Furylethylene	C_6H_6O		61.28	60.10	1.18	0.25

TABLE VI. *Benzene derivatives.*

Compound	Formula	E	E'	Resonance energy	Extra resonance energy
Phenyl cyanide	C_6H_5CN	66.89	64.97	1.92	0.21
Benzoic acid	C_6H_5COOH	74.91	71.82	3.09	0.18
Benzaldehyde	C_6H_5CHO	69.64	67.78	1.86	0.15
Acetophenone	$C_6H_5COCH_3$	82.24	80.22	2.02	0.31
Benzophenone	$C_6H_5COC_6H_5$	123.37	119.50	3.87	0.45
Sym.-diphenylurea	$C_6H_5NH\cdot CO\cdot NHC_6H_5$	137.35	131.79	5.56	0.55
Unsym.-diphenylurea	$(C_6H_5)_2N\cdot CONH_2$	137.30	131.79	5.51	0.50
Phenol	C_6H_5OH	62.46	60.46	2.00	0.29
Anisole	$C_6H_5OCH_3$	74.37	72.40	1.97	0.26
Hydroquinone	$C_6H_4(OH)_2$	66.83	64.35	2.48	0.77
Aniline	$C_6H_5NH_2$	64.89	62.99	1.90	0.19
Methylaniline	$C_6H_5NHCH_3$	76.99	75.01	1.98	0.27
Dimethylaniline	$C_6H_5N(CH_3)_2$	88.84	87.03	1.81	0.10
Diphenylamine	$(C_6H_5)_2NH$	118.26	114.29	3.97	0.55

in which a benzene (or anthracene or phenanthrene) nucleus is formed by changing the C=O bond to a single bond, leaving an odd electron on each oxygen (the two being formally paired).

TABLE VII. *Resonance energy of quinones.*

Compound	Formula	E	E'	Resonance energy	Extra resonance energy
Quinone	$C_6H_4O_2$	61.01	60.44	0.57	0.57
Anthraquinone	$C_{14}H_8O_2$	130.54	125.70	4.84	1.42
Phenanthraquinone	$C_{14}H_8O_2$	130.5	125.70	4.8	1.4

UREIDES AND PURINES

Values of E for some ureides and purines are given in Table VIII. For many of the substances it was necessary to estimate heats of vaporization or sublimation, in which cases E is given only to 0.1 v.e. The values of E' and the resonance energy $E-E'$ refer to the ketonic structures shown in the table; similar calculations may be easily made for enolic structures, leading usually to somewhat larger resonance energies. The ketonic resonance energies given do not include the energy of resonance of carbonyl between the structures $\mathrm{C}::\ddot{\mathrm{O}}:$ and $\overset{+}{\mathrm{C}}:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:^{-}$, inasmuch as the ketone value $C=O=7.71$ v.e. was used in calculating E'.

The ureides hydantoin, parabanic acid, alloxan, barbituric acid, and 4-methyluracil show resonance energies of between 2.3 v.e. and 3.1 v.e., resulting from resonance of the double bonds among the various possible positions. These values seem not unreasonable when compared with the value 1.59 v.e. for urea. However, we should expect the resonance energy for hydantoin to be somewhat smaller than for the other four rather than somewhat larger.

Allantoin would be expected to have a resonance energy somewhat smaller than the sum for two urea groups and one amide group, since the amide and one urea group interfere through the sharing of NH. The experimental value, 4.7 v.e., is, however, somewhat larger than the corresponding sum $2\times 1.59+0.91=4.09$ v.e.

The resonance energies of the seven purine derivatives given in Table VIII vary in an easily interpretable manner between 2.5 and 5.5 v.e. The value 2.5 v.e. for 7-methylpurine is probably a little too low, for the five-membered ring would be expected to contribute about 1.0 v.e. in addition to the 1.7 v.e. for the benzene-type six-membered ring. The introduction of an oxygen atom, with its accompanying increase in the number of possible positions for the double bond, increases the resonance energy to 3.5 v.e. for 8-oxypurine. Two oxygen atoms, in caffeine, theobromine, and xanthine, lead to an additional increase to 4.4 v.e., 4.7 v.e., and 4.9 v.e., respectively (the differences of the three values being probably without significance). Uric acid, containing three oxygen atoms, has a resonance energy of 5.2 v.e. In guanine, with one oxygen and one nitrogen atom providing extra resonance, the resonance energy is 5.5 v.e. Hence we learn

TABLE VIII. *Ureides and purines.*

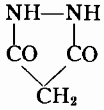
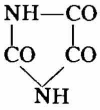
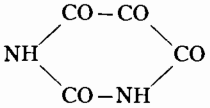
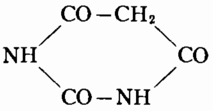
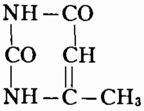
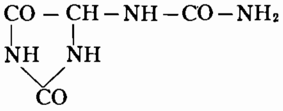
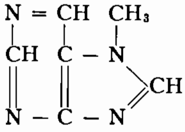
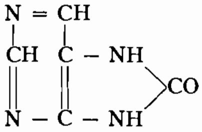
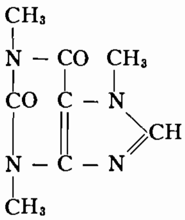
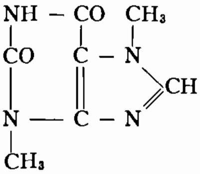
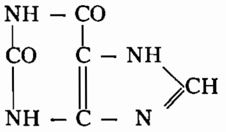
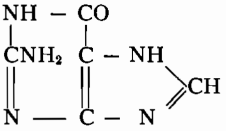
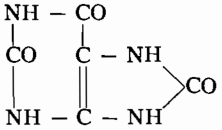
Compound	Formula	Structure	*E*	*E′*	Resonance energy
Hydantoin	$C_3H_4N_2O_2$		49.6	46.5	3.1
Parabanic Acid	$C_3H_2N_2O_3$		49.0	46.4	2.6
Alloxan	$C_4H_2N_2O_4 \cdot H_2O$		70.27	67.95	2.32
Barbituric Acid	$C_4H_4N_2O_3$		61.5	58.7	2.8
4-methyluracil	$C_5H_6N_2O_2$		69.0	66.2	2.8
Allantoin	$C_4H_6N_4O_3$		75.9	71.2	4.7
7-methylpurine	$C_6H_6N_4$		73.6	71.1	2.5
8-oxypurine	$C_5H_4N_4O$		67.1	63.6	3.5
Caffeine	$C_8H_{10}N_4O_2$		108.5	104.1	4.4
Theobromine	$C_7H_8N_4O_2$		96.7	92.0	4.7

TABLE VIII. (*Continued*).

Xanthine	$C_5H_4N_4O_2$		73.0	68.1	4.9
Guanine	$C_5H_5N_5O$		75.4	69.9	5.5
Uric Acid	$C_5H_4N_4O_3$		77.7	72.5	5.2

that each oxygen atom attached to the purine group carries with it a contribution of about 0.9 v.e. to the resonance energy of the molecule, in addition to the resonance energy included in the ketonic C=O bond energy value. The data for guanine indicate that the contribution of a nitrogen atom is still larger, though this may be due to experimental error.

It may be mentioned that in heterocyclic systems as well as in hydrocarbon condensed ring systems the contribution to the normal state of structures associated with all of the possible positions of the double bonds is dependent on the existence of a coplanar arrangement of the pertinent atoms, with bond angles of about 120°, which requires that the rings contain five or six or possibly seven atoms.

CONCLUSION

This study of thermochemical data for a very large number of substances has shown that in every case for which the data are reliable the observed energy of the molecule is equal to that calculated for an assumed distribution of bonds or differs from it in the direction corresponding to greater stability, in accord with the quantum-mechanical requirement that the actual energy for the normal state of any system is the lower limit for values of the energy integral calculated for any wave function. For molecules for which several electronic structures make appreciable contributions to the wave function for the normal state, values of the resonance energy of 0.2 v.e. to 10 v.e. are found. Thus in benzene, pyridine, etc., the resonance energy is about 1.7 v.e. or 39,000 cal./mole, in naphthalene and quinoline about 3.1 v.e., and larger in larger condensed ring systems. In the carboxylic acids and other compounds in which a double bond resonates between two positions the energy of this resonance is about 1.2 v.e.; and in compounds such as urea, with three positions for the double bond, the resonance energy is about 1.8 v.e. Additional resonance energy is also found to accompany any increase in length of the conjugated system, as in phenylethylene, biphenyl, etc. In the preceding paper there has been given the quantum-mechanical discussion of benzene and naphthalene, and a similar treatment of open-chain conjugated systems, biphenyl, the hydroaromatic hydrocarbons and other systems will be published later.

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The Nature of the Chemical Bond. VII. The Calculation of Resonance Energy in Conjugated Systems

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The quantum-mechanical treatment previously applied to benzene, naphthalene, and the hydrocarbon free radicals is used in the calculation of extra resonance energy of conjugation in systems of double bonds, the dihydronaphthalenes and dihydroanthracenes, phenylethylene, stilbene, isostilbene, triphenylethylene, tetraphenylethylene, biphenyl, *o*, *m*, and *p*-diphenylbenzene, and 1,3,5-triphenylbenzene. The calculated values, which are in approximate agreement with empirical values from thermochemical data, are used in the discussion of chemical properties and in the formulation of rules regarding conjugation in overlapping systems.

WITH the aid of the recently developed method[1] of calculating matrix elements for various electronic structures of molecules, based on Slater's treatment,[2] we have carried out a quantum-mechanical discussion of a number of conjugated systems involving double bonds and aromatic nuclei. This discussion, which is presented in the following pages, is closely similar to that previously given benzene and anthracene and the hydrocarbon free radicals,[3] and has similarly led to an illuminating qualitative and semi-quantitative explanation of the properties of the systems.

ADDITION PRODUCTS OF NAPHTHALENE

The measurements of heats of combustion made by Roth and Auwers[4] show that liquid 1,2-dihydronaphthalene, in which the benzene ring is conjugated with a double bond, is 4.9 kcal. more stable than liquid 1,4-dihydronaphthalene, in which this conjugation does not occur. It is probable that these isomers differ by about 0.1 kcal. in heat of vaporization, the boiling points being 206.5 and 212.0°C, respectively, leading to a difference in energy of the gaseous molecules of 5.0 kcal. This information permits us to discuss the effect of change in carbon-carbon distance on the exchange integral between adjacent atoms. A canonical set of fourteen independent structures for 1,2-dihydronaphthalene (in all of which single bonds between adjacent atoms are left unchanged) is shown in Fig. 1. Of these the two unexcited structures 1 and 2 will contribute most to the normal state of the molecule, so that the carbon-carbon distance for the 3–4 bond and for the six bonds of the unbroken benzene ring will be the double-bond distance of 1.38A, and the corresponding exchange integral will be that previously[3] designated by the symbol α, and found to have a value of about -1.5 v.e. The carbon-carbon distance connecting the 3–4 bond with the benzene ring

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* Contribution No. 370.

[1] Linus Pauling, J. Chem. Phys. **1**, 280 (1933). The same calculations could be made by the use of the method of Eyring and Kimball, J. Chem. Phys. **1**, 239 (1933).

[2] J. C. Slater, Phys. Rev. **38**, 1109 (1931).

[3] Linus Pauling and G. W. Wheland, J. Chem. Phys. **1**, 362 (1933).

[4] W. A. Roth and K. v. Auwers, Liebig's Ann. **407**, 145 (1915).

will be somewhat larger, lying somewhere between 1.38 and 1.54A, inasmuch as the structures which make this bond a double bond are first-excited structures, and hence play a subordinate rôle in the normal state of the molecule. The corresponding exchange integral, which we may designate as β, will thus have a somewhat different value from α (presumably smaller in absolute value). The remaining three carbon-carbon distances will have the single-bond value 1.54A, for neither the unexcited nor the first-excited structures make them double bonds. The corresponding exchange integral β' will hence differ from α by an amount somewhat larger than for β.

If we assume that structures 1 and 2 have the same coefficients in the wave function for the normal state, and similarly 3, 4, 5; 6, 7, 8; 9, 10, 11; and 12, 13, 14, we obtain the following secular equation, in which x represents the quantity $(Q-W')/\alpha$, and b the ratio β/α. The energy $W_{1,2}$ of the molecule is equal to $W'-3/2\beta$, the latter term being omitted in the secular equation for convenience.

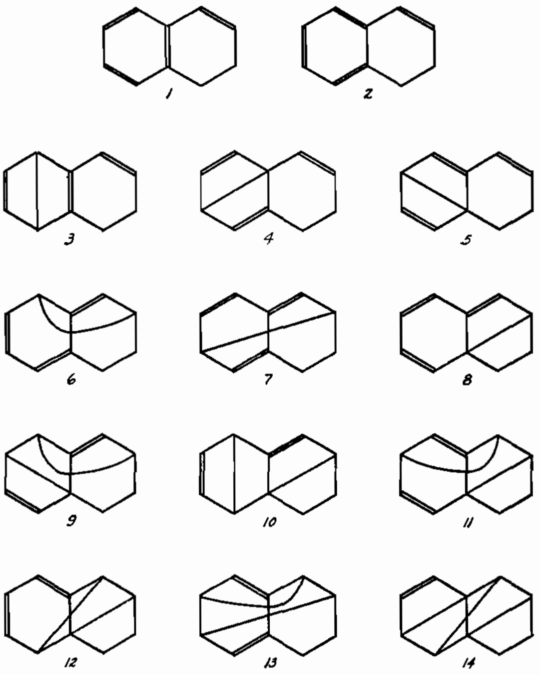


FIG. 1. Complete set of canonical structures for 1,2-dihydronaphthalene.

$$\begin{vmatrix} 5x/2+17/2-5b/4 & 3x+12-3b/2 & 7x/4+25/4+7b/4 & 7x/4+25/4-b/8 & x+4+b \\ 3x+12-3b/2 & 9x/2+27/2-9b/4 & 9x/4+33/4+9b/4 & 9x/4+33/4 & 3x/2+9/2+3b/2 \\ 7x/4+25/4+7b/4 & 9x/4+33/4+9b/4 & 11x/2+7/4+11b/2 & 5x/2+53/8+5b/2 & 5x/2+7/4+5b/2 \\ 7x/4+25/4-b/8 & 9x/4+33/4 & 5x/2+53/8+5b/2 & 11x/2+5/2-11b/4 & 11x/8+4+11b/8 \\ x+4+b & 3x/2+9/2+3b/2 & 5x/2+7/4+5b/2 & 11x/8+4+11b/8 & 5x/2-11/4+5b/2 \end{vmatrix} = 0.$$

Because of the small contribution of the second and third-excited states, we may neglect them, which reduces the equation to a cubic, of the form

$$b^2(198z-63)+b(234z^2+132z-390) + (68z^3+44z^2-884z-582)=0, \quad (1)$$

in which $z=-x-b$.

If as an approximation we assume $b=1(\beta=\beta'=\alpha)$, we find as the pertinent root of this equation $z=2.3062$, corresponding to $W_{1,2}=Q+1.8062\alpha$. A similar treatment applied to 1,4-dihydrobenzene (which involves no interaction between the benzene ring and the double bond) leads to $W_{1,4}=Q+3.6055\alpha-2\beta'$, or, in this case, $Q+1.6055\alpha$. (In this paper as in the previous one interactions involving the single bonds between adjacent atoms are neglected, on the reasonable assumption that they are effectively the same for all the structures considered.) Hence the 1,2 compound is calculated to be more stable than the 1,4 compound by -0.2007α or, for $\alpha=-1.5$ v.e., 0.301 v.e. This is in rough agreement with the experimental value 5.0 kcal. or 0.22 v.e. given above. The comparison indicates that β and β' differ from α by a few percent. If we assume, as is reasonable because of the relative interatomic distances, that β lies midway between β' and α, and that a safe lower limit for the extra stability of the 1,2 compound is 4.6 kcal. or -0.14α, we write as a second equation connecting b and z

$$z=4.2455-2b. \quad (2)$$

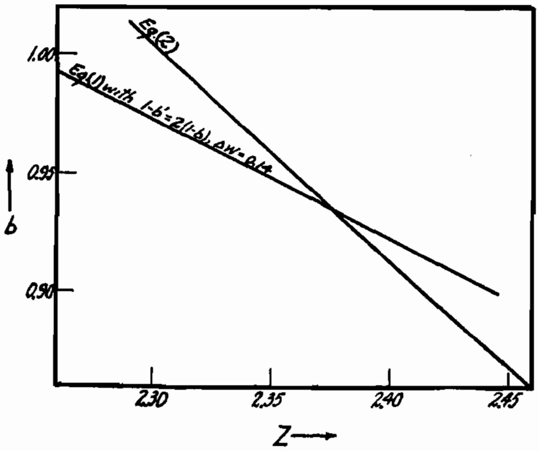


FIG. 2.

The simultaneous solution of Eqs. (1) and (2) is shown in Fig. 2, in which the two curves represent the two relations between the variables. Their intersection corresponds to $\beta = 0.935\alpha$ and $\beta' = 0.87\alpha$, which are thus minimum values for these exchange integrals.

It is probable that the errors introduced by the neglect of all except unexcited and first-excited structures and by equating β and β' to α cancel each other to a considerable extent, especially for more complicated molecules than the dihydronaphthalenes. These approximations are made throughout the rest of this paper.

Calculated resonance energies for $1,2-C_{10}H_{10}$, $1,4-C_{10}H_{10}$, $1,5-C_{10}H_{10}$, and $9,10-C_{10}H_{10}$, the last two involving a chain of four and two chains of two conjugated double bonds (discussed in a following section), are given in Table I. No data are available regarding the two least stable dihydronaphthalenes.

TABLE I. *Calculated resonance energies for dihydronaphthalenes.*

	W	$W-W_{1,2}$	$W-W_{1,2}$
$1,2-C_{10}H_{10}$	$Q+1.8062\alpha$	0	0
$1,4-C_{10}H_{10}$	$Q+1.6055\alpha$	-0.2007α	0.301 v.e.
$1,5-C_{10}H_{10}$	$Q+1.225\alpha$	-0.581α	0.872
$9,10-C_{10}H_{10}$	$Q+0.964\alpha$	-0.842α	1.263

ADDITION PRODUCTS OF ANTHRACENE

The secular equation for 1,2-dihydroanthracene resulting from the consideration of (I) the symmetrical unexcited structure, (II) the two unsymmetrical unexcited structures, (III) the sixteen first-excited structures not involving conjugation of the double bond and the naphthalene nucleus, and (IV) the six first-excited structures involving this conjugation, is

$$\begin{vmatrix} x+5/2 & x/2+7/2 & 35x/8+361/16 & 19x/16+7 \\ x/2+7/2 & 17x/8+103/16 & 19x/2+47 & 35x/16+403/32 \\ 35x/8+361/16 & 19x/2+47 & 557x/8+4627/16 & 427x/32+2599/32 \\ 19x/16+7 & 35x/16+403/32 & 427x/32+2599/32 & 119x/8+595/16 \end{vmatrix} = 0.$$

The pertinent root of this is $x = -4.599$, corresponding to the energy $W_{1,2} = Q - x\alpha - 3\alpha/2 = Q + 3.099\alpha$, of which $Q+2.976\alpha$ results from resonance within the naphthalene nucleus (calculated by neglecting all structures other than the three unexcited and the sixteen naphthalene first-excited structures), and the difference, 0.123α, is the energy of conjugation of the naphthalene nucleus and the double bond. The total energy of 1,4-dihydroanthracene, in which this conjugation does not occur, is $W_{1,4} = Q + 2.976\alpha$, and that of 9,10-dihydroanthracene, involving two unconjugated benzene rings, is $W_{9,10} = Q + 3.190\alpha$ (Table II). Table II could be easily extended to include additional less stable and as yet unprepared dihydroanthracenes and higher addition products. No thermal data are available for comparison with the calculated energy values of Table II.

TABLE II. *Calculated resonance energies for dihydroanthracenes.*

	W	$W-W_{9,10}$	$W-W_{9,10}$
$9,10-C_{14}H_{12}$	$Q+3.190\alpha$	0	0
$1,2-C_{14}H_{12}$	$Q+3.099\alpha$	-0.091α	0.137 v.e.
$1,4-C_{14}H_{12}$	$Q+2.976\alpha$	-0.214α	0.321 v.e.

The resonance energies are essentially independent of the nature of the atoms attached to the nucleus; hydrogen is mentioned for convenience.

It is, however, reasonable to assume that, in the case of closely similar reactions, that reaction leading to the most stable product will occur most easily. This hypothesis leads to a complete explanation of the observed courses of hydrogenation of benzene, naphthalene, and anthracene, which are represented by the following schemes, showing only the reactions for which data are available.[5]

$$C_6H_6+H_2\rightarrow 1,2-C_6H_8+H_2 \rightarrow 1,2,3,4-C_6H_{10}+H_2\rightarrow C_6H_{12}.$$

$$C_{10}H_8+H_2\rightarrow 1,2-C_{10}H_{10}+H_2\rightarrow 1,2,3,4-C_{10}H_{12}.$$

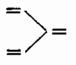
$$C_{14}H_{10}+H_2\rightarrow 9,10-C_{14}H_{12}+H_2 \rightarrow 1,2,3,4-C_{14}H_{14}+2H_2 \rightarrow 1,2,3,4,5,6,7,8-C_{14}H_{18}+3H_2\rightarrow C_{14}H_{24}.$$

With this hypothesis, the calculated stability of the 9,10 addition compound of anthracene provides an explanation of the ease of attack of the 9,10 positions for addition. A similar calculation for phenanthrene shows that for this molecule too the 9,10 positions should be most reactive.

CONJUGATED DOUBLE-BOND SYSTEMS

In Table III are given calculated values of the resonance energy for straight conjugated chains containing two, three, and four double bonds and a branched chain with three double bonds (the list could be easily extended). In each case the secular equation was solved as a quadratic, all first-excited structures being given the same coefficient. No reliable thermochemical data are available for comparison with these values. It may be mentioned that our hypothesis provides no information regarding addition in various positions (1,2 *vs.* 1,4 in dienes), which must instead be discussed on the basis of detailed mechanisms.

TABLE III. *Resonance energies in systems of double bonds.*

System	Number of first-excited structures	Resonance energy
= — =	1	$-0.232\alpha=0.348$ v.e.
= — = — =	3	$-0.482\alpha=0.723$ v.e.
= — = — = — =	6	$-0.725\alpha=1.09$ v.e.
	2	$-0.438\alpha=0.657$ v.e.

PHENYLETHYLENE, STILBENE, ETC.

The secular equation for phenylethylene, in which a phenyl group is conjugated with a double bond, is the same as for 1,2-dihydronaphthalene, and leads to the same value for the resonance energy.

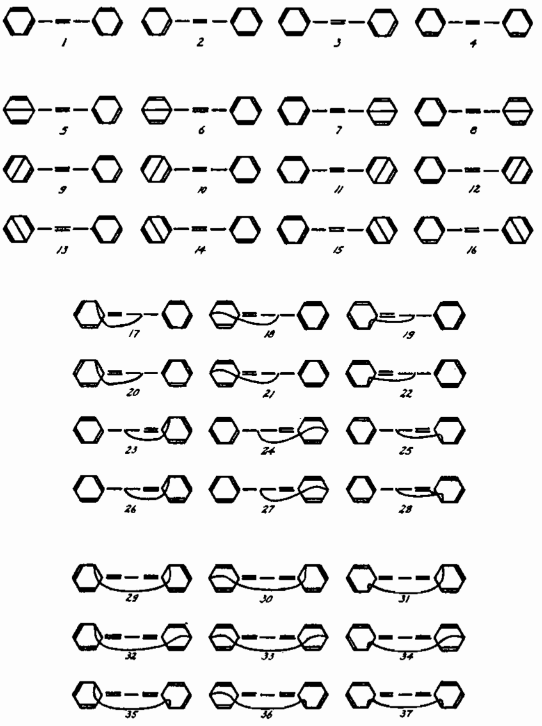


FIG. 3. Unexcited and first-excited canonical structures of sym.-diphenylethylene.

For stilbene, sym.-diphenylethylene, we consider the thirty-seven structures shown in Fig. 3, grouping together the four unexcited structures, the twelve first-excited structures not involving conjugation, the twelve in which there is conjugation of the double bond and a phenyl group, and the nine in which there is conjugation of the two phenyl groups by way of the double bond. This leads to the biquadratic secular equation

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[5] W. Hückel, *Theoretische Grundlagen der organischen Chemie*, 1, p. 359, Akad. Verlag. M. B. H., Leipzig, 1931.

$$\begin{vmatrix} 25x/4+30 & 15x+81 & 35x/4+453/8 & 49x/16+399/16 \\ 15x+81 & 81x/2+207 & 87x/4+1185/8 & 63x/8+519/8 \\ 35x/4+453/8 & 87x/4+1185/8 & 269x/8+1107/8 & 77x/4+753/8 \\ 49x/16+399/16 & 63x/8+519/8 & 77x/4+753/8 & 121x/4+759/8 \end{vmatrix} = 0,$$

which on solution as a biquadratic leads to $W=Q+5.5889\alpha$. The energy the molecule would have without resonance, found by equating the upper left-hand quadratic part of the secular determinant to zero, is $W'=Q+5.1898\alpha$, corresponding to an extra resonance energy of conjugation of 0.3891α.

The secular equation for isostilbene, in which there is no conjugation of the two phenyl groups with each other, is just the cubic equation obtained from the stilbene determinant by omitting the fourth row and column.

The secular equation for triphenylethylene, corresponding to 8, 36, 36, and 36 structures of the four kinds described for stilbene, is

$$\begin{vmatrix} 125x/8+1675/16 & 225x/4+3285/8 & 525x/16+4395/16 & 245x/16+4921/32 \\ 225x/4+3285/8 & 1755x/8+25{,}569/16 & 1935x/16+17{,}019/16 & 231x/4+2379/4 \\ 525x/16+4395/16 & 1935x/16+17{,}019/16 & 2385x/16+31{,}653/32 & 3423x/32+12{,}465/16 \\ 245x/16+4921/32 & 231x/4+2379/4 & 3423x/32+12{,}465/16 & 2959x/16+3985/4 \end{vmatrix} = 0.$$

That for tetraphenylethylene, with 16, 96, 196, and 144 structures, respectively, of these four kinds, is

$$\begin{vmatrix} 625x/16+5375/16 & 375x/2+1725 & 875x/8+17{,}975/16 & 1225x/16+7315/8 \\ 375x/2+1725 & 3825x/4+35{,}685/4 & 4275x/8+91{,}815/16 & 3045x/8+18{,}699/4 \\ 875x/8+17{,}975/16 & 4275x/8+91{,}815/16 & 9175x/16+41{,}245/8 & 12{,}845x/32+273{,}911/64 \\ 1225x/16+7315/8 & 3045x/8+18{,}699/4 & 12{,}845x/32+273{,}911/64 & 74{,}761x/64+557{,}465/64 \end{vmatrix} = 0.$$

The energy values obtained on solution of these equations are given in Table IV.

Conjugated Benzene Rings

For biphenyl we consider four unexcited structures, twelve first-excited structures not involving conjugation, and nine involving conjugation, as shown in Fig. 4. These lead to the secular equation

$$\begin{vmatrix} 25x/4+215/8 & 15x+147/2 & 49x/8+301/8 \\ 15x+147/2 & 81x/2+747/4 & 63x/4+393/4 \\ 49x/8+301/8 & 63x/4+393/4 & 121x/4+319/4 \end{vmatrix} = 0,$$

whose solution is given in Table V.

For ortho, meta, and para diphenylbenzene we consider eight unexcited structures of the type indicated by the letter *A* in Fig. 5, thirty-six first-excited structures of type *B*, and thirty-six of type *C*, in which there is conjugation with the central ring. This includes all first-excited structures for *m*-diphenylbenzene. For ortho and para diphenylbenzene, however, there are in addition nine first-excited structures of type *D*, in which the two end rings are conjugated together. The secular equation for the ortho compound is

$$\begin{vmatrix} 125x/8+775/8 & 225x/4+765/2 & 245x/8+3941/16 & 245x/64+1169/32 \\ 225x/4+765/2 & 1755x/8+11{,}907/8 & 231x/2+1917/2 & 231x/16+4527/32 \\ 245x/8+3941/16 & 231x/2+1917/2 & 5771x/32+7813/8 & 539x/16+3367/16 \\ 245x/64+1169/32 & 231x/16+4527/32 & 539x/16+3367/16 & 121x/4+110 \end{vmatrix}=0.$$

The secular equation for the meta compound is obtained from this by omitting the fourth row and column. That for the para compound is:

$$\begin{vmatrix} 125x/8+775/8 & 225x/4+765/2 & 245x/8+3941/16 & 49x/16+497/16 \\ 225x/4+765/2 & 1755x/8+11{,}907/8 & 231x/2+1917/2 & 399x/32+981/8 \\ 245x/8+3941/16 & 231x/2+1917/2 & 2959x/16+16{,}151/16 & 77x/2+1891/8 \\ 49x/16+497/16 & 399x/32+981/8 & 77x/2+1891/8 & 121x/4+110 \end{vmatrix}=0.$$

For 1,3,5-triphenylbenzene, with 16 unexcited, 96 unconjugated first-excited, and 108 conjugated first-excited structures, the secular equation is

$$\begin{vmatrix} 625x/16+10{,}125/32 & 375x/2+6525/4 & 3675x/32+9135/8 \\ 375x/2+6525/4 & 3825x/4+67{,}545/8 & 9135x/16+23{,}481/4 \\ 3675x/32+9135/8 & 9135x/16+23{,}481/4 & 50{,}265x/64+799{,}227/128 \end{vmatrix}=0.$$

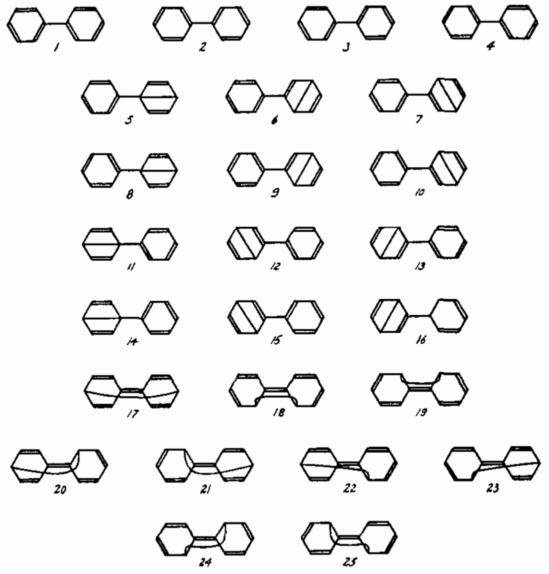

FIG. 4. Unexcited and first-excited structures of biphenyl.

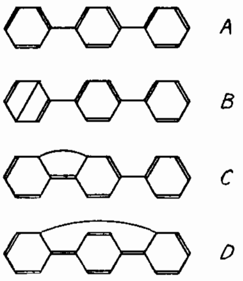

FIG. 5.

TABLE IV. *Calculated resonance energies for phenyl-substituted ethylenes.*

Molecule	W	W'	$W'-W$
Phenylethylene	$Q+3.3062\alpha$	$Q+3.1055\alpha$	$-0.2007\alpha=0.301$ v.e.
Sym. diphenyl-ethylene	$Q+5.589\alpha$	$Q+5.190\alpha$	$-0.389\alpha=0.584$ v.e.
Unsym. diphenyl-ethylene	$Q+5.545\alpha$	$Q+5.190\alpha$	$-0.355\alpha=0.533$ v.e.
Triphenylethylene	$Q+7.804\alpha$	$Q+7.285\alpha$	$-0.519\alpha=0.779$ v.e.
Tetraphenyl-ethylene	$Q+10.080\alpha$	$Q+9.362\alpha$	$-0.719\alpha=1.08$ v.e.

The energy values found on solution of these equations and of the non-conjugated parts of them, together with their differences, the energy of conjugation, are given in Table V.

TABLE V. *Calculated resonance energies for conjugated benzene rings.*

Molecule	W	W'	$W'-W$
Biphenyl	$Q+4.867\alpha$	$Q+4.690\alpha$	$-0.177\alpha=0.266$ v.e.
m-Diphenylbenzene	$Q+7.086\alpha$	$Q+6.785\alpha$	$-0.301\alpha=0.452$ v.e.
p-Diphenylbenzene	$Q+7.094\alpha$	$Q+6.785\alpha$	$-0.309\alpha=0.464$ v.e.
o-Diphenylbenzene	$Q+7.103\alpha$	$Q+6.785\alpha$	$-0.318\alpha=0.477$ v.e.
1,3,5-Triphenylbenzene	$Q+9.273\alpha$	$Q+8.862\alpha$	$-0.411\alpha=0.617$ v.e.

COMPARISON WITH EXPERIMENT

The meager existant results of experiments on heats of combustion, given in the previous paper of this series,[6] are in rough agreement with the theoretical calculations, the discrepancies in most cases lying within the experimental error. The calculated energy of conjugation of a benzene ring and a double bond, 0.30 v.e., is in excellent agreement with the extra resonance energy 0.29 v.e. for phenylethylene. For stilbene and isostilbene[7] the empirical values 0.67 and 0.45 v.e. agree less well with the calculated values 0.58 and 0.53 v.e., respectively. For biphenyl the agreement is good, 0.35 v.e. empirical, 0.27 v.e. calculated; for 1,3,5-triphenylbenzene the difference of 0.5 v.e. between the empirical value 1.1 v.e. and the calculated value 0.62 v.e., while large, may be due to error in the reported heat of combustion or in part in the estimated heat of sublimation.

CONCLUSIONS REGARDING CONJUGATION

The calculations provide us with sufficient information to permit the formulation with considerable confidence of a set of rules regarding conjugation.

A phenyl group is 20 or 30 percent less effective in conjugation than a double bond, and a naphthyl group is less effective than a phenyl group. Thus the resonance energy of biphenyl is only 77 percent of that for two conjugated double bonds, and the ratios of energy of conjugation of a double bond with another double bond, a phenyl group, and a naphthyl group are 1 : 0.86 : 0.53.

If a conjugated system can be resolved into two overlapping parts with a common double bond or benzene ring, and with no conjugation from one part to the other by way of the double bond or benzene ring, the total conjugation energy is 10 or 15 percent less than the sum of the conjugation energies for the two parts. Examples are isostilbene, with conjugation energy 1.77 times that for phenylethylene, metadiphenylbenzene, 1.70 times the biphenyl energy, and branched triene, 1.89 times the diene energy. The conjugation energy of 1,3,5-triphenylbenzene, in which the central benzene ring forms a part of three biphenyl systems, is 23 percent less than three times the biphenyl conjugation energy.

In an overlapping system in which there is conjugation from one part to another by way of a double bond this extra conjugation may counteract the effect of overlapping, so that the total conjugation energy is approximately equal to the sum for the parts. Thus the conjugation energy of stilbene is 1.94 times that for phenylethylene, that for unbranched triene 2.08 times that for diene, and for unbranched tetraene 3.12 times that for diene. A phenyl group is not so effective as a link in a conjugated chain, however; no doubt for the reason that, because of resonance between the two Kekulé structures, the average path between ortho or para positions is three bonds long. In consequence the conjugation energy for *p*-diphenylbenzene is only three percent greater than for the meta compound, and that for the ortho compound (in which the bridge is more effective) only six percent greater.

Conjugation of phenyl groups and double bonds is of quite appreciable effect in stabilizing molecules, as is, of course, evident from the early recognition of the phenomenon by chemists. The extra resonance energy of tetraphenylethylene, amounting to 1.08 v.e., is more than enough to overcome the unsaturation of the double bond, amounting to 0.74 v.e. (the difference in energy of two carbon-carbon single bonds and a double bond), in consequence of which the properties of the substance differ radically from those of an

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[6] L. Pauling and J. Sherman, J. Chem. Phys. 1, 606 (1933).

[7] The value for this compound, omitted from the previous paper, is calculated from the heat of combustion by the methods described there.

unsaturated compound such as ethylene.[8] Using the bond-energy values given in earlier papers,[9] we calculate for ΔH for the reactions $C_2(C_6H_5)_4 + X_2 \rightarrow C_2(C_6H_5)_4X_2$ the values -0.30 v.e., -0.42 v.e., and $+0.24$ v.e. for $X_2 = H_2$, Cl_2, and Br_2, respectively. Assuming that ΔF and ΔH do not differ greatly, these values suggest that tetraphenylethylene will add hydrogen and chlorine but not bromine.[10] This is in agreement with experiment; tetraphenylethylene has been hydrogenated catalytically to tetraphenylethane,[11] and has been shown to add chlorine directly,[12] but it does not add bromine, and attempts to prepare tetraphenyldibromethane have led to tetraphenylethylene itself.[13]

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[8] We are indebted to Professor G. E. K. Branch and to Dr. G. W. Wheland for pointing this out to us.

[9] L. Pauling and J. Sherman, J. Chem. Phys. **1**, 606 (1933); L. Pauling, J. Am. Chem. Soc. **54**, 3570 (1932).

[10] The values of ΔH for addition to a non-conjugated double bond are 1.08 v.e. less than these, so that such addition reactions are all exothermic.

[11] W. H. Zartman and H. Adkins, J. Am. Chem. Soc. **54**, 1668 (1932).

[12] H. Finkelstein, Ber. Dtsch. Chem. Ges. **43**, 1533 (1910); J. F. Norris, R. Thomas and B. M. Brown, ibid. **43**, 2940 (1910). See also J. Schmidlin and R. v. Escher, ibid. **43**, 1153 (1910). The resultant dichlortetraphenylethane decomposes easily, mainly with the liberation of HCl and the formation of tetraphenylethylene with Cl substituted in the para position in one of the phenyl groups.

[13] H. Biltz, Ann. d. Chemie **296**, 231 (1897). H. Finkelstein, reference 12.

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Covalent Radii of Atoms and Interatomic Distances in Crystals containing Electron-Pair Bonds

By

Linus Pauling and **M. L. Huggins**

With 4 figures

1934
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Z. Krist. (A)

(Contribution from Gates Chemical Laboratory, California Institute of Technology, No. 375, and from the Chemical Laboratory of the Johns Hopkins University.)

Covalent Radii of Atoms and Interatomic Distances in Crystals containing Electron-Pair Bonds.

By

Linus Pauling and **M. L. Huggins** in Pasadena and Baltimore.

(With 4 figures.)

Abstract.

A simple quantum-mechanical discussion of the orbitals (one-electron orbital eigenfunctions) of an atom is shown to lead to the possibility of formation of various sets of covalent bonds, differing in number and spatial distribution. Among these are tetrahedral sp^3 bonds, octahedral d^2sp^3 bonds, square dsp^2 bonds, etc. After a discussion of the criteria which may be applied to distinguish crystals of essentially covalent rather than ionic or metallic character, observed interatomic distances are used as a basis for formulating sets of radii corresponding to different bond types, including tetrahedral, octahedral, square, trigonal-prism, and normal-valence bonds. It is found that these radii show various reasonable interrelations, and that they are in general agreement with the interatomic distances determined experimentally, cognizance being taken when necessary of resonance among several electronic structures. A remarkable and puzzling exception is the octahedral radius of manganese in the pyrite-type crystals MnS_2 and $MnTe_2$, the observed value being over 0.30 Å larger than expected. A somewhat detailed discussion is then given of the structures of several crystals, including palladous oxide, niccolite, breithauptite, iodyrite, wolfsbergite, eulytite, and the triiodides of arsenic and bismuth.

Of the three principal classes of crystals, ionic crystals, crystals containing electron-pair bonds (covalent crystals), and metallic crystals, we feel that a good understanding of the first class has resulted from the work done in the last few years. Interionic distances can be reliably predicted with the aid of the tables of ionic radii obtained by Goldschmidt¹) by the analysis of the empirical data and by Pauling²) by a treatment based on modern theories of atomic structure. The stability,

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1) V. M. Goldschmidt, Geochemische Verteilungsgesetze der Elemente. 1926.

2) L. Pauling, J. Am. Chem. Soc. 49, 765. 1927. See also W. H. Zachariasen, Z. Krist. 80, 137. 1931 and Huggins and Mayer, J. chem. Physics 1, Nov. 1933.

crystal energy, and other properties of simple ionic crystals have been extensively discussed by Born, Goldschmidt, Mayer, and others[1]; and the nature of complex ionic crystals has been elucidated by the recent extensive structure determinations of silicates and related minerals carried out mainly by W. L. Bragg[2] and his school and by the formulation[3] of a set of structural principles for such crystals.

The application of the Lewis theory of the electron-pair bond to crystals was begun early by Huggins[4], who in 1922 ascribed to diamond, sphalerite, wurtzite, carborundum, chalcopyrite, pyrite, marcasite, cobaltite, arsenic, antimony, bismuth, and related crystals the electron-pair-bond structures which are now accepted for them, and which were independently suggested for tetrahedral crystals (diamond, sphalerite, wurtzite, carborundum) by Grimm and Sommerfeld[5] four years later. In 1926 Huggins[6] published a set of atomic radii for use in crystals containing electron-pair bonds. Goldschmidt in the same year published "atomic radii" obtained from observed interatomic distances in metallic crystals as well as covalent crystals; more recently[7] he has collected these and additional radii into a table of radii for use in metals and intermetallic compounds.

During the last two years the application of the quantum mechanics to the problem of the nature of the electron-pair bond and the development of a theory of the paramagnetic susceptibility of molecules and crystals containing electron-pair bonds[8] has clarified the field considerably, and has led us to attack the problem of the formulation of a set of principles governing the structure of crystals containing electron-pair bonds, the first step being the discussion of interatomic distances. In the following sections of this paper there are given a discussion of the covalent bond according to the quantum mechanics, the application of criteria as to the nature of the bonds in various crystals to segregate those containing covalent bonds, the determination of sets of electron-pair-bond or covalent radii, and the discussion of the structures of some covalent crystals.

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1) J. Sherman, Chem. Rev. **11**, 93. 1932.

2) W. L. Bragg, Z. Krist. **74**, 237. 1930.

3) Linus Pauling, J. Am. Chem. Soc. **51**, 1010. 1929.

4) M. L. Huggins, J. Am. Chem. Soc. **44**, 1841. 1922. A structure of this type was also assigned to calcite, for which an ionic structure (Ca^{++} and $CO_3^{=}$) is now accepted.

5) H. G. Grimm and A. Sommerfeld, Z. Physik **36**, 36. 1926.

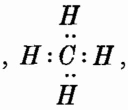
6) M. L. Huggins, Physic. Rev. **28**, 1086. 1926.

7) V. M. Goldschmidt, Trans. Faraday Soc. **25**, 253. 1929.

8) Linus Pauling, J. Am. Chem. Soc. **53**, 1367. 1931.

The Electron-Pair Bond.

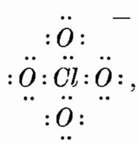
The electron-pair bond as postulated by Lewis consists of two electrons held jointly by two atoms. By assuming that atoms tend to surround themselves with an outer shell of either shared or unshared electron pairs, usually four in number, but sometimes more or less, Lewis accounted for the formation of molecules such as $:\ddot{\underset{..}{F}}:\ddot{\underset{..}{F}}:$, $H:H$,



$H:\overset{H}{\underset{H}{\ddot{\underset{..}{C}}}}:H$,

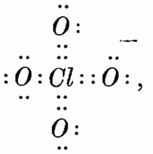
etc., and of crystals such as diamond, in which each atom has an outer shell of four shared electron pairs. The quantum-mechanical treatment of the hydrogen molecule by Heitler and London[1]) and others showed that it is the resonance or interchange energy of the two electrons which causes the electron-pair bond to be stable, and later studies of Heitler and London led to a somewhat more complete formal quantum-mechanical justification of the Lewis theory, aside from the concept of directed valence bonds.

Lewis's theory and Heitler and London's extension permitted the reasonably certain attribution of specific electronic formulas to a great many compounds. In other cases, however, it was possible to set up a number of alternative electronic formulas for a molecule or crystal, and often no sound argument could be advanced supporting any one of them against the others. For example, Lewis gave the perchlorate ion the structure



$\overset{:\ddot{O}:\;\;-}{\underset{:\underset{..}{O}:}{:\ddot{\underset{..}{O}}:\ddot{\underset{..}{Cl}}:\ddot{\underset{..}{O}}:}}$,

while London wrote



$\overset{\ddot{O}:\;\;-}{\underset{\underset{..}{O}:}{:\ddot{\underset{..}{O}}:\ddot{Cl}::\ddot{O}:}}$,

in which three of the oxygen atoms are held by double bonds, and one by a single bond. Other structures deserving consideration are the more ionic ones, such as that containing Cl^{7+} and $O^{=}$. Moreover, the theory permits no predictions regarding the spatial arrangement of bonds, other than the assumed tetrahedral arrangement of four outer pairs.

These questions can often be answered with the aid of a set of rules regarding the properties of electron-pair bonds derived from the quantum mechanics, and of a semi-quantitative method of treatment of bond eigenfunctions leading to information on the strengths and relative orientation of bonds[2]). The rules are the following.

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1) W. Heitler and F. London, Z. Physik **44**, 455. 1927.

2) Linus Pauling, Pr. Nat. Acad. **14**, 359. 1928; J. Am. Chem. Soc. **53**, 1367. 1931. (Hereafter called Ref. I). A detailed treatment of the theory is given by J. C. Slater, Physic. Rev. **38**, 1109. 1931.

1. The single electron-pair bond between two atoms involves one orbital[1] for each atom and one pair of electrons.

2. In such a bond the spins of the electrons are opposed, and hence make no contribution to the magnetic moment of the molecule.

3. Two electrons which form a shared pair cannot take part in forming additional pairs.

4. The main resonance terms for a single electron-pair bond are those involving the two orbitals (one from each atom) associated with the bond.

5. Of two orbitals with the same dependence on r, the one with the larger value in the bond direction will give rise to the stronger bond, and for a given orbital the bond will tend to be formed in the direction in which the orbital has its maximum value.

6. Of two orbitals with the same dependence on ϑ and φ, the one corresponding to the lower energy level for the atom will usually give rise to the stronger bond.

Here r, ϑ, and φ are polar coordinates used in the description of the orbitals of an atom, the nucleus being at the origin of the coordinate system.

We should not expect s orbitals to lead to strong bonds (except in the K-shell), on account of their spherical symmetry. Somewhat stronger bonds, tending to make angles of 90° with each other, are formed by p orbitals. In most cases when bonds are formed, however, the s und p orbitals do not retain their identity, but instead combine linearly to new orbitals especially suited to bond formation. The criterion for the occurrence of this change in quantization or hybridization of bond orbitals involves the relative bond energies for s and p orbitals and hybrid orbitals, and the difference in energy of s and p orbitals in the atom[2].

. It has been found that a simple and powerful approximate method of treatment of bond orbitals can be developed by assuming that the dependence on r of s, p, and d orbitals corresponding to about the same energy is nearly the same, so that the r-portion of the resonance terms can be taken as the same. The consideration of the ϑ, φ portion of the orbitals then leads directly to the determination of the best bond orbitals which can be formed under given circumstances.

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[1] Following Mulliken, we shall use the word "orbital" to represent a one-electron orbital eigenfunction of an atom.

[2] A detailed discussion of this question and of the assumptions underlying our approximate treatment of bond strengths is given in the interesting papers of J. H. Van Vleck, J. chem. Physics 1, 177, 219. 1933.

Putting

$$\Psi_{n0}(r,\vartheta,\varphi) = R_{n0}(r)\, s(\vartheta,\varphi) \quad \text{for } s \text{ orbitals,}$$

$$\left.\begin{array}{l} \Psi_{n1}(r,\vartheta,\varphi) = R_{n1}(r)\, p_x(\vartheta,\varphi) \\ \qquad\qquad\qquad\qquad\quad p_y(\vartheta,\varphi) \\ \qquad\qquad\qquad\qquad\quad p_z(\vartheta,\varphi) \end{array}\right\} \text{for } p \text{ orbitals,}$$

$$\left.\begin{array}{l} \Psi_{n2}(r,\vartheta,\varphi) = R_{n2}(r)\, d_z(\vartheta,\varphi) \\ \qquad\qquad\qquad\qquad\quad d_{x+z}(\vartheta,\varphi) \\ \qquad\qquad\qquad\qquad\quad d_{y+z}(\vartheta,\varphi) \\ \qquad\qquad\qquad\qquad\quad d_{x+y}(\vartheta,\varphi) \\ \qquad\qquad\qquad\qquad\quad d_x\quad(\vartheta,\varphi) \end{array}\right\} \text{for } d \text{ orbitals,}$$

the parts s, p_x, etc. of the orbitals depending on ϑ and φ, normalized to 4π, are

$$\begin{array}{ll} s = 1 & d_{x+z} = \sqrt{15}\,\sin\vartheta\,\cos\vartheta\,\cos\varphi \\ p_x = \sqrt{3}\,\sin\vartheta\,\cos\varphi & d_{y+z} = \sqrt{15}\,\sin\vartheta\,\cos\vartheta\,\sin\varphi \\ p_y = \sqrt{3}\,\sin\vartheta\,\sin\varphi & d_{x+y} = \sqrt{15/4}\,\sin^2\vartheta\,\sin 2\varphi \\ p_z = \sqrt{3}\,\cos\vartheta & \quad d_x = \sqrt{15/4}\,\sin^2\vartheta\,\cos 2\varphi\,. \\ d_z = \sqrt{5/4}\,(3\cos^2\vartheta - 1) & \end{array}$$

Now by Rule 5 the bond-forming power of an orbital in a given direction increases as the magnitude of the orbital in that direction increases, and it may be conveniently expressed in a qualitative manner by that magnitude, which we shall call the bond-strength of the orbital. Thus the maximum bond-strength of an s orbital is 1, that of a p orbital $\sqrt{3} = 1.732$, and that of a d orbital $\sqrt{5} = 2.237$. In constructing a bond orbital our problem is to find a normalized linear combination of these orbitals which has a large concentration in one direction. When two or more bonds are formed by an atom, a bond orbital must be constructed for each bond with large concentration in the direction of that bond, and these orbitals must be mutually orthogonal. The nature of the bond orbital depends on the orbitals available for linear combination. By Rule 6 orbitals corresponding to unstable states of the atom will not be useful. Thus in carbon or any atom of the first horizontal row of the periodic system the $2s$ and $2p$ levels of the L-shell are stable, and all outer levels, in the M, N, etc. shells, are very unstable, so that the only orbitals to be considered are $2s$, $2p_x$, $2p_y$, and $2p_z$. In general ns and np are to be grouped together, for the difference in term values is usually small. This group of four orbitals ns, np_x, np_y, and np_z gives rise to the octet of Lewis and Langmuir. Even in the M-shell and outer shells where there is a group of five d orbitals they usually correspond to energy values considerably higher than the *s* and *p* levels of the same shell (the *p*—*d* separation being over twice the *s*—*p* separation) and so are not usually brought into use in forming bond orbitals. There are exceptions to this rule, however, especially for very heavy atoms. *d* orbitals usually become important when the *d* level of a shell lies close to the *s* and *p* levels of the next outer shell, as $3d$, $4s$, $4p$ for the iron group, $4d$, $5s$, $5p$ for the palladium group, and $5d$, $6s$, $6p$ for the platinum group. Then the nature of the bond orbitals which can be formed depends very largely on the number of available *d* orbitals. The principal types of bond orbitals other than the *p* orbitals already mentioned are described in the following paragraphs.

The most important case is that of s, p_x, p_y, and p_z. On setting up a general expression for a linear combination of these and varying the coefficients to make the bond-strength a maximum (for details of the calculation see Ref. I), it is found that the best *sp* bond orbital which exists, shown in Fig. 1, has a strength of 2.000. The orbital corresponding to a second bond formed by this atom must be orthogonal to this; on evaluating it it is found to be equivalent to the first, with a strength of 2.000, and to make an angle of 109° 28′, the tetrahedral angle, with it. A third and a fourth equivalent orbital, also at tetrahedral angles and orthogonal to the others, can be constructed. These four may be written as

$$\begin{aligned}\psi_{111} &= \tfrac{1}{2}(s + p_x + p_y + p_z)\\ \psi_{1\bar{1}\bar{1}} &= \tfrac{1}{2}(s + p_x - p_y - p_z)\\ \psi_{\bar{1}1\bar{1}} &= \tfrac{1}{2}(s - p_x + p_y - p_z)\\ \psi_{\bar{1}\bar{1}1} &= \tfrac{1}{2}(s - p_x - p_y + p_z).\end{aligned}$$

Thus we have shown that when *s* and *p* orbitals are available and *s*—*p* quantization is broken an atom can form four (or fewer) equivalent bonds which are directed towards tetrahedron corners. To the approximation involved in these calculations the strength of a bond is independent of the nature of other bonds. This result gives us at once the justification for the tetrahedral carbon atom and other tetrahedral atoms, such as silicon, germanium, and tin in the diamond-type crystals of the elements and, in general, all atoms in tetrahedral structures.

In bivalent nickel, palladium, or platinum there are eight electrons in the outer *d* subshell. Putting them two to an orbital, they occupy a minimum of four of the five *d* orbitals, leaving only one *d* orbital available for bond formation through combination with s, p_x, p_y, and p_z of the next outer shell. It is found that only four strong bond orbitals can be formed. These four lie in a plane and are directed towards the four corners of a

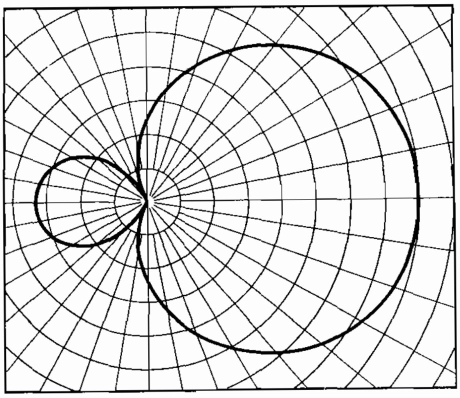

Fig. 1. Polar graph showing the dependence on ϑ and φ of a tetrahedral bond orbital. The value of $|\psi|$ in cross-section is shown; the function is cylindrically symmetrical about the midline of this cross-section.

square so that we may conveniently call them square bond orbitals. They have a strength of 2.694. The fifth orbital, p_z, has its maxima normal to the plane. Usually it is not engaged in bond formation, on account of its small strength 1.732. Square bond orbitals are involved in $K_2Ni(CN)_4$, K_2PdCl_4, K_2PtCl_4, $KAuCl_4$, etc.

When six or fewer d electrons are present there are two d orbitals available for bond formation, which, on combination with s, p_x, p_y, and p_z, are found to give rise to six equivalent d^2sp^3 orbitals of strength 2.923, with their maxima directed towards the corners of a regular octahedron. These octahedral bond orbitals are involved in a great many complexes, such as $[Co(CN)_6]^{\equiv}$, $[PtCl_6]^{=}$, etc, and are of great importance in crystals containing transition group elements.

When more d orbitals are available, six stronger equivalent eigenfunctions with their maxima directed towards the corners of a trigonal prism of unit axial ratio can be formed[1]. The bond-strength of these is 2.985, nearly equal to the maximum 3.000 possible for dsp orbitals.

It is probable that eight equivalent bond orbitals can be constructed when four d orbitals are available, as in $[Mo(CN)_8]^{==}$ and $[W(CN)_8]^{==}$. The arrangement of these in space has not yet been determined either experimentally or theoretically.

The Determination of the Type of Bond in Crystals. Resonance of Molecules and Crystals Among Several Electronic Structures.

Questions such as, for example, whether sphalerite contains Zn^{++} and $S^{=}$ ions or has a covalent structure similar to that of diamond, and whether ionic or covalent bonds are present in complexes such as $[FeF_6]^{\equiv}$, $[Fe(CN)_6]^{\equiv}$, etc., have been extensively discussed; it has, indeed, until recently not been at all clear whether or not they could be definitely

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1) These were discovered by R. Hultgren, Physic. Rev. **40**, 891. 1932.

answered. The quantum mechanics has thrown much light on this subject[1]. By the methods developed by Slater it is possible to formulate a wave function corresponding to a given Lewis structure for a molecule or crystal, and it has been found that for many molecules and crystals such a wave function provides a good approximation to the normal state. In other cases, however, two or more such functions may be formulated which correspond to nearly the same energy value. If these functions satisfy certain conditions permitting them to combine with one another, in particular if they have the same multiplicity[2], then a more general wave function formed by linear combination of these will provide a better approximation to the normal state than any one of the original functions. The molecule or crystal is then said to resonate among the various electronic structures corresponding to the original wave functions. This resonance phenomenon is closely similar to that discovered by Heisenberg and Dirac in treating many-electron atoms and applied by Heitler and London to the hydrogen molecule. It should be pointed out that the resonance obtained depends on the initial choice of wave functions. For example, if hydrogen-atom wave functions are selected originally in discussing the hydrogen molecule-ion H_2^+, as was done by Pauling[3], then the electron may be said to resonate between the two protons; on the other hand, resonance does not appear in Burrau's treatment[4] of the molecule-ion by the numerical solution of the wave equation for an electron in the field of two protons. It is consequently the lucidity and convenience of a treatment based on Lewis electronic structures (with some extensions, such as the one-electron bond, the three-electron bond, etc.) which recommends their choice in formulating initial wave functions and discussing their combination.

Arguments based mainly on bond energies[5] and interatomic distances[6] have recently led to the determination of the normal electronic structures of a number of molecules. The hydrogen halides resonate between the extreme ionic structure H^+X^- and the covalent structure $H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{X}}:$, the contribution of the former being largest for HF and of the latter for HI.

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1) For a detailed discussion see L. Pauling, J. Am. Chem. Soc. 54, 988. 1932.

2) That is, the same number of unpaired electrons (one less than the multiplicity of the state).

3) L. Pauling, Chem. Rev. 5, 173. 1928.

4) Ø. Burrau, Det. Kgl. Danske Vid. Selsk. Math.-fys. Meddeleker 7, 14. 1927.

5) L. Pauling and D. M. Yost, Pr. Nat. Acad. 18, 414. 1932; L. Pauling, J. Am. Chem. Soc. 54, 3570. 1932.

6) L. Pauling, Pr. Nat. Acad. 18, 293, 498. 1932.

Carbon monoxide resonates between the structures $:C::\ddot{O}:$ and $:C:::O:$, nitrous oxide between the structures $:\ddot{N}::N::\ddot{O}:$ and $:N:::N:\underset{\cdot\cdot}{\ddot{O}}:$, etc.

In such cases as these it is evident that a continuous transition from one extreme structure to another could occur. If, however, the structures have different multiplicities, they cannot be combined with one another (so long as spin-orbit interactions are negligible), so that the transition from one extreme bond type to the other would be effectively discontinuous.

Both the ionic and the covalent structure of sphalerite, for instance, are singlet structures, with no unpaired electrons, so that either extreme or any intermediate is possible, and in such a case evidence from various properties of the particular substance must be considered to decide which extreme is more closely approached. On the other hand, in a crystal such as $(NH_4)_3FeF_6$ or $(NH_4)_3Fe(CN)_6$ the lowest ionic state of the $[FeX_6]^{\equiv}$ complex does not combine with the lowest covalent state, so that the transition from one extreme to the other is discontinuous. The actual state of the complex in the crystal can be determined from the multiplicity. With an ionic state, Fe^{+++} and $:\underset{\cdot\cdot}{\ddot{F}}:^-$ or $(:C:::N:)^-$, the F^- or $(CN)^-$ groups contain no unpaired electrons. Fe^{+++} contains five d electrons, which, in accordance with the rules of line spectra, distribute themselves among the five $3d$ orbitals in such a way as to avoid pairing unless required. In this case they remain unpaired, and the ion assumes a sextet state, ${}^6S$, the state of the complex being ${}^6\Sigma$. If covalent bonds are formed, two of the d orbitals are used in the octahedral d^2sp^3 bonds, leaving only three d orbitals for the five d electrons. Hence two pairs are formed, leaving one unpaired electron, and the complex[1] acquires the doublet state, ${}^2\Sigma$. The actual multiplicity, r, of the complex can be determined experimentally from the paramagnetic susceptibility, the magnetic moment being given by the equation

$$\mu = \sqrt{r^2 - 1} = 2\sqrt{S\,(S+1)}\,.$$

S is the spin quantum number. The expected magnetic moments for a sextet and a doublet state are 5.91 and 1.73 respectively, measured in Bohr magnetons. The values calculated from the observed paramagnetic susceptibilities of the crystals are 5.88 for $(NH_4)_3FeF_6$ and 2.0 for

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[1] On account of the quenching of the orbital mechanical and magnetic moment of atoms on bond formation, all electron-pair-bond complexes are to be represented as Σ states.

Table I. Predicted Magnetic Moments of Complexes Containing Transition Elements.

			For ion or $4sp^3$ (tetrahedral) bonds	For 4 dsp^2 (square) bonds	For 6 d^2sp^3 (octahedral) bonds	For 8 d^4sp^3 bonds
$K^{I}\,Ca^{II}\,Sc^{III}\,Ti^{IV}$, etc.	$Rb^{I}\,Sr^{II}\,Y^{III}\,Zr^{IV}\,Nb^{V}\,Mo^{VI}$	$Cs^{I}\,Ba^{II}$—$Hf^{IV}\,Ta^{V}\,W^{VI}$	0.00	0.00	0.00	0.00
V^{IV}	$Nb^{IV}\,Mo^{V}$	W^{V}	1.73	1.73	1.73	1.73
$V^{III}\,Cr^{IV}$	$Mo^{IV}\,Ru^{VI}$	$W^{IV}\,Os^{VI}$	2.83	2.83	2.83	0.00
$V^{II}\,Cr^{III}\,Mn^{IV}$	Mo^{III}		3.88	3.88	3.88	
$Cr^{II}\,Mn^{III}\,Fe^{IV}$	$Mo^{II}\,Ru^{IV}$	Os^{IV}	4.90	4.90	2.83	
$Mn^{II}\,Fe^{III}\,Co^{IV}$	Ru^{III}	$Os^{III}\,Ir^{IV}$	5.91	3.88	1.73	
$Fe^{II}\,Co^{III}$	$Ru^{II}\,Rh^{III}\,Pd^{IV}$	$Ir^{III}\,Pt^{IV}$	4.90	2.83	0.00	
$Co^{II}\,Ni^{III}$	Rh^{II}		3.88	1.73		
Ni^{II}	$Rh^{I}\,Pd^{II}\,Ag^{III}$	$Pt^{II}\,Au^{III}$	2.83	0.00		
Cu^{II}			1.73			
$Cu^{I}\,Zn^{II}\,Ca^{III}\,Ge^{IV}$, etc.	$Ag^{I}\,Cd^{II}\,In^{III}\,Sn^{IV}\,Sb^{V}\,Te^{VI}$	$Au^{I}\,Hg^{II}\,Tl^{III}\,Pb^{IV}\,Bi^{V}\,Po^{VI}$	0.00			

$K_3Fe(CN)_6$. Accordingly we can say with certainty that the $[FeF_6]^{\equiv}$ ion contains essentially ionic bonds, and the $[Fe(CN)_6]^{\equiv}$ ion covalent bonds.

Further statements can be made with the aid of the available data. In Table I, taken from Ref. I, there are given the magnetic moments for transition atoms in various conditions. Magnetic moments for these atoms in a few crystals calculated from the observed susceptibilities with the use of Curie's law and the Langevin equation are given in Table II. It is seen on reference to Table IV of Ref. I that in most compounds atoms of the palladium and platinum groups form covalent bonds. The iron-group atoms form covalent bonds with cyanide, sulfur, etc., but usually ionic or ion-dipole bonds with H_2O, NH_3, SO_4, F, Cl, Br, I, etc. The presence of some covalent bonds facilitates the formation of more; thus five CN bonds in $[Fe(CN)_5NH_3]^{\equiv}$ stabilize a covalent bond to NH_3.

In the discussion so far it has been assumed that d

Table II. Observed Magnetic Moments of Atoms of Transition Elements in Crystals[1]).

Ionic or Ion-dipole Bonds		Octahedral Covalent Bonds	
	μ		μ
$(NH_4)_3FeF_6$ [2])	5.88	$K_3Fe(CN)_6$	2.0
$(NH_4)_2FeF_5 \cdot H_2O$ [2])	5.91		
$FeCl_3$	5.84		
$(NH_4)_2FeCl_5 \cdot H_2O$	5.45		
$FeSO_4 \cdot 7H_2O$	4.99	$K_4Fe(CN)_6 \cdot 3H_2O$	0.00
$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	5.33	$Na_3Fe(CN)_5 \cdot NH_3$	0.00
$FeCO_3$	5	FeS_2 (pyrite)	0.5
$FeCl_2$	5.4		
$FeBr_2$	5.4		
FeI_2	5.4		
$FeCl_2 \cdot 6NH_3$	5.4		
$CoSO_4 \cdot 7H_2O$	4.65		
$CoSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	4.56		
$Co(NH_3)_6Cl_2$	5		
$MnCl_2$	5.66		
$MnBr_2$	5.83		
MnI_2	5.81		
$MnSO_4$	5.62		
$Mn(NO_3)_2 \cdot 6H_2O$	5.51		
MnF_2	5.77		

orbitals of an inner shell contribute to the formation of bond orbitals. Under certain conditions the *d* orbitals of the outermost shell of an atom may play a part. Thus in PCl_5 there are five bonds formed from the $3s$, $3p$, and $3d$ orbitals, and in IF_7 there are seven bonds formed from $5s$, $5p$, and $5d$ orbitals. Other examples are *Sn*, *Sb*, *Te*, *I*, etc. with coordination number six, as in K_2SnCl_6, $KSb(OH)_6$, K_2TeBr_6, $K_2H_3IO_6$, etc.

When the multiplicity of a complex is the same for ionic or ion-dipole bonds and for covalent bonds, the decision as to which extreme bond type is the more closely approached in any actual case must be made with the aid of less straightforward arguments. Sometimes theoretical energy diagrams can be constructed with sufficient accuracy to decide the question. A discussion of crystals based on the Born-Haber thermochemical cycle has been given by Rabinowitsch and Thilo[3]), and more accurate but less extensive studies have been made by Sherman and Mayer[4]).

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[1]) The data are taken mostly from the International Critical Tables.

[2]) E. Cotton-Feytis, Ann. Chim. **4**, 9. 1925.

[3]) E. Rabinowitsch and E. Thilo, Z. physikal. Ch. (B) **6**, 284. 1930.

[4]) J. Sherman, Chem. Rev. **11**, 93. 1932. J. E. Mayer, J. chem. Physics **1**, 327. 1933.

Sometimes the atomic arrangement of a crystal is such as not to permit the formulation of a covalent structure. This is the case for the sodium chloride arrangement, as the alkali halides do not contain enough electrons to form bonds between each atom and its six equivalent nearest neighbors. This criterion must be applied with caution, however, for in some cases electron pairs may jump around in the crystal, giving more bonds than there are electron pairs, each bond being of an intermediate type. It must also be mentioned that determinations of the atomic arrangement are sometimes not sufficiently accurate to provide evidence on this point; an atom reported equidistant from six others may be somewhat closer to three, say, than to the other three.

Agreement or non-agreement with the rules governing the structures of ionic crystals also gives evidence regarding the bond type. The complex silicates, which conform excellently to the rules, are probably largely ionic in nature. The tetrahedral arrangement of four oxygen atoms about a silicon atom would be expected whether the bonds are ionic or covalent. An ionic structure would allow the oxygen bonds to assume any angles, large angles being favored, whereas covalent bonds of oxygen would tend to the angles 90° or 109.5°. The observed angles of 180° in β-tridymite suggest that the bonds are largely ionic, and the smaller angles in the α-forms and in quartz suggest that the bonds may also have considerable covalent character. Corundum and hematite contain coordinated octahedra which share faces with one another, and the edges of these octahedra are shortened, as is expected for ionic crystals. The shared octahedral edges in rutile, anatase and brookite are similarly shortened. But the shared edges of octahedra in marcasite are larger than unshared edges, an indication that in this substance the bonds are not ionic. In As_4O_6 three of the six oxygen atoms about each arsenic atom are closer to it than the other three, and an ionic structure provides no explanation of this fact. The observed square arrangement of four chlorine atoms about each platinum atom in K_2PtCl_4 and the trigonal prism of sulfur atoms about molybdenum in molybdenite are not expected for crystals built of ions. These atomic arrangements are, on the other hand, just those expected if covalent bonds are formed. Such agreement or disagreement with the rules governing covalent bonds, especially bond angles, is another valuable criterion of bond type. Light electronegative atoms such as oxygen can form only p-bonds or tetrahedral bonds, at angles of about 90°—110°. The structure of cuprite is such as to surround each oxygen by four copper atoms, so that covalent bonds may well be present in Cu_2O (and Ag_2O).

Ionic bonds may be fully as strong as covalent bonds, so that properties such as hardness, solubility, melting point, ionization in solution, and chemical character are not especially valuable criteria as a rule. Sometimes comparison of properties with those of compounds of known bond type permits reasonably certain conclusions to be drawn. Thus the similarity in physical properties as well as in atomic arrangement of *SiC*, *AlN*, and diamond suggests that all three substances contain covalent bonds. *PbS* is like FeS_2, MoS_2, etc. in properties rather than like *CaS*, so that it is improbable that *PbS* is an ionic substance.

Covalent Radii of Atoms.

We have constructed a number of sets of atomic radii for use in compounds containing covalent bonds. These radii have been obtained from the study of observed interatomic distances. They are not necessarily applicable only to crystals containing pure covalent bonds (it is indeed probable that very few crystals of this type exist); but also to crystals and molecules in which the bonds approach the covalent type more closely than the ionic or metallic type. The crystals considered to belong to this class are "tetrahedral" crystals, pyrite and marcasite-type crystals, and others which have been found on application of the various criteria discussed in the preceding section to contain covalent bonds or bonds which approach this extreme.

Standard Tetrahedral Radii. Table III, which is closely similar to the table published by Huggins[1]) in 1926, contains radii for atoms which form four covalent bonds involving the four tetrahedral sp^3 orbitals (see also Fig. 2). These radii are primarily for use in tetrahedral crystals (Strukturbericht types *B*3, *B*4, *B*5, *B*6, *B*7, etc.), but are also valid for tetrahedral atoms in other crystals.

In constructing this table, the radii for *C*, *Si*, *Ge*, and *Sn* were taken as half the observed interatomic distances in diamond-type crystals of the elements. It was next

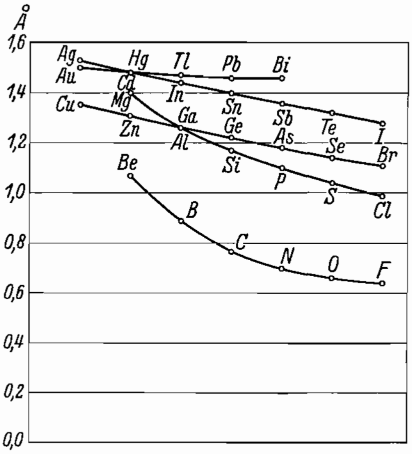

Fig. 2. Tetrahedral radii of atoms forming sp^3 bonds.

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[1]) M. L. Huggins, Physic. Rev. 28, 1086. 1926.

tentatively assumed that (*S*) equals half of *S*—*S* in pyrite, FeS_2, and hauerite, MnS_2. (The symbol (*S*) means the radius of sulfur, *S*—*S* the distance between two sulfur atoms.) Using Ewald's values for the parameters, *S*—*S* equals 2.10 Å in the former and 2.12 Å in the latter. Parker and Whitehouse obtain the value 2.14 Å in pyrite. We therefore take *S*—*S* = 2.12 Å and (*S*) = 1.06 Å. The radii of *Zn*, *Cd*, and *Hg* were then obtained by subtracting this sulfur radius from the observed interatomic distances in their sulfides, and from these radii and the interatomic distances in the selenides and tellurides radii for *Se* and *Te* were calculated. The radius of oxygen was obtained from (*Zn*) and *Zn-O*. Smooth curves were then drawn for each row of the table in such a way as to give as good agreement as possible with the observed distances in other tetrahedral crystals involving only elements in these rows. It was then noticed that whereas the radius of iodine obtained in this way was 0.02 Å less than half of *I*—*I* in I_2 (from band spectral data), the chlorine radius was 0.01 Å greater than half of *Cl*—*Cl* in Cl_2 and the fluorine radius was also about the same amount greater than half of *F*—*F* in F_2. As it seems unreasonable that the discrepancy should be in different directions for *Cl* and *I*, the radius of sulfur was taken as 1.04 Å, and the above procedure repeated to obtain most of the other radii in the table. The agreement with the observed distance in F_2 and Cl_2 is now perfect; a discussion of the discrepancy in the case of I_2 is given in the following section. The slight disagreement (which is hardly larger than the possible experimental error) between (*S*) and $\frac{1}{2}$ (*S*—*S*) in pyrite and haue-

Table III.

Standard Tetrahedral Radii.

	Be	*B*	*C*	*N*	*O*	*F*
	1.07	0.89	0.77	0.70	0.66	0.64
	Mg	*Al*	*Si*	*P*	*S*	*Cl*
	1.40	1.26	1.17	1.10	1.04	0.99
Cu	*Zn*	*Ga*	*Ge*	*As*	*Se*	*Br*
1.35	1.31	1.26	1.22	1.18	1.14	1.11
Ag	*Cd*	*In*	*Sn*	*Sb*	*Te*	*I*
1.53	1.48	1.44	1.40	1.36	1.32	1.28
Au	*Hg*	*Tl*	*Pb*	*Bi*		
1.50	1.48	1.47	1.46	1.46		

rite may indicate that the radii should show a small dependence on the structure of the crystal.

The radii in the lowest row of the table were obtained by a number of approximate considerations. For instance, if we assume the bismuth radius to bear the same ratio to the interatomic distance in elementary bismuth as in the case of arsenic and antimony, we obtain $(Bi) = 1.46$—1.47 Å. A similar conclusion is reached from a study of $NiSb$ and $NiBi$ (with the nickel arsenide structure). Although the structures of the aurous halides have not been determined, it may be pointed out that if they are assumed to be tetrahedral ($B3$ or $B4$) the interatomic distances in the chloride, bromide, and iodide calculated from the observed densities[1]) are 2.52, 2.66, and 2.75 Å, to be compared with 2.49, 2.66, and 2.78 Å, respectively, from our table.

The radius curve for the first row was extrapolated smoothly to a value of (Be) giving good agreement with Be—S and Be—Se. This value for the beryllium radius may be in error by as much as 0.05 Å, for it is probable that several perturbing effects enter in the case of beryllium compounds. As is seen from Table IV, Be—O observed is about 0.09 Å less than the sum of the radii. This we believe to be largely or entirely due to the partially ionic nature of the bonds in this crystal, the properties of which are equally compatible with an ionic and a covalent structure. The large observed interatomic distance in $BeTe$ may be due to the effect of contact (large repulsion) between the large tellurium atoms, a phenomenon similar to "anion contact" and "double repulsion" in ionic crystals. This effect may also be important in $MgTe$.

In the foregoing treatment the assumption of additivity of interatomic distances in the compounds under discussion has been tacitly made. Examination of Table IV shows that this assumption is approximately substantiated by experiment. The agreement between the observed distances and the calculated radius sums is excellent in most cases. Aside from those just discussed, the exceptional crystals are AlN and SiC with observed interatomic distances slightly smaller than the radius sums. It seems doubtful that these deviations are to be attributed to a partially ionic character of the bonds, and the number of other factors which might conceivably be operative is so large that no single one can be selected with confidence as responsible.

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1) W. Biltz, Z. anorg. Ch. **159**, 96. 1926.

Table IV.

Comparison of Radius Sums from Table III with Observed Interatomic Distances in Tetrahedral Crystals.

(The upper number in each case is the radius sum)

C 1.54 *A*4 1.54 *B, E*	*Si* 2.34 *A*4 2.33 *De* 2.34 *Ge, L* 2.35 *Hul, KR, P,* 1) 2)	*Ge* 2.44 *A*4 2.43 *K, G* 2.44 *Hul*	*Sn* 2.80 *A*4 2.80 *K*	*SiC* 1.94 *B*3,5,6,7 1.90 *Ot* 1.88 3)
AlN 1.96 *B*4 1.89 *Ot*	*AlP* 2.36 *B*3 2.35 *Na* 2.36 *G*	*AlAs* 2.44 *B*3 2.43 *Na* 2.44 *G*	*AlSb* 2.62 *B*3 2.64 *G* 2.65 *OP*	
	GaP 2.36 *B*3 2.35 *G*	*GaAs* 2.44 *B*3 2.44 *G*	*GaSb* 2.62 *B*3 2.64 *G*	
			InSb 2.80 *B*3 2.79 *G*	
BeO 1.73 *B*4 1.64 *A, Haa* 1.65 *McK, G*	*BeS* 2.11 *B*3 2.10 *G*	*BeSe* 2.21 *B*3 2.22 *G*	*BeTe* 2.39 *B*3 2.43 *G*	
			MgTe 2.72 *B*4 2.76 *G*	
ZnO 1.97 *B*4 1.96 *B* 1.97 *G*	*ZnS* 2.35 *B*3 2.34 *Har, deJ* 2.35 *L, G* 2.36 *R* *B*4 2.34 *A,* 4) 2.35 *G* 2.36 *R*	*ZnSe* 2.45 *B*3 2.45 *D, G*	*ZnTe* 2.63 *B*3 2.64 *G*	

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1) Nasini and Cavallini, Atti III congresso, naz. chim. pura applicata **1930**, 463.

2) van Arkel, Z. Krist. **67**, 235. 1928.

3) Braekken, Z. Krist. **75**, 572. 1930.

4) Fuller, Phil. Mag. 8, 658. 1929.

Interatomic distances in *B*4 type crystals were calculated on the assumption that the distances from an atom to each of its four neighbors are equal.

Table IV (continuation).

CdS	*CdSe*	*CdTe*
2.52 *B*3	2.62 *B*3	2.80 *B*3
2.52 *G*	2.62 *G*	2.80 *G*
*B*4	*B*4	
2.53 *G*	2.63 *G*	
HgS	*HgSe*	*HgTe*
2.52 *B*3	2.62 *B*3	2.80 *B*3
2.52 *Har, G*	2.62 *deJ*	2.78 *deJ*
2.53 *K, L, vO*	2.63 *G, Har*	2.79 *G, Har*
2.54 *BV*		
CuCl	*CuBr*	*CuI*
2.34 *B*3	2.46 *B*3	2.63 *B*3
2.32 *D*	2.46 *G*	2.61 *A*
2.34 *G*	2.49 *D*	2.62 *G*
2.38 *W*	2.52 *W*	2.63 *D*
		2.64 *W*
		AgI
		2.81 *B*3
		2.81 *Wi, G*
		2.83 *D*
		*B*4
		2.81 *Wi, A, K*

Key to References to the "Strukturbericht"[1]).

A	Aminoff	*Hug*	Huggins
Al	Alsen,	*Hul*	Hull
B	Bragg	*HM*	Hassel and Mark
Boz	Bozorth	*HMB*	Harris, Mack and Blake
Brad	Bradley	*K*	Kolkmeijer, Bijl, Bijvoet, Boekenoogen, Claasen, Karssen, van Dobbenburgh
BV	Buckley and Vernon	*KR*	Küstner and Remy
D	Davey	*L*	Lehmann
De	Debye, Scherrer	*Le*	Levi and Fontana
DeJ	deJong, Willems	*Ma*	Machatschki
Di	Dickinson, Raymond	*McK*	McKeehan
E	Ehrenberg	*MP*	Mark and Pohland
Ew	Ewald	*Na*	Natta, Passerini
FV	Frederickse and Verweel	*Nit*	Nitta
G	Goldschmidt, Barth, Lunde, Oftedahl, Thomassen, Ulrich, Zachariasen	*Og*	Ogg
Ge	Gerlach	*Ot*	H. Ott
Haa	Haase	*OP*	Owen and Preston
Haag	Haag	*P*	Phragmen
Har	Hartwig	*Pa*	Pauling, Ewing, Hendricks

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1) References to papers not abstracted in the "Strukturbericht" are given in full.

R	Rinne
Ra	Ramsdell
SB	Strukturbericht
St	Stoll
T	Terpstra, Westenbrink, Jaeger
V	Vegard, Sollesnes
vA	van Arkel
vO	von Olshausen
W	Wyckoff, Dennis, Posnjak
Wi	Wilsey

Observed distances between tetrahedral atoms in other crystals, given in Table V, are also in satisfactory agreement with the radius sums. One interesting crystal is B_2H_6. Various investigators have suggested different structures for the B_2H_6 molecule. Two such suggestions are that the structure is isosteric with that of ethylene[1], with a double bond between

Table V.

Comparison of Tetrahedral Radius Sums with Observed Interatomic Distances in Other Crystals.

Crystal	Structure Type	*d* calculated	*d* observed	Reference and remarks
			2.14 Å	Parker and Whitehouse, Phil. Mag. **14**, 939. 1932.
FeS_2	*C* 2	$S—S = 2.08$Å	2.09	a_0 by *B* or *Ra, u* by *Ew*
			2.10	a_0 by *deJ, u* by *Ew*
FeS_2	*C* 18	$S—S = 2.08$	2.25	M. J. Buerger, Am. Min. **16**, 361. 1931. Parameters probably inaccurate.
MnS_2	*C* 2	$S—S = 2.08$	2.12	a_0 by Onorato, Periodica di Mineralogia **1**, 109. 1930, and by Pauling (unpublished); *u* by *Ew*
CoS_2	*C* 2	$S—S = 2.08$	2.05	*deJ.*
NiS_2	*C* 2	$S—S = 2.08$	2.09	*deJ.*
$FeAs_2$	*C* 18	$As—As = 2.36$	2.46	Buerger, Z. Krist. **82**, 165. 1932.
$FeSb_2$	*C* 18	$Sb—Sb = 2.72$	2.44	*Hä*
$CoAs_3$	*D* 2	$As—As = 2.36$	2.46	*G*
$N(CH_3)_4Cl$	*OB* 10	$C—N = 1.47$	1.38	*W*
			1.48	*V*
$N(CH_3)_4Br$	*OB* 10	$C—N = 1.47$	1.49	*V*
$N(CH_3)_4I$	*OB* 10	$C—N = 1.47$	1.51	*V*
B_2H_6	*D* 41	$B—B = 1.78$	1.82	*MP*
C_2H_6	*D* 41	$C—C = 1.54$	1.55	*MP*
$K_2S_2O_6$		$S—S = 2.08$	2.06	Huggins and Frank, Am. Min. **16**, 580. 1931.

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[1] G. Herzberg, Leipziger Vorträge 1931.

the two boron atoms, or with that[1]) of $O_2\,{}^3\Sigma$, in which the interatomic distance is within 2% of the double-bond distance, whereas a third structure[2]) involves a single *B—B* bond. The observed *B—B* distance agrees with the last structure and not with the other two.

Normal-valence Radii for Non-metallic Atoms.

In normal-valence compounds of non-metallic atoms each atom forms covalent bonds to a number given by its valence: one for the halogens, two for oxygen, three for nitrogen, and four for carbon. Examples of such compounds are CH_4, F_2, OF_2, NF_3, diamond, etc. In Table VI[3]) and Fig. 3 there are given radii for use in compounds of this type. The sum of the singlebond radii for two atoms gives the expected distance between these two atoms in such a compound when they are connected by a covalent bond. The sum of their double-bond or triple-bond radii similarly gives the expected distance when they are connected by a double or a triple bond.

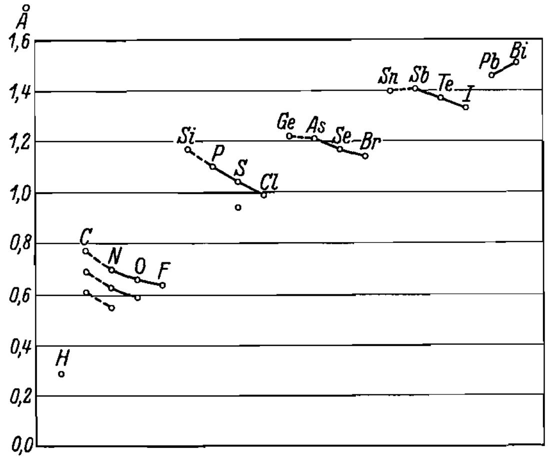

Fig. 3. Normal valence radii of atoms.

The values in Table VI were obtained in the following way. Values for *C*, *Si*, *Ge*, and *Sn* are the same as in Table III, for the tetrahedral configuration is the normal one for these atoms. Radii for *F*, *Cl*, *Br*, and *I* were taken as one-half the band-spectral values for the equilibrium separation in the diatomic molecules of these substances. Inasmuch as these radii for *F* and *Cl* are numerically the same as the tetrahedral radii for these atoms, the values for *N*, *O*, *P*, and *S* given in Table III were also accepted as normal-valence radii for these atoms. The differences of 0.03 Å between the normal-valence radius and the tetrahedral radius for *Br* and

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1) R. S. Mulliken, Physic. Rev. 41, 751. 1932.

2) Linus Pauling, J. Am. Chem. Soc. 53, 3225. 1931.

3) This table has been published by L. Pauling, Pr. Nat. Acad. 18, 293. 1932, in connection with the discussion of the resonance of molecules among several electronic structures.

Table VI.

Normal-valence Radii for Non-metallic Atoms.

Single-bond Radii

	H			
	0.28 Å	(0.375 Å in H_2)		
B	*C*	*N*	*O*	*F*
0.89	0.77	0.70	0.66	0.64
	Si	*P*	*S*	*Cl*
	1.17	1.10	1.04	0.99
	Ge	*As*	*Se*	*Br*
	1.22	1.21	1.17	1.14
	Sn	*Sb*	*Te*	*I*
	1.40	1.41	1.37	1.33
	Pb	*Bi*		
	1.46	1.51		

Double-bond Radii (factor 0.90)

B	*C*	*N*	*O*
0.80	0.69	0.63	0.59
			S
			0.94

Triple-bond Radii (factor 0.79)

C	*N*	*O*
0.61	0.55	0.52

of 0.05 Å for *I* we believe to be due largely to a difference in the nature of the bond orbitals involved. In a tetrahedral atom the bonds are formed by the four tetrahedral bond orbitals. When less than four bonds are formed, the bond orbitals may be pure *p*-orbitals, tetrahedral orbitals, or some intermediate type, depending on the ratio of *s*—*p* separation to difference in bond energy for different bond orbitals. We believe that in *N*, *O*, *F*, *P*, *S*, and *Cl* the bond orbitals for normal valence compounds lead to about the same radii as tetrahedral orbitals, whereas in atoms below these in the periodic system normal valence bonds involve orbitals which approach *p*-orbitals rather closely, and so lead to weaker bonds, and to radii larger than the tetrahedral radii. This effect should be observed in *Br*, *Se*, and *As*, but not in *Ge*, and in *I*, *Te*, and *Sb*, but not *Sn*. For this reason we have added 0.03 Å to the tetrahedral radii for *As* and *Se* and 0.05 Å to those for *Sb* and *Te* to obtain normal-valence radii for these

atoms. The normal-valence radii for *Pb* and *Bi* are related to their tetrahedral radii in the same way as for *Sn* and *Sb*, respectively.

The effective radius of H in H_2 is 0.375 Å. In other compounds, however, a lower value is operative; from the hydrogen halides and other compounds this is found to be 0.29 Å, as given in Table VI.

It seems probable also that, to within one or two percent, double-bond and triple-bond radii for various atoms should bear constant ratios to single-bond radii. We have chosen 0.79 for the triple-bond factor, which gives agreement with the observed distance in the N_2 molecule, and 0.90 for the double-bond factor. The radii given in Table VI are obtained with these factors.

Table VII.

Comparison of Radius Sums from Table VI with Observed Distances from Band Spectra.

Molecule	*d* calculated	*d* observed	Molecule	*d* calculated	*d* observed
F_2	$F{-}F = 1.28$ Å	1.27 Å			
Cl_2	$Cl{-}Cl = 1.98$	1.98	$O_2\ {}^1\Sigma$	$O = O = 1.18$ Å	1.22 Å
Br_2	$Br{-}Br = 2.28$	2.28			
I_2	$I{-}I = 2.66$	2.66	H_2CO	$C = O = 1.28$	1.25
ICl	$I{-}Cl = 2.32$	2.31	N_2	$N \equiv N = 1.10$	1.10
HF	$H{-}F = 0.93$	0.92	CN	$C \equiv N = 1.16$	1.17
HCl	$H{-}Cl = 1.28$	1.28	HCN	$C \equiv N = 1.16$	1.16[4]
HBr	$H{-}Br = 1.43$	1.42	C_2H_2	$C \equiv C = 1.22$	1.21[5]
HI	$H{-}I = 1.62$	1.62			
H_2O	$H{-}O = 0.95$	0.97[1]			
NH_3	$H{-}N = 0.99$	0.98			
CH_4	$H{-}C = 1.06$	1.08[2]			
CH_3F	$C{-}F = 1.41$	1.43[3]			

In Table VII radius sums from Table VI are compared with observed distances from band spectral data. Agreement to within 0.01 or 0.02 Å is usually found; in the exceptional case H_2CO the experimental value is not very accurate. In Table VIII a similar comparison is made with observed distances in crystals. These distances depend in all cases on

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1) R. Mecke and W. Baumann, Physikal. Z. **33**, 833. 1932.

2) R. G. Dickinson, R. T. Dillon, and F. Rasetti, Physic. Rev. **34**, 582. 1929.

3) R. Mecke, Leipziger Vorträge 1931.

4) From R. M. Badger and J. L. Binder, Physic. Rev. **37**, 800. 1931, assuming $C{-}H = 1.06$ Å.

5) From $I = 23.509 \times 10^{-40}$. R. Mecke, Z. Elektrochem. **36**, 803. 1930.

one or more parameters determined from intensity data, and are accurate to ± 0.05 Å only in exceptional cases. Here too the agreement is satisfactory.

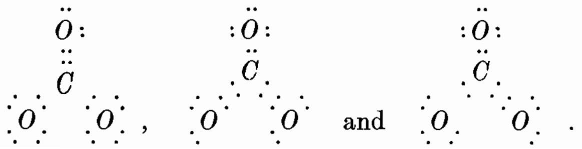
Table VIII.

Comparison of Radius Sums from Table VI with Observed Distances in Crystals.

Single Bonds

Crystal	Structure Type	d calculated	d observed	Reference and remarks
I_2		$I—I = 2.66$ Å	2.70 Å	*HMB*
Se	$A\,8$	$Se—Se = 2.34$	2.32	Brad; Parravano and Cagliotti, Gazz. Chim. Ital. **60**, 923. 1930.
Te	$A\,8$	$Te—Te = 2.74$	2.88	Brad
As	$A\,7$	$As—As = 2.42$	2.51	Brad; Jung, Ctbl. Min. (A.) 1926, page 107.
			2.57	*vO*
Sb	$A\,7$	$Sb—Sb = 2.82$	2.87	Brad
			2.62	*Og*
Bi	$A\,7$	$Bi—Bi = 3.02$	3.11	Brad; Ehret and Fine, Phil. Mag. **10**, 551. 1930.
			3.09	*HM*
			3.10	*McK*
SiI_4	$D\,11$	$Si—I = 2.50$	2.46	Hassel and Kringstad, Z. physik. Ch. (B) **13**, 1. 1931.
GeI_4	$D\,11$	$Ge—I = 2.55$	2.57	T. Parameters only roughly determined.
SnI_4	$D\,11$	$Sn—I = 2.73$	2.63	*Di*
CHI_3	$O\,11$	$C—I = 2.10$	> 2.07	*Nit*
			> 2.06	Huggins and Noble, Am. Min. **16**, 519. 1931.
As_4O_6	$D\,61$	$As—O = 1.87$	2.01	*Boz*
Sb_4O_6	$D\,61$	$Sb—O = 2.07$	2.22	*Boz*
$C_6H_{12}N_4$	$O\,81$	$C—N = 1.47$	1.44	*Di*

Often no single electronic structure can be assigned to a molecule or complex ion, which instead resonates between two or more Lewis structures, as discussed before. An example is the carbonate ion, $CO_3^=$, which assumes all three of the structures



Thus each oxygen atom is held to the carbon atom by a single electron-pair bond two-thirds of the time, and by a double bond one-third of the time. But the extra resonance energy associated with the combination of the three structures makes the molecule more stable than would correspond to any one of the structures, and indeed causes each carbon-oxygen bond to be about as strong as a double bond. In support of this, we observe (Table IX) that the C—O and N—O distances in $CO_3^=$ and NO_3^- are about equal to those calculated for double bonds. In NO_2^- the observed distance is rather small, perhaps because of a small error in the parameters. In urea and thiourea the observed C—N distance as well as the C—O and C—S distances agree well with the double bond radii, showing that in these molecules the double bond resonates among the three possible positions in just the same way as in the carbonate ion¹).

Table IX.

Distances in Molecules and Complex Ions in Crystals Resonating between Two or More Electronic Structures.

Crystal	Type	d calculated	d observed	Reference
$CaCO_3$	G 1	$C = O = 1.28$ Å	1.23 Å	W
$NaNO_3$	G 1	$N = O = 1.22$	1.22	W
$LiNO_3$	G 1	$N = O = 1.22$	1.25	G
$NaNO_2$		$N = O = 1.22$	1.13	Ziegler, Physic. Rev. **38**, 1040. 1931.
$(NH_2)_2CO$	O 21	$C = O = 1.28$	1.24	R. W. G. Wyckoff, Z. Krist. **81**, 102. 1932; **75**, 529. 1930.
		$C = N = 1.32$	1.33	
$(NH_2)_2CS$	O 22	$C = S = 1.63$	1.64	R. W. G. Wyckoff and R. B. Corey, Z. Krist. **81**, 386. 1932.
		$C = N = 1.32$	1.35	

Many other distances determined to within 0.1 or 0.2 Å could be tabulated, but the limit of experimental error is so large as to make a comparison with these values no test of the radii.

Octahedral Radii from Pyrite-type Crystales.

In crystals such as pyrite, FeS_2, marcasite, FeS_2, skutterudite, $CoAs_3$, etc., each metal atom is connected by covalent bonds to

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1) Evidence from thermochemical data regarding resonance in these molecules is given by L. Pauling and J. Sherman, J. chem. Physics **1**, 606. 1933.

six tetrahedral non-metal atoms located about it at the corners of a nearly regular octahedron. Octahedral radii for such metal atoms, obtained by the following procedure, are listed in Table X. Distances ("*d* obs", Table XI) from metal atom to non-metal atom were first calculated from the observed size of unit by assuming the non-metal to non-metal distance to be equal to twice the tetrahedral radius of the non-metal plus 0.04 Å (this giving agreement with the S—S distance in FeS_2 and MnS_2). Octahedral radii ("*d* obs—(*B*)") for the metal atoms were then calculated by subtracting the tetrahedral radius for the non-metal atom (*B*). The average values for Ru^{II}, Pd^{IV}, Os^{II}, and Pt^{IV} were found to be 1.32, 1.31, 1.33, and 1.31 Å, respectively. On the basis of these figures we assume that in iso-electronic sequences among the transition elements in this part of the periodic system the radii decrease by about 0.01 Å for each increase of 1 in atomic number. Adopting the values 1.23 Å for Fe^{II} from pyrite, 1.32 for Co^{II}, 1.39 for Ni^{II}, 1.43 for Rh^{II} and Ir^{II}, and 1.50 for Pd^{II} and Pt^{II}, we obtain the values given in Table X.

Table X.

Standard Octahedral Radii (from Pyrite-type Crystals).

Valence	*Fe*	*Co*	*Ni*	*Ru* *Os*	*Rh* *Ir*	*Pd* *Pt*	*Ag* *Au*
II	1.23	1.32	1.39	1.33	1.43	1.50	1.54[1])
III		1.22	1.31		1.32	1.42	1.49
IV			1.21			1.31	1.41

Comparison of the radius sums from Tables III and X with the observed values in Table XIA shows good agreement (within 0.03 Å) except for RhS_2. The experimental data for this compound should be checked.

It may be mentioned that in CoS_2, NiS_2, etc., there are one or two electrons more than can be placed in 3*d*, 4*s*, 4*p* orbitals, so that these electrons must go into excited orbitals, probably becoming "metallic" electrons. The effect of this is to cause a large increase in radius from Fe^{II} to Co^{II}, with one extra electron, and from Co^{II} to Ni^{II}, with two. CoS_2 and NiS_2 should be more metallic in their properties than FeS_2. They

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1) Obtained by extrapolation.

are not so stable as FeS_2, $CoAsS$, $NiAs_2$, and other compounds not containing these extra electrons.

Table XI.

Comparison of Observed Interatomic Distances with Radius Sums from Tables III and X.

A. Pyrite and Similar Types.

Crystal	Structure Type	d calculated	d obs	d obs —(B)	Parameter calc	Parameter obs	Reference
MnS_2	$C2$		2.59	1.55	0.400	0.400, .3875	Onorato, Pauling
$MnTe_2$	$C2$		2.91	1.59	.388	.36—.39	G
FeS_2	$C2$	$(Fe^{II}—S) = 2.27$	2.27	1.23	.387	.388, .386	deJ, G
FeS_2	$C18$	$(Fe^{II}—S) = 2.27$	2.25	1.21	.197, .384	.203, .375	Buerger, Am. Min. **16**, 361. 1931
$FeAs_2$	$C18$		2.36	1.18	.174, .368	.175, .361	Buerger, Z. Krist. **82**, 165. 1932.
$FeSb_2$	$C18$		2.60	1.24	.182, .364	.18, .36	$Hä$
CoS_2	$C2$	$(Co^{II}—S) = 2.36$	2.37	1.33	.392	.395	deJ
$CoSe_2$	$C2$	$(Co^{II}—Se) = 2.46$	2.45	1.31	.386	.375	deJ
$CoAsS$	$F1$	$(Co^{III}—As) = 2.40$	2.42	1.24	.419, .653		Ra, G
		$(Co^{III}—S) = 2.26$	2.28	1.24			
NiS_2	$C2$	$(Ni^{II}—S) = 2.43$	2.42	1.38	.398	.395	deJ
$NiSe_2$	$C2$	$(Ni^{II}—Se) = 2.53$	2.53	1.39	.389	.375	deJ
$NiAsS$	$F1$	$(Ni^{III}—As) = 2.49$	2.48	1.30	.419, .648		G
		$(Ni^{III}—S) = 2.35$	2.34	1.30			
RuS_2	$C2$	$(Ru^{II}—S) = 2.37$	2.35	1.31	.390	.36—.39	G
$RuSe_2$	$C2$	$(Ru^{II}—Se) = 2.47$	2.48	1.34	.397	.38	G
$RuTe_2$	$C2$	$(Ru^{II}—Te) = 2.65$	2.64	1.32	.377	.38	G
RhS_2	$C2$	$(Rh^{II}—S) = 2.47$	2.34	1.30	.390	.38	G
$PdAs_2$	$C2$	$(Pd^{IV}—As) = 2.49$	2.49	1.31	.384	.38	G
$PdSb_2$	$C2$	$(Pd^{IV}—Sb) = 2.67$	2.67	1.31	.376	.38	G
OsS_2	$C2$	$(Os^{II}—S) = 2.37$	2.37	1.33	.392	.36—.39	G
$OsSe_2$	$C2$	$(Os^{II}—Se) = 2.47$	2.48	1.34	.387	.38	G
$OsTe_2$	$C2$	$(Os^{II}—Te) = 2.65$	2.65	1.33	.378	.38	G
PtP_2	$C2$	$(Pt^{IV}—P) = 2.41$	2.38	1.28	.386	.38	G
$PtAs_2$	$C2$	$(Pt^{IV}—As) = 2.49$	2.49	1.31	.384	.38	G
$PtSb_2$	$C2$	$(Pt^{IV}—Sn) = 2.67$	2.67	1.31	.376	.38	G
$AuSb_2$	$C2$	$(Au^{IV}—Sb) = 2.77$	2.76	1.40	.380	.36—.39	G
$CoAs_3$	$D2$	$(Co^{III}—As) = 2.40$	2.37	1.19	.353, .147	.35, .15	G

Table XI (continuation).

B. Miscellaneous Types.

Crystal	Type	*d* calculated	*d* observed	Reference
Rb_2PdBr_6	$H61$	$(Pd^{IV}—Br) = 2.45$	2.52	*St*
$(NH_4)_2SnCl_6$	$H61$	$(Sn^{IV}—Cl = 2.48$	2.46	*Di*
K_2SnCl_6	$H61$	$(Sn^{IV}—Cl) = 2.48$	2.44	*Di*
$(NH_3CH_3)_2SnCl_6$	$OH62$	$(Sn^{IV}—Cl) = 2.48$	2.44	*W*
$(NH_3C_2H_5)_2SnCl_6$	$OH67$	$(Sn^{IV}—Cl) = 2.48$	2.46	*W*
K_2PtCl_6	$H61$	$(Pt^{IV}—Cl) = 2.30$	2.33, 2.29	*Pa, FV*
K_2SeBr_6	$H61$	$(Se^{IV}—Br) = 2.54$	2.54	Hoard and Dickinson, Z. Krist.84,436.1933.
$(NH_4)_2PbCl_6$	$H61$	$(Pb^{IV}—Cl) = 2.53$	2.33—2.53	*W*
$(NH_4)_2PtCl_6$	$H61$	$(Pt^{IV}—Cl) = 2.30$	2.26	*W*
$[N(CH_3)_4]_2PtCl_6$	$OH61$	$(Pt^{IV}—Cl) = 2.30$	2.35	*Hug*
$PdTe_2$	$C6$	$(Pd^{IV}—Te) = 2.68$	2.65	*G*
PtS_2	$C6$	$(Pt^{IV}—S) = 2.35$	2.39	*G*
$PtSe_2$	$C6$	$(Pt^{IV}—Se) = 2.48$	2.49	*G*
$PtTe_2$	$C6$	$(Pt^{IV}—Te) = 2.68$	2.65	*G*
SnS_2	$C6$	$(Sn^{IV}—S) = 2.53$	2.56	*G*
TiS_2	$C6$	$(Ti^{IV}—S) = 2.40$	2.42	*G*
$TiSe_2$	$C6$	$(Ti^{IV}—Se) = 2.53$	2.53	*G*
$TiTe_2$	$C6$	$(Ti^{IV}—Te) = 2.73$	2.72	*G*
ZrS_2	$C6$	$(Zr^{IV}—S) = 2.55$	2.58	*vA*
$ZrSe_2$	$C6$	$(Zr^{IV}—Se) = 2.68$	2.68	*vA*
CdI_2	$C6$	$(Cd^{II}—I)$	2.99	*Boz*
MnI_2	$C6$	$(Mn^{II}—I)$	2.95	Ferrari and Giorgi, R. Accad. Lincei (6a) **10**, 522. 1929.
FeI_2	$C6$	$(Fe^{II}—I) = 2.56$	2.88	Same
CoI_2	$C6$	$(Co^{II}—I) = 2.65$	2.83	Same
		C.		
Cu_2HgI_4		$(Hg—I) = 2.81$ $(Cu—I) = 2.68$	2.77 2.56	J. A. A. Ketelaar, Z. Krist. **80**, 190. 1931.
Ag_2HgI_4		$(Hg—I) = 2.81$ $(Ag—I) = 2.86$	2.80 2.83	Same
HgI_2	$C13$	$(Hg^{II}—I) = 2.81$	2.77	K; Huggins and Magill, J. Am. Chem. Soc. **49**, 2357. 1927.
Cu_3SbS_3		$(Sb—S) = 2.45$	2.45	*Ma*

In calculating "*d* obs" and "Parameter calc" in Table XI A from the dimensions of the unit cell, it was assumed that the distance between adjacent negative atoms,

(S—S) etc., equals the sum of the standard tetrahedral radii plus 0.04 Å. In the $C18$ type crystals all (M—X) distances between neighboring atoms were assumed equal. In $CoAsS$ and $NiAsS$ the following were assumed: $u_{Co} = u_{Ni} = 0$. (As—S) = 2.24 Å. (Co—As) — (Co—S) = (Ni—As) — (Ni—S) = 0.14 Å.

In calculating "d observed" in $C6$ type crystals, $u = 0.25$ was assumed in all cases.

In $C2$ type crystals a change of 0.01 in u makes a change in (S—S) etc. of 0.19—0.24 Å.

In other crystals an octahedral metal atom is attached to six non-metal atoms, each of which forms one, two, or three, rather than four, bonds with other atoms. The interatomic distance in such a crystal should be equal to the sum of the octahedral radius of the metal atom and the normal-valence radius (Table VI) of the non-metal atom. This is found to be true for many crystals with the potassium chlorostannate (H 61) and cadmium iodide (C 6) structures (Table XIB). Data are included in Table XIC for crystals in which a tetrahedral atom is bonded to a non-metal atom with two or three covalent bonds. The values of d_{calc} are obtained by adding the tetrahedral radius for the former to the normal-valence radius for the latter atom.

The parameter values calculated as described above are given in Table XIA, together with the values given in the literature.

Additional Octahedral Radii. From the "d obs" values in Table XIB the following approximate octahedral radii are deduced.

Table XII. Additional Octahedral Radii.

Ti^{IV}, 1.36 Å; Zr^{IV}, 1.51 Å; Sn^{IV}, 1.49 Å; Pb^{IV}, 1.54 Å; Se^{IV}, 1.40 Å

The "d calc" values obtained from these show good agreement with the "d obs" figures, even in the $C6$ type crystals, in which the parameter was arbitrarily taken as 0.25.

The orbitals involved in the Ti^{IV} bonds are $3d^2\,4s\,4p^3$, as for Fe^{II}, the larger radius for Ti^{IV} than for Fe^{II} probably being due to the smaller effective nuclear charge of the former atom. In Sn^{IV}, however, the octahedral bond orbitals involve d-orbitals with the same total quantum number as the s and p orbitals; they are $5s5p^35d^2$ orbitals. Similar octahedral bonds can be formed by all the atoms in Table III except those in the first row, and rough values of octahedral radii for them can be obtained by assuming that the ratio of octahedral radius to tetrahedral radius given in Table III is the same as for Sn^{IV}; namely, 1.06. Because of the instability of the d-orbitals, these atoms form relatively few covalent compounds involving octahedral bonds, preferring instead the tetrahedral configuration.

The octahedral radius of Se^{IV}, which is surrounded by an outer shell of six shared electron pairs and one unshared pair, is somewhat larger than the value 1.21 Å calculated by the use of the factor 1.06 for the octahedral radius of Se^{VI}, surrounded by six shared pairs only. This increase is expected as the result of the action of the unshared pair.

Square Radii. In K_2PdCl_4, $(NH_4)_2PdCl_4$, and K_2PtCl_4 the Pd or Pt atom is surrounded by four Cl atoms at the corners of a square, in agreement with the quantum-mechanical considerations previously mentioned. In PdO also we believe each Pd to be similarly surrounded; the structure of this crystal is discussed in a following section. The same structure has been reported by Bannister[1]) for cooperite, PtS. From the observed interatomic distances in these compounds we obtain the radius 1.32 Å for both Pd^{II} and Pt^{II}, and with the assumption that the dsp^2 radius of an atom with valence v and the d^2sp^3 radius of the same atom with valence $v + 2$ are closely related (differing by 0.01 Å), the additional values given in Table XIII are found.

Table XIII. Square Radii.

Co^{I}	Ni^{II}	Cu^{III}	Rh^{I} Ir^{I}	Pd^{II} Pt^{II}	Ag^{III} Au^{III}
1.23	1.22	1.21	1.33	1.32	1.31

Calculated and observed interatomic distances are compared in Table XIV. The structure reported for pentlandite, $(Ni, Fe)S$, places four S atoms about each Ni atom at the corners of a flat pyramid; this crystal is also tentatively included in Table XIV.

Table XIV.
Crystals Containing Square Configurations.

Crystal	d calculated	d observed	Reference
PdO	$Pd^{II}\text{-}O = 1.98$	1.99	*Le*
		2.01	*G*
K_2PdCl_4	$Pd^{II}\text{-}Cl = 2.31$	2.29	*Di*
$(NH_4)_2PdCl_4$	$Pd^{II}\text{-}Cl = 2.31$	2.35	*Di*
PtS	$Pt^{II}\text{-}S = 2.36$	2.31	Bannister[1])
K_2PtCl_4	$Pt^{II}\text{-}Cl = 2.31$	2.32	*Di*
$(Ni, Fe)S$	$Ni^{II}\text{-}S = 2.26$	2.2	*Al*
CuO	$Cu^{II}\text{-}O$	1.93	Tunell, Posnjak and Ksanda, J. Wash. Acad. Sci. **23**, 195. 1933.

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[1]) F. A. Bannister, Nature **130**, 142. 1932.

Trigonal-Prism Radii. In molybdenite and the corresponding tungsten sulfide the metal atom is surrounded by six sulfur atoms at the corners of a right trigonal prism of axial ratio unity, the bond orbitals involved being those discussed in an earlier section. From the observed interatomic distances the values 1.37 and 1.44 Å are calculated for Mo^{IV} and W^{IV} in such crystals (Table XV).

Table XV.

Trigonal-Prism Radii.

Crystal	*d* observed	Radius calc.	Reference
MoS_2	2.41	1.37	*Di* and *P*
WS_2	2.48	1.44	*vA*

Other Covalent Radii. In Cu_2O and Ag_2O each metal atom is equidistant from two nearest oxygen atoms, the interatomic distances corresponding to the radius values 1.18 and 1.39 Å for Cu^I and Ag^I with coordination number two. In $KAg(CN)_2$, in which each silver atom is similarly attached to two cyanide groups¹), the effective radius of Ag^I is 1.36 Å. It has been pointed out to us by Dr. Hoard that the work of Braekken²) indicates the presence of strings $—Ag—C{\equiv}N—Ag—C{\equiv}N—Ag—$ parallel to the *c*-axis in hexagonal crystals of $AgCN$, of length 5.26 Å, which leads to an Ag^I radius of 1.32 Å, in approximate agreement with the above values.

Radii for metal atoms forming only one bond can be found from the interatomic distances obtained from band spectra of molecules such as AgI, etc. The available data for the silver halides lead to a radius of about 1.12 Å for Ag^I. The change of radius with change in number of bonds is strikingly shown by silver, with radius 1.53 Å for four bonds, 1.36 Å for two, and 1.12 Å for one.

The Discussion of the Structure of Certain Crystals.

In the preceding sections it has been shown that in a large number of crystals containing covalent bonds, cited as examples, the number and distribution of the bonds are in good agreement with a classification deduced from quantum mechanical considerations, and, moreover, there exist regularities in the observed interatomic distances which may be expressed by assigning covalent radii to the atoms, dependent in a

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1) J. L. Hoard, Z. Krist. 84, 231. 1933.

2) H. Braekken, Det. Kong. Norske Vid. Selsk. Forh. 2, 169. 1930.

reasonable way on the character of the bonds and the atomic number of the atom. It is evident that these considerations can be used as a basis for judgment regarding the correctness of a reported structure of a covalent crystal, and as a means of predicting a structure or structures for test by comparison with experimental data, in case a rigorous deduction of the structure cannot be made. A few such applications are given below. It must be emphasized, however, that our understanding of the structure of covalent crystals is not complete; occasionally the arrangement of atoms about a given atom is found not to correspond to the bond distribution characteristic of any of the types of bond orbitals described above, and even the observed interatomic distances may deviate appreciably from the expected radius sum. The most noteworthy case of such a deviation is the anomalous manganese radius in hauerite.

The Anomalous Manganese Radius. Ewald and Friedrich[1]) found for hauerite, MnS_2, with the pyrite structure, the parameter value $u = 0.400 \pm 0.001$, which, together with the value $a_0 = 6.08$ Å calculated from the density 3.46 g/cc, leads to an Mn—S separation of 2.58 Å. To check this surprisingly large value, we prepared (in 1930) oscillation photographs of molybdenum radiation reflected from (111) of large octahedral crystals of hauerite from Raddusa, Sicily, using calcite as reference substance. On measurement these plates led to the value $a_0 = 6.097 \pm 0.005$ Å. Onorato has since reported[2]) the value $a_0 = 6.11$ Å. Hence there is no doubt that in hauerite the Mn—S distance is very close to 2.59 Å, corresponding to an octahedral Mn^{II} radius of 1.55 Å. A closely similar value of 1.59 Å is given in Table XIA, calculated from Goldschmidt's determination of a_0 for $MnTe_2$.

This octahedral radius for manganese is 0.3—0.4 Å larger than expected. From Table X we extrapolate the sequence Ni^{II} Co^{II} Fe^{II} to a value of about 1.15 Å for Mn^{II}. This extrapolation might not be accurate, inasmuch as octahedral Co^{II} and Ni^{II} contain one or two electrons excited to outer orbits, as discussed above; however, the safe extrapolation of the iso-electronic sequence Ni^{IV} Co^{III} Fe^{II} leads to 1.24 Å for Mn^{I}, and this should be an upper limit for Mn^{II}. Hence the large radius of 1.55—1.59 Å found experimentally is in definite and pronounced disagreement with our

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[1]) P. P. Ewald and W. Friedrich, Ann. Physique **44**, 1183. 1914; P. P. Ewald, Physikal. Z. **15**, 399. 1914.

[2]) E. Onorato, Periodico di Mineralogia **1**, 109. 1930. Onorato gives the value of u as 0.3875; this is, however, less trustworthy than that of Ewald and Friedrich.

expectations for octahedral $3d^2\,4s\,4p^3$ bonds. We are unable to advance a plausible explanation of the anomaly.

It is worthy of mention that the properties of hauerite are in accordance with the conception that the *Mn*—*S* bonds are much weaker than the *Fe*—*S* bonds in pyrite. The hardness of hauerite is 4, as compared with 6—6.5 for pyrite. All members of the pyrite group have a bright metallic luster except hauerite, which is dull. Hauerite is said to have a much smaller electrical conductivity than the others.

The Structure of Palladous Oxide. *PdO* has been studied with x-rays by Levi and Fontana[1]) and Zachariasen[2]), who found it to be tetragonal, with a two-molecule unit having $a_0 = 3.03$ Å and $c_0 = 5.31$ Å. The suggested $B10$ type structure (the Dickinson-Friauf *PbO* structure) seems unreasonable to us, inasmuch as we expect bivalent palladium to form four dsp^2 bonds directed towards the corners of a square. Moreover, the axial ratio $c/a = 1.75$ of *PdO* differs greatly from that of *PbO* (1.26). An entirely reasonable structure, however, has been described by Huggins[3]). In this structure, with $2\,Pd$ at $0\,\frac{1}{2}\,\frac{1}{4}$, $\frac{1}{2}\,0\,\frac{3}{4}$ and $2\,O$ at 000, $00\frac{1}{2}$, as shown in Fig. 4, each oxygen atom is bonded to four palladium atoms at the corners of a nearly regular tetrahedron, and each palladium atom forms four coplanar bonds to oxygen atoms at the corners of a rectangle. The geometry of the structure requires some distortion of the bond angles. If the oxygen bonds (sp^3) were directed towards the corners of a regular tetrahedron the axial ratio c/a would have the value 1.414, and if the palladium bonds (dsp^2) were directed towards the corners of a square c/a would be equal to 2.000; the observed value 1.75 shows the distortion to be divided about equally between the two atoms.

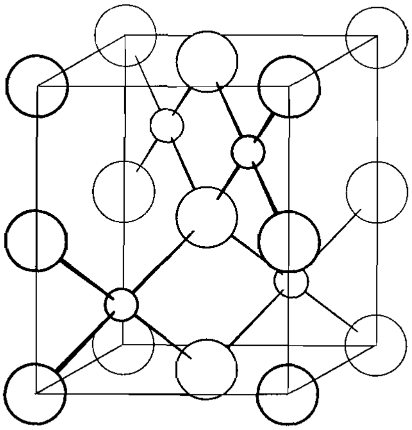

Fig. 4. The structure of *PdO* (referred to axes 45° from those of the smallest unit). Large circles represent oxygen, small circles palladium atoms.

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[1]) G. R. Levi and C. Fontana, Gazz. Chim. Ital. **56**, 388. 1926.

[2]) W. Zachariasen, Z. physikal. Ch. **128**, 412. 1927.

[3]) M. L. Huggins, Chem. Rev. **10**, 427. 1932.

Cooperite, *PtS*, has been shown by Bannister[1]) to have the same structure, with $a = 3.47$ Å, $c = 6.10$ Å, $c/a = 1.76$. It is probable that the structure of braggite, $PdPtS_2$, is closely similar.

Tenorite, *CuO*, has also recently been reported[2]) to have a distorted *PdO* type structure. The distortion is probably due to the extra electron (more than in *NiO*), probably occupying the p_z orbital which has its maxima normal to the plane of the four bonding orbitals.

The Niccolite Structure. The substances which crystallize with the niccolite structure (*B*8) are compounds of transition elements with *S*, *Se*, *Te*, *As*, *Sb*, *Bi*, or *Sn*. The physical properties of the substances indicate that the crystals are not ionic, and this is substantiated by the lack of agreement with the structural rules for ionic crystals. Thus each metal atom is surrounded by an octahedron of non-metal atoms; but these octahedra share faces, and the edges of the shared faces are longer than other edges (rather than shorter, as in ionic crystals). Hence we conclude that the bonds are covalent, with probably some metallic character also.

However, assuming the usual valences for the metal atoms, the number of valence electrons available is not sufficient to permit a shared-electron-pair bond to be formed between each non-metal atom and each of the six metal atoms surrounding it (at the corners of a trigonal prism). There are several electronic structures possible under these conditions. Thus the electron pairs may resonate among the six bonds in such a way as to keep them equivalent. This resonance would give the crystals pronounced metallic properties, as observed for niccolite and other minerals of the group. A second possibility is that the parameter may differ somewhat from the value $\frac{1}{4}$, bringing each atom closer to three atoms than to the other three of the circumscribed polyhedron. A bit of evidence indicating such a structure for *FeS* is the observation by Groth that artificial crystals formed by heating iron wire in hydrogen sulfide appear to be polar. It is very probable that breithauptite, *NiSb*, has such a structure, inasmuch at it shows definite basal cleavage, in contradistinction to niccolite and pyrrhotite. Unfortunately the available x-ray data do not provide a sufficiently accurate determination of the parameter to test this possibility.

A similar distortion may occur in some crystals with the wurtzite structure. Wurtzite and greenockite show easy prismatic cleavage and difficult basal cleavage, whereas iodyrite, *AgI*, cleaves perfectly on the

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[1]) F. A. Bannister, Nature **130**, 142. 1932.

[2]) G. Tunell, E. Posnjak, and C. J. Ksanda, J. Wash. Acad. Sci. **23**, 195. 1933.

base. This suggests that the parameter differs somewhat from 3/8, each silver atom being more strongly bound to three of the surrounding iodine atoms than to the fourth.

The Wolfsbergite Structure. The interesting structure of wolfsbergite, $CuSbS_2$, and emplectite, $CuBiS_2$, determined by Hofmann[1]), provides a good example for comparison with our rules and radii. Each copper atom is surrounded tetrahedrally by four sulfur atoms, corresponding to sp^3 bond orbitals, the Cu—S distance being 2.25—2.33 Å, slightly smaller than the radius sum 2.39 Å. We expect trivalent antimony to form three bonds; this is observed, the three nearest sulfur atoms being 2.44, 2.57, and 2.57 Å distant, with others no nearer than 3.11Å. The radius sum for Sb^{III} and S is 2.45Å, in good agreement with one of the reported values but somewhat smaller than the other (2.57 Å). It is not unlikely that small changes should be made in the eight parameters, such as to decrease the high Sb—S distance somewhat. It is also noteworthy that the structure is a layer structure on (001), the atoms within the layers being held together by covalent bonds, so that the layers can be separated without any of these bonds being broken. In consequence complete basal cleavage, similar to that in metallic antimony, is observed[2]).

Eulytite. In his investigation of eulytite, $Bi_4Si_3O_{12}$, Menzer[3]) used the assumption that each bismuth atom should be equidistant from six oxygen atoms. We, however, believe that trivalent bismuth would form three bonds of considerable covalent character, and would hence have as nearest neighbors only three oxygen atoms, at a distance of about 2.17 Å.

AsI_3 and BiI_3. Heyworth and Braekken[4]) in their studies of the hexagonal crystals AsI_3 and BiI_3 assigned to them structures in which each arsenic or bismuth atom is surrounded by six equidistant iodine atoms, the interatomic distances reported being As—I = 2.97 Å and Bi—I = 3.09 Å. As in the case of eulytite, we believe that the trivalent atoms are displaced towards three and away from three of these six atoms, until the smallest interatomic distances become As—I = 2.54 Å and Bi—I = 2.84 Å[5]).

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1) W. Hofmann, Z. Krist. **84**, 177. 1933.

2) It is very improbable that this cleavage should occur in such a way as to rupture Cu—S bonds, as suggested by Hofmann.

3) G. Menzer, Z. Krist. **78**, 136. 1931.

4) D. Heyworth, Physic. Rev. **38**, 351, 1792. 1931; H. Braekken, Z. Krist. **74**, 67. 1930; **75**, 574. 1930.

5) The possibility of such a displacement was mentioned by Miss Heyworth.

Conclusion. There is no need to multiply examples of the type considered, especially since our knowledge of the principles determining the structures of covalent crystals is still so incomplete that we can offer no explanation for the anomalous manganese radius; indeed, even the observed arrangement[1]) of the bonds formed by sulfur in sulvanite, Cu_3VS_4, was entirely unexpected and has been given only an ad hoc explanation.

A number of questions related to those taken up in this paper, such as the distances between atoms not directly connected by bonds, the use of interatomic distances as a criterion for distinguishing between ionic and covalent bonds, etc., have been discussed in a paper by Huggins[2]).

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1) L. Pauling and R. Hultgren, Z. Krist. **84**, 204. 1933.

2) M. L. Huggins, Chem. Rev. **10**, 427. 1932.

A WAVE-MECHANICAL TREATMENT OF THE MILLS-NIXON EFFECT

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A WAVE-MECHANICAL TREATMENT OF THE MILLS-NIXON EFFECT.

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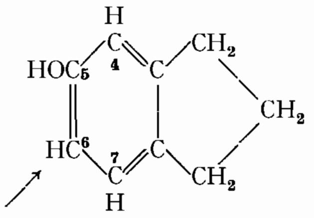
In 1930, W. H. Mills and I. G. Nixon[1] showed that by attaching saturated carbon rings of different sizes to two *ortho* valencies of a benzene molecule it is possible to make the benzene ring react as though it had either one or other of the two Kekulé structures. Thus, they found that 5-hydroxyhydrindene undergoes substitution by bromine or by diazo residues in the 6 position, and so behaves as though the benzene ring in this compound had that Kekulé structure with the single bond common to the two rings (formula 1), whereas *ar*-tetrahydro-*β*-naphthol undergoes these substitutions in the 1 position, and so behaves as though it had the other structure (formula 2).



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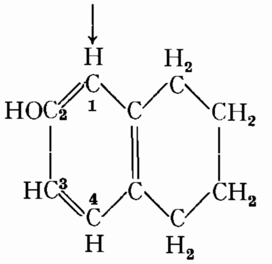

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These facts they explained by pointing out that since the angle between two single bonds is less than that between a single bond and a double bond, when the bonds come from a four-covalent van't Hoff-le Bel atom (the angles being 109° 28′ and 125° 16′, respectively) the angles between successive pairs of external valencies of a single benzene structure should alternate, as shown in Fig. 1, angle *α* being less than angle *β*. They then stated that, while in ordinary benzene there could be a tautomerism between the two Kekulé structures with equal concentrations of both present, if two adjacent valencies are pulled together (as they would be if a five-membered ring were attached to them) one structure—the one with the single bond between the valencies in question—is made much more stable than the other, and predominates.

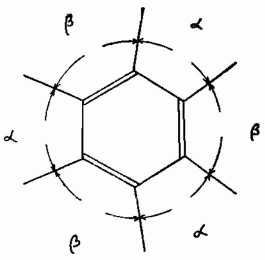

Fig. 1.

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[1] Mills and Nixon, *J. Chem. Soc.*, 1930, 2510.

In this way Mills and Nixon explained the behaviour of 5-hydroxyhydrindene. The reason for the behaviour of *ar*-tetrahydro-β-naphthol could not be expressed so simply, but they advanced arguments from a comparison of the strains in the two structures to show that when a six-membered ring is attached the structure with the double bond common to the two rings is the more stable, although according to their calculations the difference is small and vanishes if the angle between the valencies of a methylene group is 112·8°.

The conception of the benzene molecule which has been developed from the ideas of wave mechanics calls for some modification of the above interpretation of the facts. Two approximate methods of treatment have been applied to the problem of the structure of benzene, the method of molecular orbitals and the method of valency-bond wave functions[2]; the results of these are essentially in agreement.[3] In our discussion of the present problem we shall make use of the second method, inasmuch as the first one does not offer an approach to it. It appears very definitely that benzene is a single molecular species and from the second method we can say that it is a hybrid of the two Kekulé structures and various excited structures, and that the angles between the pairs of external valencies are all 60°. In the wave function for the whole molecule, the wave functions corresponding to the two Kekulé structures occur with equal coefficients, because these structures, regarded as separate entities, have equal energies. If, however, two *ortho* valencies are displaced from a mutual inclination of 60°, the two Kekulé structures no longer correspond to equal energies; if the angle is increased the structure with the double bond between the *ortho* valencies in question, hereinafter called structure I, will have the lower energy and its coefficient will therefore increase, while that of the other structure, hereinafter called structure II, will decrease. The reverse will occur if the angle is decreased. Owing to the great energy corresponding to resonance between the two structures, these changes of coefficient will, however, be relatively small.

In order to treat the problem quantitatively we shall ignore the excited structures (whose contribution to the resonance energy is small), and shall set up and solve the quadratic secular equation for the wave functions of the two Kekulé structures. In the simple treatment of benzene,[2] the matrix elements $H_{I,\,I}$ and $H_{II,\,II}$ are both equal to $Q - W + \frac{3}{2}\alpha$, and the elements $H_{I,\,II}$ and $H_{II,\,I}$ are equal to $\frac{1}{4}(Q - W) + \frac{3}{2}\alpha$, Q being the Coulomb energy, W the total energy, and α the exchange integral, which has the value 34,000 cal./gm. mole. This Q includes the strain energy caused by altering the angles of the two *ortho* valencies from ϕ_I or ϕ_{II} to 60°. In the present problem its value is different in the different matrix elements, and therefore it is necessary to express the strain energy explicitly in each. The strain energy in $H_{I,\,I}$ is that which there would be if the molecule had structure (I) only, *i.e.*, $\frac{1}{2}k(\phi - \phi_I)^2$ where k is a force constant and ϕ_I is the angle between the unstrained valencies in structure (I). Similarly in $H_{II,\,II}$ it is $\frac{1}{2}k(\phi - \phi_{II})^2$. In the resonance integrals $H_{I,\,II}$ and $H_{II,\,I}$ it may reasonably be assumed that it is approximately the mean of those in the two structures, *i.e.*,

$$\tfrac{1}{4}K[(\phi - \phi_I)^2 + (\phi - \phi_{II})^2].$$

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[2] Slater, *Physic. Rev.*, 1931, **38**, 1109; *ibid.*, **37**, 489; Hückel, *Z. Physik.*, 1931, **70**, 204; Pauling, *J. Chem. Physics*, 1933, **1**, 280; Pauling and Wheland, *bid.*, 1933, **1**, 362.

[3] Wheland, *J. Chem. Physics*, 1934, **2**, 476.

The secular equation is therefore :

$$\begin{vmatrix} Q' - W + \tfrac{1}{2}k(\phi - \phi_{\mathrm{I}})^2 + \tfrac{3}{2}\alpha & \tfrac{1}{4}\{Q' + \tfrac{1}{4}k[(\phi - \phi_{\mathrm{I}})^2 + (\phi - \phi_{\mathrm{II}})^2] - W\} + \tfrac{3}{2}\alpha \\ \tfrac{1}{4}\{Q' + \tfrac{1}{4}k[(\phi - \phi_{\mathrm{I}})^2 + (\phi - \phi_{\mathrm{II}})^2] - W\} + \tfrac{3}{2}\alpha & Q' - W + \tfrac{1}{2}k(\phi - \phi_{\mathrm{II}})^2 + \tfrac{3}{2}\alpha \end{vmatrix} = 0.$$

For numerical roots to be obtained, values must be ascribed to ϕ_{I}, ϕ_{II}, and k.

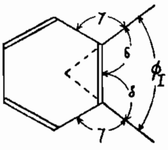

FIG. 2.

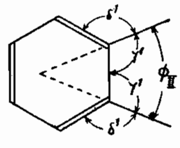

FIG. 3.

The natural values of the angles γ (or δ') and δ (or γ') shown in Figs. 2 and 3, are 109° 28′ and 125° 16′, respectively. These values cannot be achieved simultaneously because the benzene angle is 120°. If we assume that the strain is equally divided between γ and δ and between γ' and δ', we are led to the values $\phi_{\mathrm{I}} = 75{\cdot}5°$ and $\phi_{\mathrm{II}} = 44{\cdot}5°$. k is a bending force constant ; since the bending of each bond is one half of the total, say $\dfrac{\phi - \phi_{\mathrm{I}}}{2}$, the total bending energy is $a\dfrac{(\phi - \phi_{\mathrm{I}})^2}{4}$, where a is the energy necessary to bend one bond through 1°, and therefore $k = a/2$. According to Stuart[4] a is 16 cal./gm. mole. for the C—H bond in hydrogen cyanide, and hence $k = 8$ cals./gm. mole. We shall use this value for our C—C bonds in default of a better one.

The secular equation has been solved for $Q' - W$, with ϕ assuming values between 45° and 75°, and the ratios of the coefficients κ_{I} and κ_{II} of the wave functions for structures I and II in the wave function of the actual molecule, $\psi = \kappa_{\mathrm{I}}\psi_{\mathrm{I}} + \kappa_{\mathrm{II}}\psi_{\mathrm{II}}$, have been evaluated. The resonance energy, E, is the difference between W and Q (Q includes the strain energy), and since it can easily be shown that in this case

$$W \cong Q + \tfrac{12}{5}\alpha(1 - \tfrac{3}{20}\delta^2), \quad \text{where} \quad \delta = \frac{\kappa_{\mathrm{II}}}{\kappa_{\mathrm{I}}} - 1,$$

E can be calculated, and also ΔE, the change of resonance energy relative to that in normal benzene, wherein $\phi = 60°$ and $\kappa_{\mathrm{II}}/\kappa_{\mathrm{I}}$ is unity. From $Q' - W$ and E the strain energy S can be calculated for any value of ϕ, and can be compared with that, S', which there would have been if $\kappa_{\mathrm{II}}/\kappa_{\mathrm{I}}$ had remained equal to unity; this latter quantity is the mean of the strain energies in I and II for any particular value of ϕ, which is equal to the sum of the strain in normal benzene (961 cals./gm. mole.) and the quantity $\frac{1}{2}k(\phi - 60°)^2$. The stability of the molecule as a whole, relative

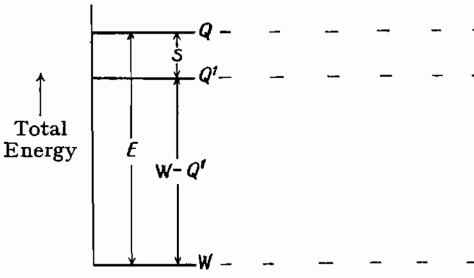

FIG. 4a.

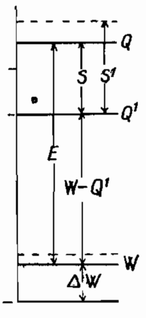

FIG. 4b.

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[4] Stuart, *Molekülstruktur*, Springer, Berlin, 1934, p. 86.

to normal benzene, is given by the differences in total energy, ΔW. The energy relations involved are illustrated in Figs. 4*a* and 4*b*, 4*a* showing the situation in normal benzene and 4*b* that in a strained benzene. Fig. 4*a* is explained by the foregoing and so is most of Fig. 4*b*; the upper broken line, in the latter, shows the value which Q would have if $\kappa_{\rm II}/\kappa_{\rm I}$ remained equal to unity, and the lower broken line shows what the total energy would have been if also the resonance energy had been the same as in normal benzene. The values of these quantities for a series of values of ϕ are collected together in Table I.; the energies are expressed in cals./gm. mole.

TABLE I.

ϕ.	W.	ΔW.	$\kappa_{\rm II}/\kappa_{\rm I}$.	E.	ΔE.	S.	S'.	$\Delta S'$.	$S'-S$.
45°	$Q' - 79{,}784$	855	1·063	− 81,552	48	1,768	1,861	900	− 93
50°	$Q' - 80{,}259$	380	1·041	− 81,579	21	1,320	1,361	400	−41
55°	$Q' - 80{,}543$	96	1·020	− 81,595	5	1,052	1,061	100	− 9
60°	$Q' - 80{,}639$	0	1·000	− 81,600	0	961	961	0	0
65°	$Q' - 80{,}543$	96	0·980	− 81,595	5	1,052	1,061	100	− 9
70°	$Q' - 80{,}259$	380	0·960	− 81,579	21	1,320	1,361	400	−41
75°	$Q' - 79{,}784$	855	0·941	− 81,552	48	1,768	1,861	900	−93

It will be observed that the resonance energy is decreased numerically by the change in $\kappa_{\rm II}/\kappa_{\rm I}$, but that the strain energy is decreased about twice as much by this same cause, so that the nett result is that the destabilisation of the molecule by the bending of the bonds is slightly less than it would have been if $\kappa_{\rm II}/\kappa_{\rm I}$ had remained equal to unity or if there had been no resonance at all.

The changes in $\kappa_{\rm II}/\kappa_{\rm I}$ are relatively small, and it remains to discuss whether or not they could account for the experimental facts. If a five-membered ring is attached to two *ortho* valencies of benzene the sum of the bond angles has to decrease from 568° 24′ to 540°, and if the simplifying assumption be made that the reduction of each bond angle is equal, this means that ϕ is reduced by about 12°, *i.e.*, to about 48°, and therefore that $\kappa_{\rm II}/\kappa_{\rm I}$ is approximately 1·05. This 5 per cent. change in the ratio of the coefficients of the two Kekulé structures is small. It may well be large enough, however, to cause one of the two substitution reactions to be favoured over the other to the extent shown by experiment. Thus we need only recall the important effects of substituents in the benzene ring in influencing the rates of further substitution in order to obtain support for the view that a small influence exerted on the benzene ring can produce important changes in rates of reaction. It is not unreasonable to expect that the effect consists primarily in a change in the heat of activation. If we represent the activation energy for the reaction of substitution in position 4 of the hydrindene derivatives by $A_{\rm I}$ and that for position 6 by $A_{\rm II}$ (these corresponding to positions 1 and 3 of the tetrahydronaphthalene derivatives), we may tentatively assume, in order to make a quantitative calculation, that the ratio $A_{\rm I}/A_{\rm II}$ is given by the equation

$$\frac{A_{\rm I}}{A_{\rm II}} = \left(\frac{\kappa_{\rm II}}{\kappa_{\rm I}}\right)^2,$$

the occurrence of the second power being characteristic of wave-mechanical calculations. In the absence of pronounced steric effects, it is probable that the ratio of the rates r_{I} and r_{II} of the reactions is given by the expression

$$\frac{r_{\mathrm{II}}}{r_{\mathrm{I}}} = \frac{e^{-A_{\mathrm{II}}/RT}}{e^{-A_{\mathrm{I}}/RT}}, \quad \text{whence} \quad \frac{r_{\mathrm{II}}}{r_{\mathrm{I}}} = e^{A_{\mathrm{II}}\left[\left(\frac{\kappa_{\mathrm{II}}}{\kappa_{\mathrm{I}}}\right)^2 - 1\right]\Big/RT}.$$

Since a 5 per cent. increase in $\kappa_{\mathrm{II}}/\kappa_{\mathrm{I}}$ produces a 10 per cent. increase in the square, it follows that the ratio anticipated for the rates of reaction would be $e^{0{\cdot}1\,A_{\mathrm{II}}/RT}$, and if A_{II} lies between 10,000 and 20,000 cals./gm. mole., as is probable, the rate ratio is between 5 and 27, approximately. Thus, since the ratio of the quantities of product is that of the rates of reaction, the product of reaction II would form between 83 per cent. and 96·5 per cent. of the total yield.

The prediction of the effect of attaching a six-membered reduced ring is less simple, owing to the more complex steric relations. Our procedure here is different from that of Mills and Nixon,[1] for they assumed that the molecule had *either* structure I *or* structure II, whereas we consider that initially it has the symmetrical resonating structure and then calculate how much it is distorted when a ring is attached. The reduced ring cannot have a stable configuration in which it is coplanar with the benzene ring : the carbon atoms 6 and 7 may either be both on one side of this plane or one on either side. Assuming the carbon-carbon distances [5] to be 1·39 Å in the benzene ring and 1·54 Å elsewhere, it is found on calculation that the *ortho* valency angle is decreased for the first configuration and increased for the second. The resultant total strain energy is less for the second than for the first configuration by about 300-500 cal./gm. mole. Moreover, it is known empirically that cyclohexane derivatives [6] and 1·4-dioxane [7] exist predominantly in the " Z " or chair form, presumably because of steric repulsion of the hydrogen atoms of the methylene groups. Therefore it is very probable that tetrahydronaphthalene and its derivatives also exist predominantly in the second configuration, which is approximately a " Z " configuration. For this configuration the angle ϕ is increased by 10° to 70°, $\kappa_{\mathrm{II}}/\kappa_{\mathrm{I}}$ becomes 0·96, and the ratio of the rate of reaction I to that of reaction II will, on the previous hypothesis, be $e^{0{\cdot}08\,A_{\mathrm{I}}/kT}$, which for values of A_{I} between 10,000 and 20,000 cals./gm. mole. is 3·8 to 14·5, so that the product from reaction I should form from 79 per cent. to 93·5 per cent. of the total yield.

The exact experimental facts as adduced by Mills and Nixon are the following. The bromination of 5-hydroxyhydrindene goes smoothly to give the 6-bromo derivative, with very little, if any, by-product, and 90 per cent. of the coupling of it with diazotised *p*-chloroaniline takes place in the 6 position ; the coupling with diazotised *p*-toluidine also occurs mainly in the 6 position but gives a small quantity of by-product which although not identified completely is isomeric with the main product.[1] Bromination of 5-acetoamido-hydrindene yields the 6-bromo derivative only, judging by the description of the reaction given by Borsche and Bodenstein.[8] The only product isolated in the bromination

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[5] Pauling and Brockway, *J. Chem. Physics*, 1934, **2.**

[6] Dickinson and Bilicke, *J. Am. Chem. Soc.*, 1928, **50**, 764 ; Hassel, *Trans. Faraday Soc.*, 1934, **30**, 874.

[7] Schwingel and Greene, *J. Am. Chem. Soc.*, 1934, **56**, 653 ; Sutton and Brockway, *ibid.*, 1935, **57**, 473.

[8] Borsche and Bodenstein, *Ber.*, 1926, **59**, 1910.

of *ar*-tetrahydro-β-naphthol is the 1-bromo derivative the structure of which was decided by elimination rather than by direct determination.[9] Coupling with diazotised sulphanilic acid occurs only in the 1 position; no definite mono-nitro derivative can be prepared because of the ease with which poly-nitration occurs; sulphonation is anomalous, occurring readily and completely in the 3 position.[9] Two mono-bromo derivatives are obtained directly from 2-acetamido-tetrahydronaphthalene, one in 82 per cent. yield and the other in 12 per cent.; [10] one must have the bromine atom attached to position 1 and the other must have it on position 4, but there is no direct chemical evidence to show which is which. It should be observed, however, that since the base derived from the main product is more volatile in steam than the other, it must certainly have the bromine atom on the 1 position, *i.e.*, *ortho* to the amino group, because *o*-chloro and *o*-bromoanilines are more volatile than the *m*- or *p*-compounds.[11] Thus it may be said that the brominations and diazo couplings go to the extent of 90 per cent. or more in the 4 position of the hydrindene derivatives, and to a similar extent in the 1 position of the tetrahydronaphthalene derivatives. There is, therefore, good agreement between the experimental facts and the theoretical predictions which have just been made. This shows that the wave-mechanical concept of the structure of the benzene molecule is capable of accounting for the facts interpreted by Mills and Nixon in terms of stabilisation of the individual Kekulé structures. It may be pointed out also that our treatment is based on the old contention that for some purposes, and within limitations, the substitution reactions of benzene derivatives can be discussed by considering the properties of the double bonds of the Kekulé structures.

One further question which merits discussion is that of the effect which forcibly altering the angle between two *ortho* valencies would have upon the angles between the other four. On the classical ideas it would obviously be expected that if the angle between one pair were fixed at ϕ then the angles between the alternate pairs would also be ϕ. Using wave-mechanical ideas the method of answering the question is the following. The expression for the total energy W,

$$W = \frac{\int(\kappa_{\mathrm{I}}\psi_{\mathrm{I}} + \kappa_{\mathrm{II}}\psi_{\mathrm{II}})H(\kappa_{\mathrm{I}}\psi_{\mathrm{I}} + \kappa_{\mathrm{II}}\psi_{\mathrm{II}})d\tau}{\int(\kappa_{\mathrm{I}}\psi_{\mathrm{I}} + \kappa_{\mathrm{II}}\psi_{\mathrm{II}})^2 d},$$

consists, when evaluated, of the Coulomb terms and exchange terms. The sum of the former terms has already been subdivided into two parts, the strain energy of a pair of external valencies, and the remainder of the energy, but this latter can be further subdivided, inasmuch as it also contains strain energy terms for the other two pairs of external valencies, the sum of which is

$$\frac{2\left\{\kappa_{\mathrm{I}}^2 \frac{k}{2}(\phi' - \phi_{\mathrm{I}})^2 + \frac{\kappa_{\mathrm{I}}\kappa_{\mathrm{II}}}{2}\frac{k}{4}[(\phi' - \phi_{\mathrm{I}})^2 + (\phi - \phi_{\mathrm{II}})^2] + \kappa_{\mathrm{II}}^2 \frac{k}{2}(\phi' - \phi_{\mathrm{II}})^2\right\}}{\kappa_{\mathrm{I}}^2 + \frac{1}{2}\kappa_{\mathrm{I}}\kappa_{\mathrm{II}} + \kappa_{\mathrm{II}}^2},$$

ϕ' being the angle between either of the two alternate pairs. In order to get the minimum energy, when $\kappa_{\mathrm{II}}/\kappa_{\mathrm{I}}$ has been fixed by the forcible

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[9] Schroeter, *Annalen*, 1922, **426**, 83.

[10] Smith, *J. Chem. Soc.*, 1904, **85**, 730.

[11] Sidgwick and Rubie, *J. Chem. Soc.*, 1921, **119**, 1013; Fittig and Mager, *Ber.*, 1874, **7**, 1179; *ibid.*, 1875, **8**, 364; Nemurowski, *Ber.*, 1891, **24**, ref. 271; Holleman, *Rec. Trav. chim. Pays Bas*, 1906, **25**, 186. We are indebted to Professor H. J. Lucas for suggesting this line of argument.

bending of one pair, this sum must be minimised with respect to ϕ', and from the differential relation which we thereby obtain the equilibrium value of ϕ' for any value of κ_{II}/κ_I can be calculated :—

$$\phi' = \tfrac{1}{2}(\phi_I + \phi_{II}) + \frac{1 - (\kappa_{II}/\kappa_I)^2}{2 + (\kappa_{II}/\kappa_I) + 2(\kappa_{II}/\kappa_I)^2}(\phi_I - \phi_{II}).$$

For $\phi_I = 75{\cdot}5°$, $\phi_{II} = 44{\cdot}5°$, and $\kappa_{II}/\kappa_I = 1{\cdot}063$, ϕ' is found to be 59° 15′, and for $\kappa_{II}/\kappa_I = 0{\cdot}941$, ϕ' is 60° 45′. It is seen that the bending of two valencies affects the disposition of the other four to only a very small extent. There are at present no published data by which this conclusion can be tested, and since the introduction of substituents in order to obtain such data from, say, measurements of electric dipole moment or electron-diffraction photographs would usually cause complications, as most substituents set up resonance of types other than that considered above, the interpretation of the results might be by no means straightforward.*

Summary.

The Mills-Nixon effect has been examined by a very simple wave-mechanical treatment. This has led to the conclusion that the effect of saturated side rings upon the ratio of the coefficients of the wave-functions of the two Kekulé structures is relatively small, being not more than about 6 per cent., and that the benzene ring retains the greater part of its stabilising resonance energy. Nevertheless, making the reasonable assumption that the ratio of the activation energies, for reaction as either one of the two Kekulé structures, depends upon the square of the ratio of coefficients, it is possible to account for the experimental facts. The effect which bending two valencies has upon the angles between the other valencies projecting from the benzene ring is found to be very small.

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* It may be pointed out, however, that although certain complications might be expected to arise in the previous considerations relating to the phenolic derivatives, there was no apparent indication of this happening.

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A Quantum Mechanical Discussion of Orientation of Substituents in Aromatic Molecules

BY G. W. WHELAND AND LINUS PAULING

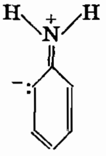
Introduction

When a substituent is introduced directly into an aromatic molecule, it may enter into certain of the available positions more readily than into others. This phenomenon of *orientation* has been exhaustively studied, and empirical rules have been found which describe the experimental results fairly satisfactorily. In a monosubstituted benzene C_6H_5R, for example, the introduction of a second substituent is governed by the nature of the atom or group, R, already present. Thus, for R = F, Cl, Br, I, OH, NH_2, and so on, the further substitution takes place largely in the ortho and para positions, while for R = COOH, CHO, NO_2, $(CH_3)_3N^+$, SO_3H, and so on, the substitution takes place largely in the meta position. Most ortho–para directing substituents, with the exception of fluorine, chlorine and bromine, activate the molecule so that the second substitution takes place more easily than in benzene itself. The meta directing substituents, on the other hand, produce deactivation. For other aromatic molecules similar rules have been found: in naphthalene substitution takes place largely at the α-position; in furan, pyrrole, and thiophene it takes place at the α-position; in pyridine it takes place at the β-position; and so on. In all the cases named except the last the molecule is more reactive than benzene.

Several qualitative theories have been proposed to explain the phenomenon of orientation, but of these we shall mention only a single one, which has been developed during the last fifteen years. This theory, which has achieved a considerable measure of success, and which we believe to be essentially correct, presents the following picture of the process of directed substitution. For definiteness we shall consider a mono-substituted benzene, since this is the type of molecule which has been most carefully studied from both the experimental and the theoretical standpoints. In the molecule C_6H_5R, with R attached to carbon atom 1, the electron distribution may be such as to place an excess or a deficiency of electrons on the various carbon atoms 2–6. Moreover, the electron distribution may be changed somewhat on the approach of a group R′ to one of the carbon atoms ("polarization" of the molecule by the group). We assume that *the rate of substitution of R′ for hydrogen on the* i*th carbon atom increases with increase in the negative charge of the* i*th carbon atom when the group R′ approaches it.* We thus take into consideration, in addition to the permanent charge distribution, the changes in it caused by the approaching group.

There are two principal ways in which the charge distribution is affected by the substituent R. The first, called the *inductive effect*, results when the electron affinity of this group is appreciably larger, or smaller, than that of the hydrogen atom which it replaces. Thus, for example, if its electron affinity is larger, it will attract to itself a larger proportion of the electrons which form the bond between it and the carbon atom. This carbon atom will accordingly be left with a small positive charge, compared with the others, and its own electron affinity will be correspondingly increased. Consequently, it will tend to appropriate some of the electrons belonging to its neighbors, and so on around the ring. The net effect is, then, a transference of negative electricity from the ring to the substituent R. In an analogous manner, if R has a smaller electron affinity than the hydrogen atom which it replaces, it will give up negative electricity to the ring. In order to obtain agreement with experiment, it is necessary to assume that the *o*- and *p*-positions are affected by this redistribution of charge to approximately equal extents, and that the *m*-positions remain nearly unaffected. This is at variance with the simple classical picture, which predicts the order ortho > meta > para, but it finds its explanation in the quantum mechanical treatment given later.

The second way in which the substituent R affects the charge distribution of the molecule is called the *resonance effect* (or sometimes the *tautomeric* or *electromeric effect*). This results when the molecule resonates among several electronic structures. For example, for aniline the structures



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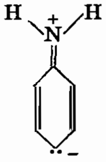

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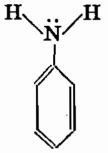
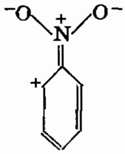


contribute to the normal state of the molecule, and for nitrobenzene



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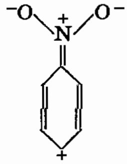

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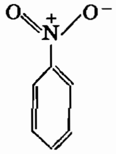
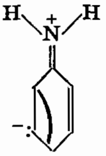


In the first molecule the resonance produces an increased concentration of electrons on the *o* and *p* carbon atoms, and in the second it produces a decreased concentration. As with the inductive effect, the meta positions remain nearly unaffected, since structures of the type



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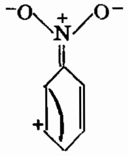

make relatively small contributions to the state of the molecule.

Some examples will illustrate the application of the theory to particular molecules. In toluene, the observed direction of the dipole moment shows that electrons have been transferred from the methyl group to the ring. Hence substitution takes place readily, particularly at the *o*- and *p*-positions, which have the greatest excess of electrons.

In nitrobenzene the nitro group has a large electron affinity, and accordingly draws electrons away from the ring. The resonance effect works in the same direction, and, as a result, all positions have a deficiency of electrons. The meta positions are least affected, and the substitution takes place there with difficulty. In aniline, the inductive effect and the resonance effect oppose each other, but the latter wins out, and very easy *o-p* substitution takes place.

These ideas have arisen through the combined efforts of a large number of different workers, among whom may be mentioned Fry, Stieglitz, Lapworth, Lewis, Lucas, Lowry, Robinson, and especially Ingold. For details the reader is referred to the excellent review articles of the last named author.[1]

With the development of a detailed quantum mechanical theory of the structure of aromatic molecules, it has become possible to attack the problem of orientation quantitatively. An attempt to do this was made by Hückel,[2] who showed that a polarizing substituent in benzene induces alternating charges in the ring. He limited his calculations, however, to the inductive effect, and neglected the resonance effect as well as the polarization of the molecule by the attacking group. As a result of these over-simplifications, he was led to make incorrect physical and chemical assumptions in order to obtain a rough correlation between his calculations and experiment. Thus, he assumed that "negative" groups, such as Cl, NH_2, and so on, increase the electron affinity of the attached carbon atom, while "positive" groups, such as NO_2, SO_3H, and so on, decrease its electron affinity. (Actually, all of the groups named tend to draw electrons away from the attached carbon atom, as far as the inductive effect alone is concerned, and hence to increase its electron affinity.) With this assumption, he then showed by a perturbation calculation that the negative groups induce positive charges on the *o*- and *p*-positions, while the positive groups induce negative charges there. This can be reconciled with the facts of orientation only if the ease of substitution is assumed to increase with increase of *positive* charge at the point of attack.

This is the exact opposite of the rule stated above, and appears to be in definite disagreement with other chemical evidence.[2] It is, furthermore, incapable of giving a consistent picture even of the process of orientation, as the following examples will show. (1) The observed direction of the dipole moment of toluene shows that electrons have been transferred from the methyl group to the ring. The methyl group is accordingly a positive one, in the sense of the foregoing discussion, and consequently should direct meta. Actually it directs ortho–para. (2) In pyridine the electron affinity of the nitrogen atom is larger than that of the carbon atoms. Consequently the charge distribution is the same as in benzene with a very strongly negative substituent. Substitution should accordingly take place in the α and γ positions (analogous to *o* and *p*) with great ease, but actually it takes place in the β position (analogous to *m*) with considerable difficulty.

The error in Hückel's treatment lies not in the quantum mechanical calculations themselves, which are correct as far as they go, but in the over-simplification of the problem and in the incorrect interpretation of the results. Consequently it has seemed desirable to us to make the necessary extensions and corrections in order to see if the theory can lead to a consistent picture. In the following discussion we have found it necessary to consider all of the different factors mentioned heretofore: the resonance effect, the inductive effect, and the effect of polarization by the attacking group. The inclusion of these several effects in the theory has led to the introduction of a number of more or less arbitrary parameters, and has thus tended to remove significance from the agreement with experiment which is achieved. We feel, however, that the effects included are all justified empirically and must be considered in any satisfactory theory, and that the values used for the arbitrary parameters are reasonable. The results communicated in this paper show that the quantum mechanical theory of the structure of aromatic molecules can account for the phenomenon of directed substitution in a reasonable way.

Outline of the Method

There are two principal methods available for the quantum mechanical treatment of molecular structure, the valence bond method and the molecular orbital method. In this paper we shall make use of the latter, since it is simpler in form and is more easily adapted to quantitative calculations.[3] We accordingly consider each electron

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[1] C. K. Ingold, *Ann. Rep.*, **23**, 129 (1926); *Rec. trav. chim.*, **48**, 797 (1929); *J. Chem. Soc.*, 1120 (1933); *Chem. Rev.*, **15**, 225 (1934).

[2] E. Hückel, *Z. Physik*, **72**, 310 (1931). For criticism of this work from the chemical side see A. Lapworth and R. Robinson, *Nature*, **129**, 278 (1932); **130**, 273 (1932); see also E. Hückel and W. Hückel, *ibid.*, **129**, 937 (1932).

[3] For purely qualitative arguments, on the other hand, the former is quite convenient. The description of the theory up to this point has been, in fact, merely a statement of the qualitative conclusions of the valence bond theory.

to be moving essentially alone in a self-consistent field, which is produced by the nuclei and by all the electrons other than itself, and we approximate the individual one-electron wave functions, φ_j, by means of linear combinations of the orbitals, ψ_k, belonging to the different atoms.

$$\varphi_j = \sum_k a_{jk}\,\psi_k \qquad (1)$$

In systems of the type under consideration the aromatic rings lie in a single plane. Consequently the atomic s and p orbitals, ψ_k, to which the present discussion will be limited, can be divided into two classes, depending upon whether they are symmetric or antisymmetric with respect to reflection in this plane. Since orbitals from one of these classes do not combine with orbitals from the other, each of the summations of Eq. 1 needs to be extended only over the members of a single class. Electrons will of course be assigned to molecular orbitals, φ_j, of both types, but it will be sufficient for our purposes to consider only the ones which are formed from the antisymmetric atomic orbitals—the $[p]_h$ orbitals in Hückel's nomenclature. In energy calculations this is a legitimate simplification, since it affects merely the arbitrarily chosen zero point of energy, but in the present treatment it requires further justification, since we are now interested in the charge distribution. There is, however, considerable experimental evidence to show that π bonds, such as are formed by the $[p]_h$ orbitals, are much more polarizable than σ bonds, such as are formed by the symmetric orbitals. This is in accord with their smaller binding energy, and also with the fact that orientation phenomena are not common in saturated systems. Consequently we shall assume that the inclusion of the polarization of the symmetric orbitals would result in only a negligibly small correction.

We return now to those molecular orbitals, φ_j, of Eq. 1 which are expressed in terms of the $[p]_h$ functions. The variation method shows that the best values of the coefficients a_{jk} are those which satisfy the equations

$$\sum_{k=1}^{l} a_{jk}(H_{mk} - \Delta_{mk} W_j) = 0,\ j, m = 1,2,\ldots,l \qquad (2)$$

where l is the total number of $[p]_h$ functions (one for each atom present, except the hydrogens);

$$H_{mk} = \int \psi_m^* H \psi_k\, d\tau \qquad \Delta_{mk} = \int \psi_m^* \psi_k\, d\tau$$

and W_j is the energy of an electron occupying the molecular orbital φ_j.

For each value of j there is a set of equations, but the different sets are all identical except for the replacement of the subscript j by some other, say j'. The condition for the solubility of this set of equations is that their determinants vanish. The l roots of this secular equation, $W = W_j$ ($j = 1,2,\ldots,l$) give the energies of the l molecular orbitals. We then assign two electrons (one with positive and one with negative spin) to the lowest root, two more to the next lowest root, and so on until all have been used up. The values of W_j found in this manner are then substituted back into the Equations 2, from which the ratios of the values of the coefficients a_{jk} can be derived. The absolute magnitudes of the coefficients are determined by the normalization condition, $\int \varphi_j^* \varphi_j d\tau = 1$.

$$|H_{mk} - \Delta_{mk} W| = \begin{vmatrix} H_{11} - \Delta_{11}W & H_{12} - \Delta_{12}W & \cdots & H_{1l} - \Delta_{1l}W \\ H_{21} - \Delta_{21}W & H_{22} - \Delta_{22}W & \cdots & H_{2l} - \Delta_{2l}W \\ \cdots & \cdots & \cdots & \cdots \\ H_{l1} - \Delta_{l1}W & H_{l2} - \Delta_{l2}W & \cdots & H_{ll} - \Delta_{ll}W \end{vmatrix} = 0 \qquad (3)$$

An electron occupying the molecular orbital φ_j will spend a fraction of its time given by the expression $|a_{jk}|^2$ in the atomic orbital ψ_k. Consequently the total average charge on atom k will be

$$C_k = e \sum_j |a_{jk}|^2 \qquad (4)$$

where the summation is extended over all occupied orbitals φ_j (the orbital being counted twice if occupied twice),[4] and e represents the charge of the electron.

As usual in these calculations, we make the following assumptions in regard to the magnitudes of the integrals H_{mk} and Δ_{mk}.

$$\begin{aligned} H_{kk} &= q + \delta_k\beta \\ H_{mk} &= \beta, \text{ if } \psi_m \text{ and } \psi_k \text{ are on adjacent atoms,} \\ &= 0, \text{ otherwise, for } m \neq k \\ \Delta_{kk} &= 1 \\ \Delta_{mk} &= 0, \text{ for } m \neq k \end{aligned}$$

Here q represents the coulomb energy of an electron occupying a definite $[p]_h$ orbital in unsubstituted benzene; its value has been estimated to be about -2.7 v. e. = -60 kcal./mole.[5] β is a *resonance integral* between adjacent orbitals; its value has been estimated to be about -0.85 v. e. = -20 kcal./mole.[5] δ_k is a constant, the purpose of which is to allow for the different electron affinities of the different atoms. For $\delta_k > 0$, the

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(4) Strictly speaking, the complete eigenfunction for the molecule should be made antisymmetric before the charge densities at the various positions are calculated. It is easily shown, however, that this further refinement in the treatment does not alter the results obtained.

(5) G. W. Wheland, *J. Chem. Phys.*, **2**, 474 (1934).

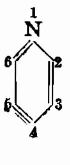
atom k has a larger, and for $\delta_k < 0$, a smaller electron affinity than a carbon atom in unsubstituted benzene.

We have attempted to estimate values of the δ's for the different kinds of atoms with which we will deal later, but we have not been able to arrive at any very consistent figures. Our procedure was to determine the values which would bring the calculated resonance energies into agreement with the empirical ones. The figures obtained in this way averaged about +4 for oxygen and +2 for nitrogen, and accordingly were of the correct sign, and of a reasonable order of magnitude, but the spread in both cases was quite large. Moreover, it is questionable if δ values obtained from energy calculations can be applied directly to calculations of charge distribution, when the method of treatment is as rough as the present. Accordingly we shall not choose a definite set of δ's which we shall use throughout, but instead shall allow the values to vary within fairly wide limits, in order to see the effect of such a variation upon the calculated polarization. Very fortunately it turns out that the decisive factor in most cases is not the magnitude of δ but its sign, which can be predicted with almost complete assurance.

Our method of calculation is now quite straightforward. We account for the permanent polarization resulting from the inductive effect by introducing suitable δ's upon the proper atoms; we account for that resulting from the resonance effect by explicitly including in the treatment all the $[p]_h$ orbitals of the problem, and not merely those on the atoms of the ring; and finally we account for the polarizing effect of the reacting group by introducing a small δ at the point of attack. For the sake of simplicity, we shall first treat only the permanent polarization, and then later consider the polarizability at the different positions.

Application to the Calculation of the Permanent Polarization

Pyridine.—We shall begin the discussion with pyridine rather than with a substituted benzene, since it offers a particularly simple example, in which only the inductive effect is operative. We number the atoms in order, beginning with nitrogen. Then δ_1, which takes into account the electron affinity of the nitrogen atom, will be positive in sign, and of the order of magnitude of perhaps 2; $\delta_2 = \delta_6$ will also be positive in sign as a result of induction, but will be much smaller in magnitude than δ_1; the remaining δ's can be considered negligibly small. The secular equation is then



$$\begin{vmatrix} x+\delta_1 & 1 & 0 & 0 & 0 & 1 \\ 1 & x+\delta_2 & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x+\delta_6 \end{vmatrix} = 0$$

where, for simplicity in writing, we have divided each row by β and set $(q-W)/\beta = x$. We cannot solve this equation rigorously unless we put into it definite numerical values for δ_1 and $\delta_2\ (=\delta_6)$. The perturbation theory, however, gives a method by which we can expand both the solutions, W_j, and the eigenfunctions, φ_j, in rising powers of the δ's. If we carry the procedure only as far as the first order, we obtain linear expressions which represent approximately the variation of the different quantities of interest for small values of the δ's. The unperturbed secular equation, which is obtained by setting $\delta_1 = \delta_2 = \delta_6 = 0$, is just the same as the one which arises in the treatment of benzene. Its roots are

$$W_j^0 = q + 2\beta \cos(2\pi j/6)$$
$$j = 1,2, \ldots, 6$$

and the corresponding wave functions are

$$\varphi_j^0 = \frac{1}{\sqrt{6}} \sum_{k=1}^{6} e^{(2\pi i/6)jk}\, \psi_k \qquad i = 1,2, \ldots, 6 \tag{5}$$

The familiar equations of the first order perturbation theory now show that the corresponding perturbed quantities are

$$\left.\begin{aligned} W_j &= \int \varphi_j^{0*} H \varphi_j^0\, d\tau = W_j^0 + \int \varphi_j^{0*} H' \varphi_j^0\, d\tau \\ \varphi_j &= \varphi_j^0 + \sum_k{}' \frac{\int \varphi_k^{0*} H' \varphi_j\, d\tau}{W_j^0 - W_k^0}\, \varphi_k^0 \end{aligned}\right\} \tag{6}$$

where H' is the part of the complete Hamiltonian operator which refers to the perturbation, such that

$$\left.\begin{aligned} \int \psi_k^* H' \psi_l\, d\tau &= \delta_1\beta \text{ if } k = l = 1 \\ &= \delta_2\beta \text{ if } k = l = 2 \text{ or } 6 \\ &= 0 \quad \text{otherwise} \end{aligned}\right\} \tag{7}$$

and the prime on the summation sign indicates that the term with $k = j$ is omitted. When Eqs. 5 and 7 are inserted in Eq. 6 and use is made of Eq. 4, the following results are obtained.

$$C_N = C_1 = \left(1 + \frac{43}{108}\delta_1 - \frac{17}{54}\delta_2\right)\beta$$

$$C_\alpha = C_2 = C_6 = \left(1 - \frac{17}{108}\,\delta_1 + \frac{22}{54}\,\delta_2\right) e$$
$$C_\beta = C_3 = C_5 = \left(1 + \frac{1}{108}\,\delta_1 - \frac{14}{54}\,\delta_2\right) e$$
$$C_\gamma = C_4 = \left(1 - \frac{11}{108}\,\delta_1 + \frac{1}{54}\,\delta_2\right) e$$

(neglecting terms in δ_1^2, $\delta_1\delta_2$ and δ_2^2). These figures differ somewhat from the corresponding ones given by Hückel,[2] because he put $\delta_2 = 0$ and also, in applying the perturbation treatment, he made use of a rather different procedure which so complicated the calculations that he did not carry them through completely.

If, now, δ_2 lies within the limits $^1/_{28}\,\delta_1 < \delta_2 < {}^1/_4\,\delta_1$, which seem quite reasonable, the over-all effect of the perturbation is a transference of negative electricity from the various carbon atoms to the nitrogen atom at position 1, with the consequence, in accordance with the rule formulated above, that the molecule is deactivated so that substitution is more difficult than in benzene; and furthermore the α and γ positions (2 and 6, and 4, respectively) are most affected by this transference of electricity, so that substitution will take place at the β positions (3 and 5), which have the smallest deficiency of electrons. Both of these conclusions are borne out by experiment.

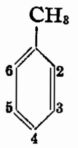
This calculation and its comparison with experiment hence provide us with a rough idea as to the magnitude of the inductive effect from atom to atom, as given by the ratio δ_2/δ_1. If this ratio were greater than $^1/_4$ the effect of δ_2 would overcome that of δ_1 and pyridine would substitute in the α and γ positions, whereas if it were less than $^1/_{28}$ substitution would occur in the β positions more readily than in benzene. A value of about $^1/_{10}$ for δ_2/δ_1 seems reasonable to us from a consideration of the electronic phenomena involved.

In order to see how accurate this perturbation treatment actually is, we have substituted numerical values for the δ's directly into the secular equation, and then solved it rigorously by numerical methods. The calculations are not given in detail, since they are quite straightforward and proceed along well-known lines. The results are shown in Table I.

TABLE I

δ_1	1	2	3	2
$\delta_2 = \delta_6$	0	0	0	0.2
$C_N = C_1$	1.37e	1.62e	1.79e	1.59e
$C_\alpha = C_2 = C_6$	0.85	0.76	0.71	0.83
$C_\beta = C_3 = C_5$	1.01	1.01	1.01	.96
$C_\gamma = C_4$	0.91	0.84	0.79	.82

It is seen that for $\delta_1 = 1$ the perturbation treatment is still fairly accurate, but that for larger values it is only qualitatively satisfactory. In any case, however, if we assume that the ease of substitution increases with increased negative charge at the point of attack, the calculations are in very good agreement with experiment; if, on the other hand, we follow Hückel in making the opposite assumption, the calculations can be reconciled with experiment only by making δ_1 negative, which seems highly improbable in view of the fact that the nuclear charge of nitrogen is greater than that of carbon.

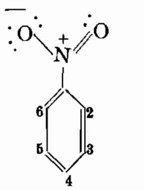


Toluene.—The toluene molecule is complicated in that it contains atomic orbitals (in the methyl group) which are neither symmetric nor antisymmetric with respect to reflection in the plane of the ring. However, since it seems very unlikely that there will be any appreciable resonance between the methyl group and the ring, we are able to avoid the difficulty by formally replacing the substituent by a small δ value on the adjacent carbon atom. The dipole moment of the molecule requires that this δ be negative in sign. It is also presumably small enough so that the same perturbation treatment as was employed in the case of pyridine will represent a good approximation.[6] The results are then just the same as those given in Eq. 8, except that C_α, C_β, and C_γ are to be replaced by C_{ortho}, C_{meta}, and C_{para}, respectively, in order to be in accord with the customary nomenclature. Here, as before, all the δ's except δ_1 and δ_2 can be set equal to zero. Since δ_1 is negative, we see, neglecting δ_2, that the ortho and para positions have excess negative charges, in agreement with the experimental result that substitution takes place there very readily. This result is not changed by the consideration of δ_2 so long as the ratio δ_2/δ_1 is less than $^1/_4$.

Phenyltrimethylammonium Ion, $N^+(CH_3)_3$-C_6H_5.—In this ion, as in toluene, we ignore the electrons involved in bonds from nitrogen to the attached groups, and consider only the inductive effect. The positive charge on the nitrogen atom increases its electron affinity to a value still greater than that for neutral nitrogen, so that we

[6] For larger δ values, the results for toluene can be read off at once from those for pyridine (Table I); reversing the sign of the δ's in a given secular equation of the present type merely reverses the direction of the induced polarization, and leaves its magnitude unchanged.

introduce in the above expressions (for toluene) a large positive value for δ_1 (and a small value for δ_2). This leads to greatly decreased values of C for ortho and para carbon atoms, with smaller decrease for meta, and in consequence to meta directed substitution, in agreement with experiment.



Nitrobenzene.—In the treatment of nitrobenzene we must consider nine $[p]_h$ orbitals and ten electrons, including an unshared pair on the negative oxygen atom in the indicated structure and one electron for each of the remaining atoms. We assume the resonance integral β to have the same value for O-N and N-C as for C-C. The results of the calculation are given in Table II, the next to the last column of which corresponds to the δ values which seem reasonable to us. It is seen that all positions are deactivated, the deactivation occurring least at the meta positions, where substitution should take place. These conclusions are in agreement with experiment.

TABLE II

δ_O	0	0	4	4	4
δ_N (δ_C)	0	2	2	2	0.8
δ_1	0	0	0	0.2	0
C_O	1.50e	1.24e	1.95e	1.94e	1.92e
C_N (C_C)	1.00	1.53	1.37	1.32	0.68
C_1	1.00	0.96	0.62	0.70	.95
$C_{\text{ortho}} = C_2 = C_6$	1.00	1.01	.79	.79	.85
$C_{\text{meta}} = C_3 = C_5$	1.00	1.00	.95	.95	1.00
$C_{\text{para}} = C_4$	1.00	1.01	.63	.61	0.83

Benzoic Acid, C_6H_5COOH.—The treatment of benzoic acid is the same as for nitrobenzene except for the δ values. The results for $\delta_O = 4$ and δ_C (of the carboxyl group) $= 0.8$ are given in the last column of Table II; it is seen that the carboxyl group, like the nitro group, is meta directing, in agreement with experiment. The calculation, however, indicates a rather too small deactivation of the meta position. This effect appears only in the third decimal place of C_{meta}, and is consequently not shown in the table.

Benzaldehyde, C_6H_5CHO, **Acetophenone,** $C_6H_5COCH_3$, **and Benzonitrile,** C_6H_5CN.—The results obtained for these molecules by considering eight $[p]_h$ orbitals and eight electrons are given in Table III.

It is seen that the aldehyde, ketone and nitrile groups are all meta directing, in agreement with experiment.

TABLE III

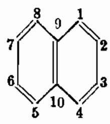
δ_O (δ_N)	0	2	2	4	4
δ_C	0	0	0.2	0	0.4
$C_O(C_N)$	1.00e	1.76e	1.75e	1.92e	1.92e
C_C	1.00	0.49	0.55	0.41	0.56
C_1	1.00	1.03	1.02	1.02	.98
$C_{\text{ortho}} = C_2 = C_6$	1.00	0.90	0.89	0.88	.85
$C_{\text{meta}} = C_3 = C_5$	1.00	1.00	1.00	1.00	1.00
$C_{\text{para}} = C_4$	1.00	0.91	0.90	0.87	0.85

Furan, Thiophene, Pyrrole.—The calculations for this case, with five orbitals and six electrons, show that when $\delta_2 (= \delta_5)$ (on the α carbon atoms) is neglected the β positions (3 and 4) are more strongly activated than the α. When, however, these δ's are given a reasonable magnitude, greater than $^1/_{25}\ \delta_1$, the situation is reversed, and the α positions are found to be the more strongly activated, as is demanded by experiment. Some calculated charge values are given in Table IV.

(X = O, S, NH)

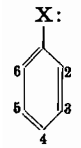
TABLE IV

δ_1	0.5	2.9	4	4	2	3
$\delta_2 = \delta_5$	0	0.29	0	0.5	0.25	0.375
$C_X = C_1$	1.38e	1.80e	1.88e	1.87e	1.69e	1.81e
$C_\alpha = C_2 = C_5$	1.14	1.08	0.98	1.13	1.10	1.13
$C_\beta = C_3 = C_4$	1.18	1.02	1.08	0.93	1.06	0.96



Naphthalene.—Naphthalene offers the first example of a molecule in which a consideration of the permanent polarization alone does not lead to the correct answer. Since this is a hydrocarbon, we might expect that no δ values would be necessary. In this case, however, the charge on each atom is found to be exactly 1.00e, so that substitution would take place at the α and β positions (1, 4, 5, 8 and 2, 3, 6, 7, respectively) with equal ease. If we attempt to avoid this difficulty by putting a δ upon the 9 and 10 carbon atoms, we find that its sign must be negative in order to produce an excess of electrons on the α positions. This seems unreasonable, however, since these carbon atoms carry no hydrogens, and would consequently be expected to have a larger rather than a smaller electron affinity than the others. We shall see later that a possible explanation of this discrepancy can be found by a consideration of the polarizing effect of the attacking group.

Aniline, Phenol, Fluorobenzene, etc.—The treatment of this group of molecules, involving seven $[p]_h$ orbitals and eight electrons, is comparatively unsatisfactory, in consequence of the fact that in them the inductive and the resonance effects work in opposite directions. In order to be able to predict which of the two will win out in any specific example, we need to have fairly accurate numerical values of the different δ's to be introduced in each case. In the absence of such information, the best we can do is to carry through a number of calculations, in order to see if any reasonable sets of values lead to agreement with experiment. The results are given in Table V.

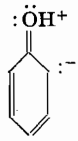


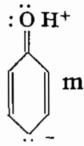
(X = NH_2, OH, F, etc.)

TABLE V

δ_X	0	2	4	6	2	4	6
δ_1	0	0	0	0	0.25	0.4	0.5
C_X	1.57*e*	1.91*e*	1.96*e*	1.98*e*	1.91*e*	1.97*e*	1.98*e*
C_1	1.00	0.93	0.95	0.95	1.02	1.10	1.15
$C_{\text{ortho}} = C_2 = C_6$	1.14	1.06	1.04	1.02	1.02	0.97	0.95
$C_{\text{meta}} = C_3 = C_5$	1.00	1.00	1.00	1.00	1.00	1.00	1.00
$C_{\text{para}} = C_4$	1.14	1.05	1.02	1.02	1.02	0.98	0.96

It will be seen that, as might be expected from purely qualitative considerations, the inductive effect, which deactivates the molecule and favors *m* orientation, is increased in importance with increase of the δ's, while the resonance effect, which activates the molecule and favors *o-p* orientation, is decreased in importance. This is in agreement with the fact that the *o-p* directing power of the halogens is in the order F < Cl < Br < I, which is the opposite of the order of electron affinities. On the other hand, it does not explain the marked difference between the halogens as a whole and the amino and hydroxyl groups—the former being relatively feeble in orienting power, and the latter being among the most powerful known. It also does not explain why the orders $NH_2 < PH_2 < AsH_2$ and OH < SH, which would be expected from analogy, are not correct.

It is possible that the explanation of these discrepancies is to be found in the fact that the resonance integral, β, may vary with the row and group of the periodic table. Such a variation must almost certainly exist, but it can be taken into account only with difficulty. Furthermore, the introduction of the large number of additional arbitrary parameters would deprive the whole procedure of much of its significance. A second possible explanation is that, with phenol for example, resonance with such structures as 

and 

may make relatively important contributions to the state of the molecule. The inclusion in the theory of such effects also would be difficult and would result in a further decrease in the significance of the treatment. Instead of resorting to such heroic measures to force the calculations into agreement with experiment, we prefer to let the matter stand as a possible weakness of the theory. It would not be surprising if our rough treatment should fall down in evaluating the relative importance of two opposed effects which differ so greatly in nature.

A further difficulty in the case of fluoro-, chloro- and bromobenzenes is that with them apparently no choice of the δ values seems to be reconcilable with the observed order of ease of substitution at the various positions: unsubstituted benzene > para > ortho > meta. Both the inductive and the resonance effects are seen to leave the charge on the *m*-position practically unchanged, and approximately equal to 1.00*e*, while the observed order demands a considerably smaller value. As in the case of naphthalene, however, we shall find later that this discrepancy can apparently be explained by taking into account the polarization of the molecule by the attacking group.

Polarization by the Attacking Group

The calculations so far have been concerned with the "permanent" charge distribution which the molecule would have when isolated, and which would be observed in its dipole moment. The factor that actually determines the orientation of the entering group, however, is the charge distribution at the instant of attack, which differs from the permanent charge distribution in consequence of polarization by the entering group. In most cases it is not necessary to take this latter effect into account explicitly, since it represents only a small correction. However, in certain cases it is apparently of decisive importance.[7]

In order to investigate the relative ease of substitution at the *i*th carbon atom, we shall introduce a small δ_i upon that atom, in addition

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(7) This was suggested originally by Ingold, *cf.* Ref. 1.

to any other δ's that may be required by the permanent polarization. This δ_i will presumably be positive in sign in all cases, since the customary reacting groups are "electron-seeking" and will accordingly tend to increase by induction the electron affinity of the near-by carbon atom.

In benzene itself the charge at the point of attack will be not 1.00e, as has been assumed heretofore, but $(1.00 + (43/108)\delta_i)e$. (Since δ_i is small, the results of the perturbation treatment can be applied directly.) In other molecules the ease of reaction at the ith carbon atom will then be greater than that of benzene if the charge at that point is greater than $(1.00 + (43/108)\delta_i)e$, and conversely.

Let us apply these considerations to pyridine. If we set $\delta_N = \delta_1 = 2$, $\delta_\alpha = \delta_2 = \delta_6 = 0.2$, and $\delta_i = 0.2$, we obtain the results given in Table VI. As might be expected, the polarizability of the molecule at the various positions is practically constant, and is very nearly the same as that of benzene. Consequently the orientation is not affected by considering the polarization by the approaching group. This state of affairs can be expected to hold whenever the permanent polarization produces marked differences, as here, between the different positions.

TABLE VI

POLARIZABILITY OF PYRIDINE

	Charge at ith atom			Charge in benzene
i[a]	$\delta_i = 0$	$\delta_i = 0.2$	Difference	$(1.00 + \frac{43}{108}0.2)e$
2	0.831e	0.920e	0.089e	1.080e
3	.960	1.038	.078	1.080
4	.825	0.905	.080	1.080

[a] For the numbering of the different atoms see the diagrams given previously.

In naphthalene, on the other hand, the permanent polarization leaves all atoms with the same or very nearly the same charge, and as a result any small difference in polarizability has an opportunity to make its effect felt. The results of perturbation treatments are given in Table VII. With $\delta_i > 0$ the α position is activated, and substitution would take place there readily, as is demanded by experiment.

TABLE VII

POLARIZABILITY OF NAPHTHALENE

i	Charge on ith atom	Charge in benzene
1	$(1.00 + 0.44\delta_i)e$	$(1.00 + 0.40\delta_i)e$
2	$(1.00 + .40\delta_i)e$	$(1.00 + .40\delta_i)e$

In the halogen benzenes the ortho and para positions are found to be more polarizable than the meta, as is shown in Table VIII.

TABLE VIII

POLARIZABILITY OF $C_6H_5\ddot{X}$

$\delta_X = 4.0$, $\delta_1 = 0.4$

i	Charge at ith atom			Charge in benzene
	$\delta_i = 0$	$\delta_i = 0.2$	Difference	
2	0.975e	1.055e	0.080e	1.080e
3	1.002	1.069	.067	1.080
4	0.984	1.064	.080	1.080

With the particular choice of the δ's used in the calculation the observed order[8] unsubstituted benzene > para > ortho > meta is not obtained, but agreement can be achieved by a suitable readjustment of the parameter values. If, with δ_X held fixed and equal to 4, the charges at the different positions are assumed to be linearly dependent upon δ_1 and δ_i (as is the case when these quantities are sufficiently small), the results of Table VIII can be expressed as

$$\begin{aligned}\text{Charge on 2} &= (1.036 - 0.152\delta_1 + 0.402\delta_i)e\\ \text{Charge on 3} &= (0.998 + 0.009\delta_1 + 0.339\delta_i)e\\ \text{Charge on 4} &= (1.024 - 0.099\delta_1 + 0.400\delta_i)e\end{aligned}$$

If we use the particular values $\delta_1 = 0.3$, $\delta_i = 0.2$ (any of several other sets would do as well), we find

$$\begin{aligned}\text{Charge on 2} &= 1.071e\\ \text{Charge on 3} &= 1.069e\\ \text{Charge on 4} &= 1.074e\end{aligned}$$

These figures are now in agreement with the observed order given above. While it is doubtful if much significance can be attached to parameter values obtained in such an arbitrary and *ad hoc* manner, it is nevertheless gratifying to observe that the ones found are not unreasonable.

Conclusion

By introducing reasonable values (about 2 for nitrogen, 4 for oxygen) for the electron affinity parameter relative to carbon, δ, and for the induced electron affinity for adjacent atoms ($\delta_2/\delta_1 \simeq 1/10$), we have shown that the calculated permanent charge distributions for pyridine, toluene, phenyltrimethylammonium ion, nitrobenzene, benzoic acid, benzaldehyde, acetophenone, benzonitrile, furan, thiophene, pyrrole, aniline, and phenol can be satisfactorily correlated qualitatively with the observed positions and rates of substitution. For naphthalene and the halogen benzenes this calculation does not lead to results

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[8] Iodobenzene substitutes more easily than benzene. In this case, however, δ_X is comparatively small, and the discrepancy does not exist.

in complete qualitative agreement with experiment; agreement is obtained, however, by the consideration of the effect of polarization of the molecule by the attacking group. Because of the presence of several adjustable parameters, this treatment cannot be considered as a pure quantum mechanical theory of directed substitution in aromatic molecules. However, the various effects which we have considered are certainly real, and there is no reason to doubt that they act in the directions calculated, and are of the general order of magnitude assumed; the parameters introduced are not completely arbitrary in value, because they are related to definite and fairly well understood atomic and molecular quantities. Furthermore, in the cases in which only one effect is important, as in pyridine, or in which all effects act in the same direction, as in nitrobenzene, the calculations lead to completely unambiguous conclusions, which are dependent to only a small degree upon the particular parameter values chosen. We accordingly feel that the degree of success realized in these quantitative considerations provides strong support for the underlying ideas as to the nature of the effects involved.

Summary

Using the method of molecular orbitals, a quantitative discussion of the charge distribution in aromatic molecules undergoing substitution reactions is carried out, taking into consideration the inductive effect, the resonance effect, and the polarizing effect of the attacking group. It is shown that, with reasonable values for the parameters involved, the calculated charge distributions for pyridine, toluene, phenyltrimethylammonium ion, nitrobenzene, benzoic acid, benzaldehyde, acetophenone, benzonitrile, furan, thiophene, pyrrole, aniline, phenol, naphthalene, and the halogen benzenes are in qualitative agreement with the experimental results regarding position and rate of substitution, the auxiliary hypothesis being made that the rate of substitution of the group R′ for hydrogen on the *i*th carbon atom increases with increase in the negative charge of the *i*th carbon atom when the group R′ is in position to react.

PASADENA, CALIFORNIA RECEIVED JULY 26, 1935

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The Dependence of Interatomic Distance on Single Bond–Double Bond Resonance[1]

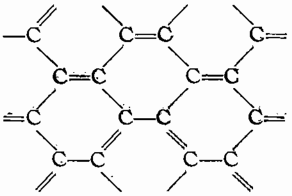
BY LINUS PAULING, L. O. BROCKWAY AND J. Y. BEACH

Introduction

Three years ago it was pointed out[2] that observed values of interatomic distances provide useful information regarding the electronic structures of molecules, and especially regarding resonance between two or more valence bond structures. On the basis of the available information it was concluded that resonance between two or more structures leads to interatomic distances nearly as small as the smallest of those for the individual structures.[3] For example, in benzene each carbon–carbon bond resonates about equally between a single bond and a double bond (as given by the two Kekulé structures); the observed carbon–carbon distance, 1.39 Å., is much closer to the carbon–carbon double bond distance, 1.38 Å., than to the single bond distance, 1.54 Å.

In benzene the two Kekulé structures contribute equally. In general, however, the coefficients of the functions corresponding to different structures in the approximate wave function of a molecule may have arbitrary values, and a bond between two atoms may have any intermediate character between the extremes of a pure single bond and a pure double bond. For a series of bonds covering the range between a pure single bond and a pure double bond we expect the interatomic distance to change continuously from the single bond value to the double bond value. In this paper we present evidence regarding the nature of the function expressing the dependence of interatomic distance on single bond–double bond resonance, and then make use of the function in order to obtain information regarding the electronic structures of resonating molecules for which experimental interatomic distance values are available. The effect of resonance on bond angles is also discussed.

The Interatomic Distance Function for Single Bond–Double Bond Resonance.—The carbon–carbon single bond distance is 1.54 Å. (diamond, aliphatic compounds). For the carbon–carbon double bond distance we shall use the value 1.38 Å. given by the table of covalent radii;[4] some support for this is given by Badger's value[5] 1.37 Å. for ethylene. These give the two extreme points of the interatomic distance function for single bond–double bond resonance. The midway point, for fifty per cent. double bond character, is provided by the value 1.39 Å. for benzene;[6] the electronic structure of benzene is represented in the main by resonance between the two Kekulé structures (the contribution of excited structures being small[7]), and this makes each bond resonate equally between a double and a single bond. Another point on the curve is provided by graphite (C–C = 1.42 Å.), in which each bond has one-third double bond character, corresponding to resonance among many structures such as



Through these four points we draw a smooth curve, as shown in Fig. 1, which we accept as representing the dependence of carbon–carbon interatomic distance on double-bond character for single bond–double bond resonance. We believe that by a suitable translation and a change of vertical scale (to give the correct end-points) the same function can be used for bonds between other atoms, and probably also for double bond–triple bond resonance. This use of the curve will be illustrated below.

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(1) Part of the material in this paper was presented at the meeting of the A. A. A. S. in Berkeley, June, 1934.

(2) L. Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932).

(3) The following argument, suggested by Professor P. M. Morse, shows that this conclusion is reasonable. Of two potential functions corresponding to two structures, the one with the smaller value of the equilibrium internuclear distance will have the greater curvature in the neighborhood of the minimum [see for example, R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934)]. Hence the more stable of the two resultant potential functions corresponding to resonance between these two structures will tend to have its minimum in the position determined by the original curve of greater curvature, that is, near the smaller value of the internuclear distance.

(4) L. Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932); L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

(5) R. M. Badger, *Phys. Rev.*, **45**, 648 (1934).

(6) L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

(7) A possibly more accurate value for the double bond character of the bonds in benzene (0.46) is obtained by considering all five canonical structures with weights equal to the squares of their coefficients in the wave function. There is some uncertainty as to the significance of this, however, because of the non-orthogonality of the wave functions for the canonical structures, and for chemical purposes it is sufficiently accurate to follow the simple procedure adopted above.

It is seen that a small amount of double bond character causes a large decrease in interatomic distance below the single bond value, whereas only a small change from the double bond value is caused by even as much as fifty per cent. single bond character.[8] In consequence, the interatomic distance criterion for resonance provides quantitative information only through about one-half of the bond character region.

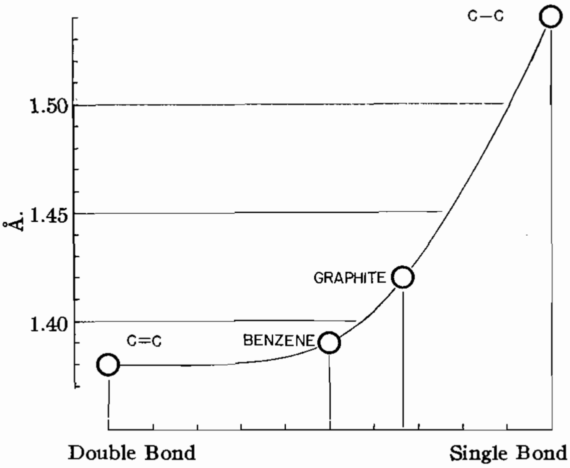

Fig. 1.—The empirical function expressing the dependence of carbon–carbon interatomic distance on bond character for single bond–double bond resonance.

The applicability of the curve to bonds other than carbon–carbon can be tested with the data for carbon–oxygen and nitrogen–oxygen bonds given in Table I, the predicted distances being obtained from the table of covalent radii for pure single and double bonds, and from the curve (with end-points determined by the table) for bonds of intermediate type. The carbonate and nitrate ions resemble graphite in that the double bond resonates among three positions, whereas in the carboxyl and nitro groups, as in benzene, the double bond resonates between two positions. It is seen that there is approximate agreement between predicted and observed values.

The Use of the Interatomic Distance Function in Discussing the Electronic Structure of Molecules.—The observed interatomic distances listed in Table II are interpreted with the aid of the curve of Fig. 1 to lead to the assignment of fractional double bond character as given in the last column. It is seen that a single bond between conjugated double bonds (cyclopentadiene) or conjugated benzene rings (biphenyl) *p*-diphenylbenzene, has about 15 or 20% double bond character,[9] whereas a single bond between conjugated

TABLE I

COMPARISON OF PREDICTED AND OBSERVED INTERATOMIC DISTANCES

Carbon–Oxygen Bonds

Amount of double bond character	Predicted distance	Observed distance
0	1.43 Å.	1.42 Å. in $(CH_3)_2O$[a] 1.44 in CH_3ONH_2[a]
$^1/_3$	1.32	1.31 (1.26) in $(CO_3)^{-}$[b]
$^1/_2$	1.29	1.29 in $(HCOOH)_2$[c]
1	1.28	

Nitrogen–Oxygen Bonds

Amount of double bond character	Predicted distance	Observed distance
0	1.36 Å.	1.37 Å. in CH_3ONH_2[a]
$^1/_3$	1.26	1.22 (1.26) in $(NO_3)^{-}$[b]
$^1/_2$	1.23	1.21 in CH_3NO_2[a]
1	1.22	

[a] Preceding papers. [b] Preliminary values obtained through redetermination of parameters in crystals (calcite and sodium nitrate) by Mr. Norman Elliot. The values in parentheses are based on older parameter determinations. [c] L. Pauling and L. O. Brockway, *Proc. Nat. Acad. Sci.*, **20**, 336 (1934). The value 1.25 Å. reported in crystals of oxalic acids and oxalates is probably less reliable.

TABLE II

INTERATOMIC DISTANCES AND BOND TYPE

Molecule	Bond	Observed distance	Amount of double bond character
Cyclopentadiene	C—C	1.46 Å.[a]	0.20
p-Diphenylbenzene	C—C	1.48[b]	.14
Biphenyl	C—C	1.48[c]	.14
Cyanogen	C—C	1.43[d]	.29
Diacetylene	C—C	1.43[d]	.29
Urea	C—N	1.37[e]	.28
Thiourea	C—N	1.37[f]	.28
Cyanuric triazide	C—N	1.38[g]	.25
Carbon suboxide	C═C	1.30[h]	.20[i]
	C═O	1.20[h]	.20[i]

[a] Preliminary result of electron diffraction study in this Laboratory. [b] L. W. Pickett, *Proc. Roy. Soc.* (London), **A142**, 333 (1933). [c] J. Dhar, *Indian J. Phys.*, **7**, 43 (1932). [d] L. O. Brockway, *Proc. Nat. Acad. Sci.*, **19**, 868 (1933). [e] R. W. G. Wyckoff and R. B. Corey, *Z. Krist.*, **89**, 462 (1934). [f] R. W. G. Wyckoff and R. B. Corey, *ibid.*, **81**, 386 (1932). [g] I. E. Knaggs, *Proc. Roy. Soc.* (London), **A150**, 576 (1935). [h] L. O. Brockway and L. Pauling, *Proc. Nat. Acad. Sci.*, **19**, 860 (1933). [i] Triple-bond character.

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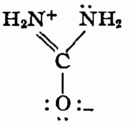
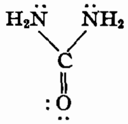
[8] Verification of the shape of the curve has been obtained with the collaboration of Dr. J. Sherman by the theoretical treatment of a somewhat similar problem (the effect of *s*-*p* hybridization of bond orbitals on interatomic distance).

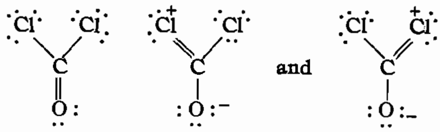
[9] The comparison of these results with the simple theory of conjugated systems [Pauling and Sherman, *J. Chem. Phys.*, **1**, 679 (1933)] is not straightforward because of non-orthogonality of the canonical structures. If we assume that the double bond character is given by the square of the coefficient of the structure — = — in the normalized wave function for a system of two conjugated double bonds the simple theory leads to the value 0.25, in approximate agreement with the experimental result.

triple bonds (cyanogen, diacetylene) has about 30% double bond character. In cyanuric triazide the reported distance for the bond linking an azide group to the cyanuric ring corresponds to about 25% double bond character.

In urea and thiourea the ionic structures such as  are of sufficient importance to give each C–N bond about 28% double bond character. In case these structures were equivalent to the structure  giving complete resonance, each bond would have one-third double bond character, as in the carbonate, nitrate, and guanidonium ions. The experimental result shows that resonance is nearly complete.

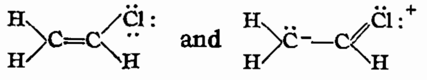
In carbon suboxide, for which the structure $:\ddot{O}{=}C{=}C{=}C{=}\ddot{O}:$ is most important, structures such as $^{-}:\ddot{O}{-}C{\equiv}C{-}C{\equiv}O:^{+}$ contribute about 20% triple bond character to each bond.

Resonance of a Carbon–Chlorine Bond and an Adjacent Double Bond.—We expect the phosgene molecule to resonate among the structures



of which the first is the most important, the second and third making only small contributions to the normal state of the molecule. The value 1.68 ± 0.02 Å. for the C–Cl distance, reported in the preceding paper,[10] corresponds to 17% double bond character for the carbon–chlorine bonds, calculated with the curve of Fig. 1, with end points C–Cl = 1.76 Å. and C=Cl = 1.58 Å. The value C–Cl = 1.70 ± 0.02 Å. in thiophosgene leads to 12% double bond character, indicating that the ionic structures make a smaller contribution for this molecule than for phosgene.

We might predict that of the six chloroethylenes the C–Cl distance would be smallest in vinyl chloride, which resonates between the structures



and largest in tetrachloroethylene, in which the effect of the double bond is divided among four carbon–chlorine bonds. This is found experimentally (Table III), except that the distance reported for *cis*-dichloroethylene is about 0.02 Å. smaller and that for vinyl chloride somewhat larger than expected. The amounts of double bond character shown in the table are reasonable—about 15% for mono- and dichloroethylenes, 10% for trichloroethylene, and 6% for tetrachloroethylene.

TABLE III

INTERATOMIC DISTANCES AND BOND TYPE FOR CARBON–CHLORINE BONDS

Molecule	C–Cl distance	Double bond character
Phosgene	1.68 ± 0.02 Å.	0.17
Thiophosgene	1.70 ± .02	.12
CH_2CHCl	1.69 ± .02	.14
CH_2CCl_2	1.69 ± .02	.14
cis-CHClCHCl	1.67 ± .03	.20
trans-CHClCHCl	1.69 ± .02	.14
$CHClCCl_2$	1.71 ± .03	.10
C_2Cl_4	1.73 ± .02	.06

The effect of this partial double bond character on the chemical properties of chlorine atoms conjugated to double bonds is well known; it corresponds in the main to a diminution in reactivity. The correlation with bond angles is discussed in a later section of this paper.

Inasmuch as the conjugation properties of a double bond and a benzene ring are closely similar,[11] we expect for the halogen substituted benzenes interatomic distances similar to those for the halogen ethylenes. De Laszlo[12] has reported the values C–Cl = 1.69 Å., C–Br = 1.88 Å., and C–I = 2.05 Å., corresponding to 14, 6, and 10% double bond character, respectively.[13]

The Dependence of Bond Angles on Single Bond–Double Bond Resonance.—In a molecule such as phosgene or 1,1-dichloroethylene the value 125°16′ for the angle Cl–C–O (β) is predicted by the theory of the tetrahedral carbon atom in case that the C–Cl bonds have no double bond character. If the double bond resonates equally among all three positions, giving the Cl–C bond one-third double bond character, we expect from symmetry

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[10] Brockway, Beach and Pauling, THIS JOURNAL, **57**, 2693 (1935).

[11] L. Pauling and J. Sherman, *J. Chem. Phys.*, **1**, 679 (1933).

[12] H. de Laszlo, *Proc. Roy. Soc.* (London), **A146**, 690 (1934).

[13] The interatomic distance values given are stated to hold for hexahalogen, *sym*-trihalogen and *p*-dihalogen benzenes. We expect the distances in these different compounds to be different, however; and investigation of these and other halogen compounds is under way in this Laboratory. De Laszlo has also reported values of C–Br and C–I distances in ethylenic and acetylenic compounds in a letter to *Nature*, **135**, 474 (1935).

the value 120° for β. Between these limits the dependence of β on the amount of double bond character of the C–Cl bonds may be postulated to be given by a curve similar in shape to the interatomic distance curve of Fig. 1. If this is so, there would be a linear relation connecting the angle β and the C–Cl distance, between the points $\beta = 125°16'$, C–Cl = 1.76 Å. and $\beta = 120°$, C–Cl = 1.64 Å. (as given by the curve for one-third double bond character). From a similar discussion, the other chloroethylenes (except vinyl chloride) would be expected to fall roughly on the same line.

A test of this relation is shown in Fig. 2, the seven points being those determined experimentally for phosgene and the six chloroethylenes.

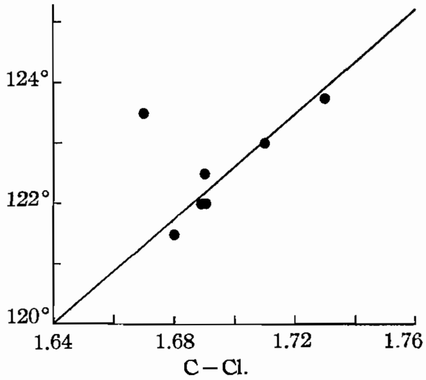
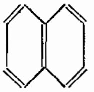
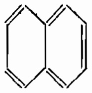


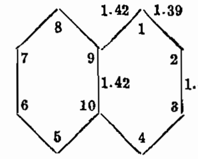
Fig. 2.—The relation between bond angle and carbon-chlorine distance for phosgene and the chloroethylenes.

It is seen that, with one exception, the points lie very close to the straight line drawn according to our assumptions, the displacements being much less than the probable errors of the experimental values. The exceptional point is that for *cis*-dichloroethylene, the discrepancy confirms the suggestion made in the preceding section that our results for this substance are slightly in error.[14] It is surprising that vinyl chloride obeys the same relation, as there is no apparent reason for the angle to be much different from 125°16′.

Interatomic Distances in Polynuclear Aromatic Hydrocarbons.—As a further example of the use of the interatomic distance function we shall discuss the polynuclear aromatic hydrocarbons.

For naphthalene there are three unexcited structures   and 

Giving these equal weights, we obtain the result that the 1–2 bonds have $^2/_3$ double bond character and all others $^1/_3$. These correspond to the values 1.39 Å. for the 1–2 interatomic distances (including 3–4, 5–6 and 7–8), and 1.42 Å. for all others, giving the configuration



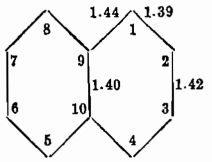
A possibly more reliable prediction can be made on the basis of Sherman's wave function for naphthalene,[15] by considering all 42 canonical structures. The fractional double bond character of a bond can be considered to be given approximately (neglecting non-orthogonality of the canonical wave functions) by the expression

$$\sum_i' a_i^2 \Big/ \sum_i a_i^2$$

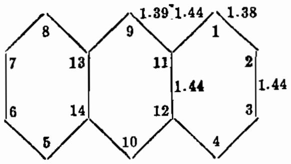
in which a_i represents the coefficient for the *i*th structure; the unprimed sum includes all structures of the set of 42, and the primed sum those for which the bond in question is a double bond. The results of this calculation are the following:[16]

Bond	1–2	2–3	9–1	9–10
Double bond character	0.60	0.33	0.26	0.43
C–C distance	1.39 Å.	1.42 Å.	1.44 Å.	1.40 Å.

corresponding to the configuration



The four unexcited structures for anthracene, given equal weights, lead to $^3/_4$ double bond character for the 1–2 bonds, $^1/_2$ for the 9–11 bonds and $^1/_4$ for others, the predicted configuration being



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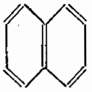
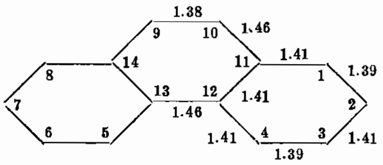
[14] The discrepancies are removed by increasing the C–Cl distance by 0.02 Å., to 1.69 Å., and decreasing the angle by 1°, to 122°30′. These changes are within the estimated probable errors of our determination, ±0.03 Å. and ±1°, respectively.

[15] J. Sherman, *J. Chem. Phys.*, **2**, 488 (1934).

[16] It may be pointed out that the changes from the simple calculation given above result mainly from the fact that the coefficient for the structure  is larger than that for the other unexcited structures.

For phenanthrene the five unexcited structures lead to $^4/_5$ double bond character for the 9–10 bonds, $^3/_5$ for the 1–2 bonds, $^2/_5$ for the 1–11, 11–12 and 4–12 bonds, and $^1/_5$ for the 10–11 and 12–13 bonds, and the predicted configuration is



Similar prediction can be made for larger molecules. It must be pointed out that the contributions of excited structures become important for bonds with small double bond character, inasmuch as in conjugated systems excited structures alone may lead to as much as 20% double bond character; it is probable that the maximum carbon–carbon bond distance in aromatic hydrocarbons is about 1.46 Å., the minimum being the double bond distance 1.38 Å.

The predicted average interatomic distance is 1.41 Å. in naphthalene, anthracene and phenanthrene, this value being somewhat larger than the benzene value (1.39 Å.). With increase in size of the hydrocarbon the carbon–carbon distances should all approach the graphite value 1.42 Å.

The only experimental values of sufficient accuracy to permit a test of the predicted values are those obtained by Robertson in his careful and thorough x-ray investigations of the structure of crystals of naphthalene[17] and anthracene.[18] In each of these molecules Robertson reports the value 1.41 Å. for the average carbon–carbon bond distance, in complete agreement with the predicted value.[19] He does not discuss individual variations from the average; however, measurements made on his reproduced electron distribution projections (Fig. 2 for naphthalene, Fig. 2 for anthracene) show differences of 2 or 3% in the predicted directions.[20]

Summary

Using experimental values for carbon–carbon bonds, a function is plotted showing the dependence of interatomic distance on bond character for single bond–double bond resonance. This function is tested with data for other bonds, and used in the discussion of the electronic structure of molecules containing conjugated double or triple bonds or aromatic nuclei and of molecules containing carbon–chlorine bonds adjacent to double bonds. The dependence of bond angles on single bond–double bond resonance is discussed. Values of carbon–carbon bond distances in polynuclear aromatic hydrocarbons are predicted and compared with the existent experimental data.

[17] J. M. Robertson, *Proc. Roy. Soc.* (London), **A142**, 674 (1933).

[18] J. M. Robertson, *ibid.*, **A140**, 79 (1933).

[19] The data for chrysene [J. Iball, *ibid.*, **A146**, 140 (1934)] are also compatible with this value.

[20] The value 1.41 Å. has also been reported for the carbon–carbon distance in benzene derivatives. We think it probable that this is 0.02 Å. too large.

PASADENA, CALIFORNIA RECEIVED SEPTEMBER 24, 1935

Reprinted from *Introduction to Quantum Mechanics, with Application to Chemistry,* by Linus Pauling and E. Bright Wilson, Jr., McGraw Hill, NY, Section 42, pp. 326–331 (1935).

CHAPTER XII

THE STRUCTURE OF SIMPLE MOLECULES

Of the various applications of wave mechanics to specific problems which have been made in the decade since its origin, probably the most satisfying to the chemist are the quantitatively successful calculations regarding the structure of very simple molecules. These calculations show that we now have at hand a theory which can be confidently applied to problems of molecular structure. They provide us with a sound conception of the interactions causing atoms to be held together in a stable molecule, enabling us to develop a reliable intuitive picture of the chemical bond. To a considerable extent the contribution of wave mechanics to our understanding of the nature of the chemical bond has consisted in the independent justification of postulates previously developed from chemical arguments, and in the removal of their indefinite character. In addition, wave-mechanical arguments have led to the development of many essentially new ideas regarding the chemical bond, such as the three-electron bond, the increase in stability of molecules by resonance among several electronic structures, and the hybridization of one-electron orbitals in bond formation. Some of these topics will be discussed in this chapter and the following one.

In Sections 42 and 43 we shall describe the accurate and reliable wave-mechanical treatments which have been given the hydrogen molecule-ion and hydrogen molecule. These treatments are necessarily rather complicated. In order to throw further light on the interactions involved in the formation of these molecules, we shall preface the accurate treatments by a discussion of various less exact treatments. The helium molecule-ion, He_2^+, will be treated in Section 44, followed in Section 45 by a general discussion of the properties of the one-electron bond, the electron-pair bond, and the three-electron bond.

42. THE HYDROGEN MOLECULE-ION

The simplest of all molecules is the hydrogen molecule-ion, H_2^+, composed of two hydrogen nuclei and one electron. This molecule was one of the stumbling blocks for the old quantum theory, for, like the helium atom, it permitted the treatment to be carried through (by Pauli[1] and Niessen[2]) to give results in disagreement with experiment. It was accordingly very satisfying that within a year after the development of wave mechanics a discussion of the normal state of the hydrogen molecule-ion in complete agreement with experiment was carried out by Burrau by numerical integration of the wave equation. This treatment, together with somewhat more refined treatments due to Hylleraas and Jaffé, is described in Section 42*c*. Somewhat simpler and less accurate methods are described in Sections 42*a* and 42*b*, for the sake of the ease with which they can be interpreted.

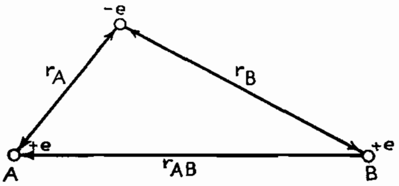


FIG. 42–1.—Coordinates used for the hydrogen molecule-ion.

42a. A Very Simple Discussion.[3]—Following the discussion of Section 34, the first step in the treatment of the complete wave equation is the solution of the wave equation for the electron alone in the field of two stationary nuclei. Using the symbols of Figure 42–1, the electronic wave equation is

$$\nabla^2\psi + \frac{8\pi^2 m_0}{h^2}\left(W + \frac{e^2}{r_A} + \frac{e^2}{r_B} - \frac{e^2}{r_{AB}}\right)\psi = 0, \qquad (42\text{–}1)$$

in which ∇^2 refers to the three coordinates of the electron and m_0 is the mass of the electron.[4]

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[1] W. PAULI, *Ann. d. Phys.* **68**, 177 (1922).

[2] K. F. NIESSEN, Dissertation, Utrecht, 1922.

[3] L. PAULING, *Chem. Rev.* **5**, 173 (1928).

[4] We have included the mutual energy of the two nuclei e^2/H_{AB} in this equation. This is not necessary, inasmuch as the term appears unchanged in the final expression for W, and the same result would be obtained by omitting it in this equation and adding it later.

If r_{AB} is very large, the normal state of the system has the energy value $W = W_{\mathrm{H}} = -Rhc$, the corresponding wave functions being u_{1s_A} or u_{1s_B}, hydrogen-atom wave functions about nucleus A or nucleus B (Sec. 21), or any two independent linear combinations of these. In other words, for large values of r_{AB} the system in its normal state is composed of a hydrogen ion A and a normal hydrogen atom B or of a normal hydrogen atom A and a hydrogen ion B.

This suggests that as a simple variation treatment of the system for smaller values of r_{AB} we make use of the same wave functions u_{1s_A} and u_{1s_B}, forming the linear combinations given by solution of the secular equation as discussed in Section 26*d*. The secular equation is

$$\begin{vmatrix} H_{AA} - W & H_{AB} - \Delta W \\ H_{BA} - \Delta W & H_{BB} - W \end{vmatrix} = 0, \tag{42–2}$$

in which

$$H_{AA} = \int u_{1s_A} H u_{1s_A} d\tau,$$
$$H_{AB} = \int u_{1s_A} H u_{1s_B} d\tau,$$

and

$$\Delta = \int u_{1s_A} u_{1s_B} d\tau.$$

Δ represents the lack of orthogonality of u_{1s_A} and u_{1s_B}. Because of the equivalence of the two functions, the relations $H_{AA} = H_{BB}$ and $H_{AB} = H_{BA}$ hold. The solutions of the secular equation are hence

$$W_S = \frac{H_{AA} + H_{AB}}{1 + \Delta} \tag{42–3}$$

and

$$W_A = \frac{H_{AA} - H_{AB}}{1 - \Delta}. \tag{42–4}$$

These correspond respectively to the wave functions

$$\psi_S = \frac{1}{\sqrt{2 + 2\Delta}}(u_{1s_A} + u_{1s_B}) \tag{42–5}$$

and

$$\psi_A = \frac{1}{\sqrt{2 - 2\Delta}}(u_{1s_A} - u_{1s_B}). \tag{42–6}$$

The subscripts S and A represent the words symmetric and antisymmetric, respectively (Sec. 29*a*); the wave function ψ_S is symmetric in the positional coordinates of the two nuclei A and B, and ψ_A is antisymmetric in these coordinates.

Introducing W_H by use of the equation

$$-\frac{h^2}{8\pi^2 m_0}\nabla^2 u_{1s_A} - \frac{e^2}{r_A}u_{1s_A} = W_H u_{1s_A}$$

(which is the wave equation for u_{1s_A}), we obtain for the integral H_{AA} the expression

$$H_{AA} = \int u_{1s_A}\left(W_H - \frac{e^2}{r_B} + \frac{e^2}{r_{AB}}\right)u_{1s_A}d\tau = W_H + J + \frac{e^2}{a_0 D}, \qquad (42\text{–}7)$$

in which

$$J = \int u_{1s_A}\left(-\frac{e^2}{r_B}\right)u_{1s_A}d\tau = \frac{e^2}{a_0}\left\{-\frac{1}{D} + e^{-2D}\left(1 + \frac{1}{D}\right)\right\}. \qquad (42\text{–}8)$$

In this expression we have introduced in place of r_{AB} the variable

$$D = \frac{r_{AB}}{a_0}. \qquad (42\text{–}9)$$

H_{BA} and H_{AB} are similarly given by the expression

$$H_{BA} = \int u_{1s_B}\left(W_H - \frac{e^2}{r_B} + \frac{e^2}{r_{AB}}\right)u_{1s_A}d\tau = \Delta W_H + K + \frac{\Delta e^2}{a_0 D}, \qquad (42\text{–}10)$$

in which Δ is the orthogonality integral, with the value

$$\Delta = e^{-D}(1 + D + \tfrac{1}{3}D^2), \qquad (42\text{–}11)$$

and K is the integral

$$K = \int u_{1s_B}\left(-\frac{e^2}{r_B}\right)u_{1s_A}d\tau = -\frac{e^2}{a_0}e^{-D}(1 + D). \qquad (42\text{–}12)$$

It is seen that J represents the Coulomb interaction of an electron in a $1s$ orbital on nucleus A with nucleus B. K may be called a resonance or exchange integral, since both functions u_{1s_A} and u_{1s_B} occur in it.

Introducing these values in Equations 42–3 and 42–4, we obtain

$$W_S = W_H + \frac{e^2}{a_0 D} + \frac{J + K}{1 + \Delta} \qquad (42\text{–}13)$$

and

$$W_A = W_H + \frac{e^2}{a_0 D} + \frac{J - K}{1 - \Delta}. \qquad (42\text{–}14)$$

Curves showing these two quantities as functions of r_{AB} are given in Figure 42–2. It is seen that ψ_S corresponds to attraction, with the formation of a stable molecule-ion, whereas ψ_A corresponds to repulsion at all distances. There is rough agreement between observed properties of the hydrogen molecule-ion in its normal state and the values calculated in this simple way. The dissociation energy, calculated to be 1.77 v.e., is actually 2.78 v.e., and the equilibrium value of r_{AB}, calculated as 1.32 Å, is observed to be 1.06 Å.

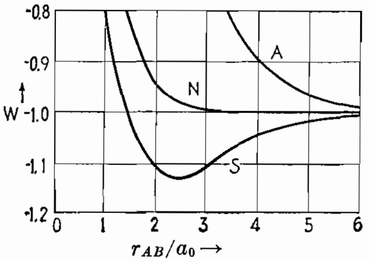

Fig. 42–2.—Energy curves for the hydrogen molecule-ion (in units $e^2/2a_0$), calculated for undistorted hydrogen atom wave functions.

The nature of the interactions involved in the formation of this stable molecule (with a one-electron bond) is clarified by the discussion of a hypothetical case. Let us assume that our system is composed of a hydrogen atom A and a hydrogen ion B, and that even for small values of r_{AB} the electron remains attached to nucleus A, the wave function being u_{1s_A}. The energy of the system would then be H_{AA}, and the difference between this and W_H, namely $\frac{e^2}{a_0}e^{-2D}\left(1 + \frac{1}{D}\right)$, would be the energy of interaction of a normal hydrogen atom and a hydrogen ion. The curve representing this energy function, which before the discovery of the resonance phenomenon was supposed to correspond to the hydrogen molecule-ion, is shown in Figure 42–2 with the symbol N. It is seen that it does not correspond to the formation of a stable bond but instead to repulsion at all distances. The difference between this curve and the other two is that in this case we have neglected the resonance of the electron between the two nuclei A and B. It is this resonance which causes the actual hydrogen molecule-ion to be stable—the energy of the one-electron bond is in the main the energy of resonance of the electron between the two nuclei. (Other interactions, such as polarization of the atom in the field of the ion, also contribute to some extent to the stability of the bond. An attempt to answer the question of the magnitude of this contribution will be given in the next section.)

It is seen from the figure that the resonance interaction sets in at considerably larger distances than the Coulomb interaction of atom and ion. This results from the exponential factor e^{-2D} in H_{AA}, as compared with e^{-D} in the resonance integral K. For values of r_{AB} larger than 2 Å the energy functions W_S and W_A are closely approximated by the values $W_H + K$ and $W_H - K$, respectively. In accordance with the argument of Section 41*b*, the resonance energy $\pm K$ corresponds to the electron's jumping back and forth between the nuclei with the frequency $2K/h$.

Problem 42–1. Verify the expressions given for H_{AA}, H_{AB}, and Δ in Equations 42–7 to 42–12.

42b. Other Simple Variation Treatments.—We can easily improve the preceding treatment by introducing an effective nuclear charge $Z'e$ in the hydrogenlike 1*s* wave functions u_{1s_A} and u_{1s_B}. This was done by Finkelstein and Horowitz.[1] On minimizing the energy W_S relative to Z' for various values of r_{AB}, they obtained a curve for W_S similar to that of Figure 42–2, but with a lower minimum displaced somewhat to the left. They found for the equilibrium value of r_{AB} the value 1.06 Å, in complete agreement with experiment. The value of the effective atomic number Z' at this point is 1.228, and the energy of the system (neglecting oscillational and rotational energy) is -15.78 v.e., as compared with the correct value -16.31 v.e.; the value of the dissociation energy $D_e = 2.25$ v.e. differing from the correct value 2.78 v.e. by 0.53 v.e. The variation of the effective atomic number from the value 1 has thus reduced the error by one-half.

The energy of the bond for this function too is essentially resonance energy. Dickinson[2] introduced an additional term, dependent on two additional parameters, in order to take polarization into account. He wrote for the (not yet normalized) variation function

$$\psi = u_{1s_A}(Z') + u_{1s_B}(Z') + \sigma\{u_{2p_A}(Z'') + u_{2p_B}(Z'')\},$$

in which the first two terms represent as before 1*s* hydrogenlike wave functions with effective nuclear charge $Z'e$ and the remain-

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[1] B. N. Finkelstein and G. E. Horowitz, *Z. f. Phys.* **48,** 118 (1928).

[2] B. N. Dickinson, *J. Chem. Phys.* **1,** 317 (1933).

[Reprint from the Journal of the American Chemical Society, 59, 1450 (1937).]

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY No. 603]

A Quantitative Discussion of Bond Orbitals

BY LINUS PAULING AND J. SHERMAN

Six years ago, in the course of the development of the quantum mechanical theory of directed valence,[1] a very simple method of discussing the bond-forming power of an atomic bond orbital (one-electron orbital wave function) in its dependence on the angular distribution of the orbital was formulated.[1b,2] The fundamental assumption of the method is that in the case of bond orbitals with the same or nearly the same radial part of the wave function the magnitude of the angular part of an orbital along the bond axis (that is, in the direction of the other atom) is a measure of its relative bond-forming power. The bond-forming power or strength S of an s orbital (normalized to 4π), defined in this way, is 1, that of a p orbital is 1.732, and that of the best bond-forming hybrid sp orbital (called a tetrahedral sp bond orbital) is 2.

In order to obtain information as to the extent to which the bond strength S of an orbital can be considered a qualitative measure of its bond-forming power and also as to the quantitative relation between the energy of a bond and the strengths of the bond orbitals involved in its formation, we have now carried out the thorough discussion of various sp and spd one-electron bonds between identical atoms.

Description of the Method

We discuss a system comprising two atomic nuclei or kernels (nuclei and completed inner shells of electrons), with residual charge $+e$, and one electron, which forms a one-electron bond between the two atoms. The energy integral $E = \int \psi^* H\psi d\tau / \int \psi^*\psi d\tau$ is evaluated for various internuclear distances to give an energy function for each choice of the wave function ψ. This wave function is assumed to be of the form $c(\psi_A + \psi_B)$, ψ_A and ψ_B being similar atomic bond orbitals for atoms A and B and c a normalization constant. The functions ψ_A and ψ_B are formed by linear combination of central-field atomic orbitals. However, in discussing s-p hybridization, we do not use $2s$ and $2p$ hydrogen-like orbitals, inasmuch as these differ somewhat in their radial parts; instead, in order to obtain results bearing directly on the effect of angular distribution of the orbital on its bond-forming power, we use the same radial function for $2s$ as for $2p$. As a result of this simplification of the radial function, the energy of the $2s$ orbital is changed from the hydrogen-like value, a term $l(l+1)/r^2$ being introduced by the kinetic energy operator acting on the radial function, and not canceled by the angular function. In order to achieve sp degeneracy we omit this term, as well as the corresponding term in the sp exchange integrals. In a later section there is then discussed the case in which the s and p orbitals correspond to different energy values. Similarly in discussing M orbitals we use the

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[1] (a) J. C. Slater, *Phys. Rev.*, **38**, 1109 (1931); (b) L. Pauling, THIS JOURNAL, **53**, 1367 (1931).

[2] See also R. Hultgren, *Phys. Rev.*, **40**, 891 (1932), for extended applications of the method, J. H. Van Vleck, *J. Chem. Phys.*, **3**, 803 (1935), for a discussion of the relation between directed bond orbitals and molecular orbitals, and C. A. Coulson, *Proc. Cambridge Phil. Soc.*, **33**, 104 (1937), for a brief discussion of the criterion of maximum overlapping.

same radial function for 3*s* and 3*p* as for 3*d*, and omit the extra terms introduced by the kinetic energy operator.

The radial wave functions used are thus the hydrogen-like 2*p* and 3*d* functions, $R_{21}(r)$ and $R_{32}(r)$, for all orbitals of the *L* and *M* shells, respectively; the symbols ψ_{2s}, ψ_{2p} and ψ_{3s}, ψ_{3p}, ψ_{3d} represent these multiplied by the angular parts 1 (for *s*), $\sqrt{3}\cos\theta$ (for *p*), and $\sqrt{5/4}\,(3\cos^2\theta-1)$ (for *d*), rather than the usual hydrogen-like orbitals. The *z*-axis for each atom points along the internuclear axis toward the other atom.

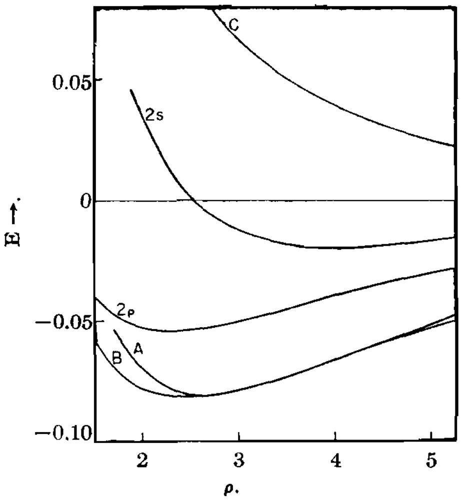

Fig. 1.—Energy curves for one-electron bonds involving 2*s*-2*p* hybridization.

The effective atomic numbers in the radial wave functions cannot be evaluated by minimizing the energy integral, because of neglect of inner shells. In all the calculations reported the effective atomic numbers were given the value 1.

This investigation involved the evaluation of thirty integrals and the computation of numerical values for each of them for values of $\rho = r_{AB}/2a_0$ at intervals of 0.5 from 1.5 to 5.0 for *L* orbitals and from 2.0 to 7.5 for *M* orbitals. The work is straightforward, though laborious, and involves no new methods. In this paper we shall discuss only the results of the calculations.

Bond Orbitals Formed by *s*-*p* Hybridization

An atomic bond orbital $\psi = a\psi_s + b\psi_p$ can be varied from a pure *s* orbital to a pure *p* orbital by varying the ratio of the coefficients *a* and *b*. Energy curves calculated for one-electron bonds between similar orbitals on two atoms, as functions of $\rho = r_{AB}/2a_0$, with r_{AB} the internuclear distance, are shown for various choices of the bond orbitals in Figs. 1 and 2, Fig. 1 representing *L* orbitals and Fig. 2, *M* orbitals. The curves A represent bonds formed by tetrahedral orbitals, with the ratio b/a equal to $3^{1/2}$. The curves B represent the strongest bonds which can be formed by *s*-*p* orbitals, the ratio of b/a being so chosen for each value of ρ as to minimize the energy integral. The curves C correspond to orbitals which are orthogonal to those for curves B; they represent the maximum repulsion given by *s*-*p* orbitals.

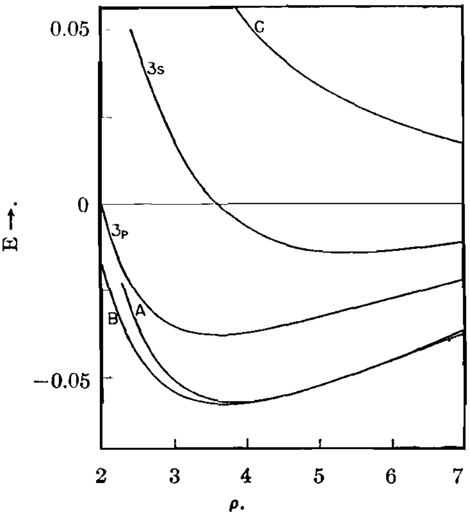

Fig. 2.—Energy curves for one-electron bonds involving 3*s*-3*p* hybridization.

The most striking characteristic of the figures is the close approximation of the tetrahedral-orbital curves (A) to the curves for strongest bonding (B), the difference being very small over the ranges 2.5 to 4.5 in ρ for *L* orbitals and 4 to 6 for *M* orbitals. This shows the extent to which the original simple treatment, which ascribes to tetrahedral orbitals the maximum bond-forming power, is applicable. Similar information is provided by Fig. 3, in which the ratio b/a for the orbitals corresponding to the curves B is shown; in each case this ratio differs from the value for tetrahedral orbitals, 1.732, by less than about 20% over a range of values of about 2 for ρ, beginning with the equilibrium value.

The internuclear distance at which the best bond orbitals are tetrahedral orbitals is in each case somewhat larger than the equilibrium distance given by the minimum of the energy curve. It is possible that in actual molecules the repulsion of inner shells increases the equilibrium internuclear separations toward the values at which the simple treatment of the strengths of bond orbitals is accurate. The results of the present investigation show that even without this effect the simple treatment can be used for qualitative and rough quantitative arguments.

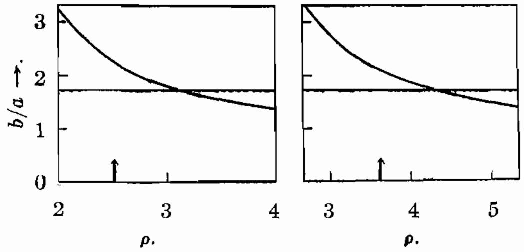

Fig. 3.—The ratios of coefficients of p and s orbitals in best s-p bond orbitals (left, L orbitals; right, M orbitals).

Bond Energies.—It is seen that the bond energies (given by the minima of the curves of Figs. 1 and 2) for s, p, and tetrahedral bonds are in the approximate ratios 1:3:4. (The actual values, in units e^2/a_0, are 0.020, 0.054, and 0.082, respectively, for L orbitals, and 0.014, 0.037, and 0.057, respectively, for M orbitals.) These ratios are the squares of the bond strengths S introduced in the simple treatment, as given by the expression $S = (a + \sqrt{3}\, b)/(a^2 + b^2)^{1/2}$. A further test of the suggested relation $D = kS^2$ connecting the bond energy D with the strength S of the two bond orbitals involved is shown in Fig. 4. The dashed curves in this figure represent S^2 for $2s$–$2p$ and $3s$–$3p$ bond orbitals (with shifted vertical scales) as a function of the coefficient a from 0 to 10, b being placed equal to $10 - a$. With this normalization S^2 increases from 3 at $a = 0$ (p orbitals) to a maximum of 4 at $a = 3.66$ (tetrahedral orbitals) and then decreases to 1 at $a = 10$ (s orbitals). The solid lines show the calculated one-electron-bond energy D with the scale changed by a factor making the energy of the best bond 4. It is seen that in each case the curve for D/k approximates the S^2 curve closely throughout the range, again showing the good approximation provided by the simple treatment.

The results suggest that for bonds between atoms with unlike orbitals ψ_A and ψ_B the bond energy is given by the expression $D = kS_AS_B$, being proportional to the product of the strengths of the two orbitals. The energy of a bond for ψ_A with ψ_B would then be the geometrical mean of the bond energies for ψ_A with ψ_A and ψ_B with ψ_B. This is of significance in connection with a related case. In a discussion of the partial ionic character of covalent bonds[3] the postulate was made that the energy of a normal covalent single bond between unlike atoms A and B is the algebraic mean $^1/_2(D_{AA} + D_{BB})$ of the bonds between like atoms of the kinds involved. The discussion above indicates that this postulate should be replaced by a similar postulate[4] with $(D_{AA}D_{BB})^{1/2}$ in place of $^1/_2(D_{AA} + D_{BB})$. In case that the bond energies D_{AA} and D_{BB} do not differ greatly in value, there is only a very small difference between their geometric and algebraic means (which for 3 and 4, for example, are 3.46 and 3.50, respectively); and for this reason the arguments based on the earlier postulate are in general valid with the new one. The new postulate is superior to the old in some ways, leading to better agreement with thermal data. In the

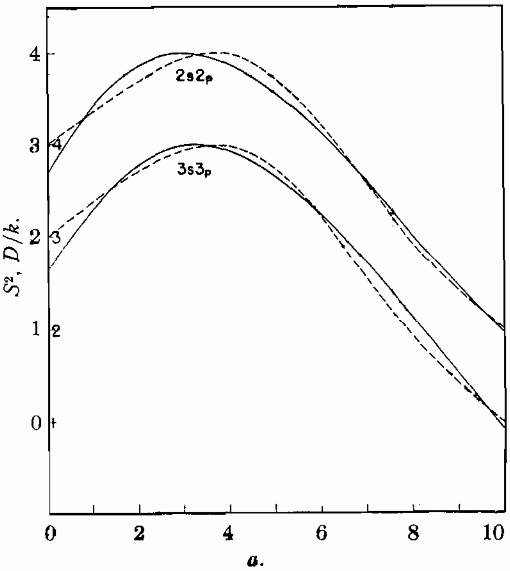

Fig. 4.—Calculated one-electron bond energy values (D/k, full curves) and squared bond strength values (S^2, dashed curves) for s-p hybridization.

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(3) L. Pauling and D. M. Yost, *Proc. Nat. Acad. Sci.*, **18**, 414 (1932); L. Pauling, THIS JOURNAL, **54**, 3570 (1932).

(4) The new postulate is presumably accurate in simple cases, such as for bonds between univalent atoms. For multivalent atoms a complication is introduced by the usual choice of the normal states of separated atoms as the origin for energy measurements, inasmuch as this changes in an erratic manner with change in term character (especially multiplicity) from row to row of the periodic system. It is probable that better results would be obtained for multivalent atoms by using as the energy of a bond the energy required to break that bond and dissociate the molecule into two parts, rather than a fraction of the energy required to dissociate the molecule completely into atoms. At present, however, accurate values of the energy required to break one bond alone in a molecule are not available.

earlier discussion use was made of the equation $D_{AB} = {}^1/_2(D_{AA} + D_{BB}) + \Delta$, in which Δ, the contribution of ionic character to the bond energy, should always be greater than or equal to zero. A few exceptions to this were noted. In case that the new postulate is used, $D_{AB} = (D_{AA}D_{BB})^{1/2} + \Delta'$, these cases are no longer troublesome, all values of Δ′ being positive. For the carbon–iodine bond, which alone of those discussed in the earlier work gave a negative value for Δ(−0.12 e. v.), the values $D_{CI} = 2.45$ e. v., $D_{CC} = 3.60$ e. v., and $D_{II} = 1.54$ e. v., lead to the positive value $\Delta' = +0.10$ e. v. Another case in which the original postulate is invalid has been pointed out by Mulliken.[5] From the values $D_0 = 4.45$ e. v. for H_2 and 1.14 e. v. for Li_2, algebraic additivity would give as a lower limit for D_0 for LiH the value 2.80 e. v., to be increased by Δ in case that the bond has some ionic character. The experimental value of D_0 for LiH is about 2.59 e. v.; this shows a discrepancy with the old additivity postulate of 0.2 e. v., and, as emphasized by Mulliken, the discrepancy is really somewhat larger, since the Li–H bond has without doubt some ionic character. The trouble is remedied by the new postulate, which gives 2.25 e. v. as the geometric mean of the values of D_0 for H_2 and Li_2; this leads to 0.34 e. v. for Δ′, corresponding to a reasonable difference in electronegativity of hydrogen and lithium. Sodium hydride and potassium hydride provide similar cases. With $D_0 = 0.76$ e. v. for Na_2, the old postulate gives $D_0 = 2.61$ e. v. + Δ for NaH, which is incompatible with the experimental value 2.24 e. v.; whereas the new postulate leads to 1.84 e. v. + Δ′, corresponding to the reasonable value 0.40 e. v. for Δ′. With $D_0 = 0.51$ e. v. for K_2, the old and new postulates give 2.48 e. v. + Δ and 1.51 e. v. + Δ′, respectively, for D_0 for KH; the experimental value is 1.91 e. v., which is incompatible with the first but compatible with the second of these, leading to 0.40 e. v. for Δ′. The sequence of values Δ′ = 0.34, 0.40, and 0.40 e. v. for LiH, NaH, KH, respectively, shows to some extent the increase expected because of the increasing electropositive character of the alkali metals with increasing atomic number; it is possible that this effect would be shown more clearly if more reliable values of D_0 were available.

Interatomic Distances.—The equilibrium internuclear distances (at which the energy curves have their minima) are given for 2*s*2*p* and 3*s*3*p* bonds by the curves of Fig. 5, showing the dependence of ρ_0 on the coefficient *a* in the hybrid orbital $a\psi_s + b\psi_p$, with $b = 10 - a$. It is seen that addition of a very small amount of *s* to a *p* orbital causes ρ_0 to decrease slightly, its minimum value being at $a = 1$, which corresponds to a state of the atom which is about 1% *s* and 99% *p* (the ratio of a^2 to b^2 being $^1/_{81}$). With further increase in *a* the equilibrium distances increase monotonically toward their values for *s* bonds.

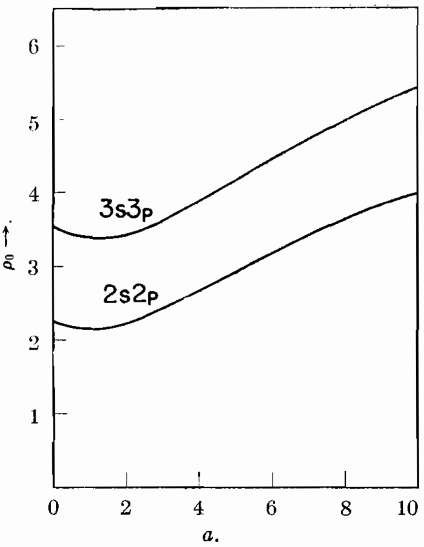

Fig. 5.—Dependence of equilibrium internuclear distance on nature of bond orbitals.

Comparison of Figs. 4 and 5 shows that there is no simple relation between bond energy and equilibrium internuclear distance for *s*-*p* bonds, the minima in ρ_0 and the maxima in *D* occurring for much different values of *a*. There is, indeed, no reason to expect bond energy to depend in a simple way on bond distance, and the non-existence of a monotonic dependence is shown directly by the fact that in many diatomic molecules r_0 has smaller values for excited states than for the normal states. In a recent discussion of single-bond–double-bond resonance Penney[6] has assumed a simple monotonic relation between bond distance and bond energy; such a relation may of course be valid in special cases, but its validity cannot be assumed in general without justification.

Bond Orbitals Formed by *s*-*p*-*d* Hybridization

The results of the calculation of one-electron bond energies for orbitals of the type $a\psi_{3s}$ +

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[5] R. S. Mulliken, *Phys. Rev.*, **50**, 1028 (1936).

[6] W. G. Penney, *Proc. Roy. Soc.* (London), **A156**, 306 (1937).

$b\psi_{3p} + c\psi_{3d}$ are shown in Fig. 6. The contour lines for the diagram 6a indicate values of $S^2 = (a + \sqrt{3}\,b + \sqrt{5}\,c)^2/(a^2 + b^2 + c^2)$, the values of a, b, and c determining the hybrid wave function being given by triangular coördinates (normalized to $a + b + c = 10$). The maximum value of S^2, 9, corresponding according to the simple treatment to the best *spd* bond orbital, occurs[1b] at $a = 2.01$, $b = 3.49$, $c = 4.50$. From this point the bond strength falls off at about the same rate in all directions. In the diagram 6b the contour lines represent similarly the calculated values of the bond energy (in units $0.022\ e^2/a_0$). It is seen that the function corresponds only roughly to S^2, the approximation being much less close than for *s-p* hybridization. The general behavior of the energy surface is similar to that of the S^2 surface; its maximum, however, is shifted by a large amount, lying near the *p-d* line. A study of the energy calculations suggests that this lack of agreement with the simple treatment is to be attributed to the occurrence for small values of ρ of negative values for the overlapping integral between a $3p$ orbital of one atom and a $3d$ orbital of the other. It is possible that in actual molecules the repulsion of inner shells increases the equilibrium values of ρ in such a way as to cause the bond energies to be more nearly proportional to S^2 than for the calculations presented here. It is, indeed, found that at a constant value of ρ in the neighborhood[7] of 4 to 6 the calculated energy curves for hybrid orbitals are closely proportional to S^2, the proportionality being nearly exact at $\rho = 5.5$.

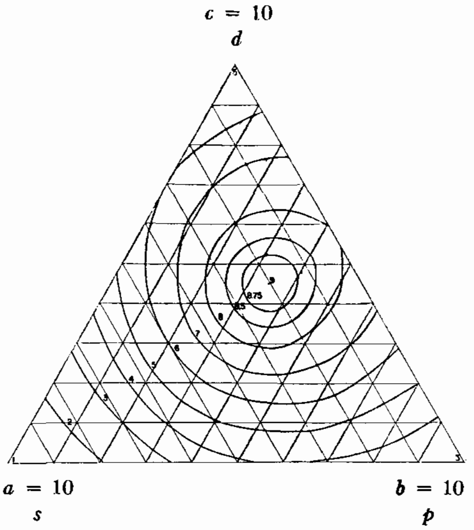

Fig. 6a.—Contour diagram of S^2 (square of bond strength of orbital) for *s-p-d* hybridization.

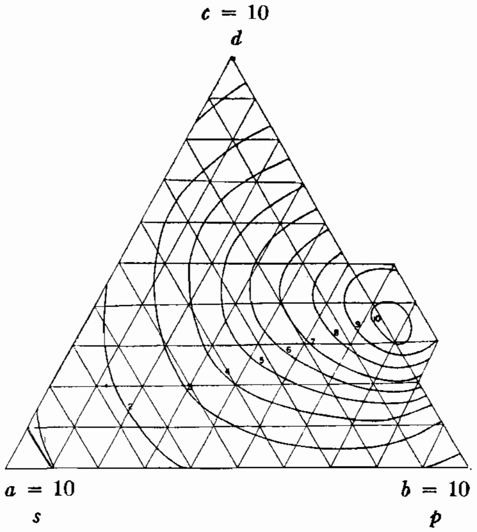

Fig. 6b.—Contour diagram of D/k (calculated one-electron bond energy divided by a constant) for *s-p-d* hybridization.

We conclude that qualitative arguments regarding *s-p-d* hybridization can be safely based on the simple bond-strength treatment, but that this treatment cannot be expected to have the same quantitative significance in this case as for *s-p* bond orbitals.

The Lithium Molecule-Ion

In the preceding calculations the orbitals $2s$ and $2p$ have been assigned the same energy value. In the lithium atom the $2p$ level lies 1.84 e. v. above the $2s$ level, as indicated by the horizontal lines (corresponding to a lithium ion and a lithium atom in the ^2P or ^2S state at large internuclear distance) in Fig. 7. We can take this *s-p* separation into account by adding 1.84 e. v. to H_{pp} and making corresponding changes in the other integrals which occur in the secular equation. The two roots of the secular equation are represented by curves B and C of Fig. 7. Curve C, the upper of the two roots, represents the interaction of a lithium ion and an excited lithium atom; according to this simple treatment only a weak bond is formed, the curve being repulsive to about $\rho = 7$, at which the bond energy is about 0.3 e. v.

Curve B, representing the combination of a lithium ion and a normal lithium atom to give a

[7] The minima of the energy curves occur at about $\rho = 4$ or 5 except in the region around $a = 0$ to 2, $b = 4$ to 6, $c = 2$ to 5, where values as low as 2 or 2.5 are found.

normal lithium molecule-ion, has its minimum value at $\rho = 2.85$, corresponding to the equilibrium internuclear distance $r_e = 3.02$ Å. The value found for the bond energy D_e is 1.19 e. v. This energy value is in good agreement with that calculated by James[8] by a reliable method, 1.27 e. v., and the value of r_e agrees well with that estimated by James, 3.0 Å. The agreement provides one more example showing the surprisingly good approximations yielded by very simple treatments of molecular problems such as that reported in this paper.

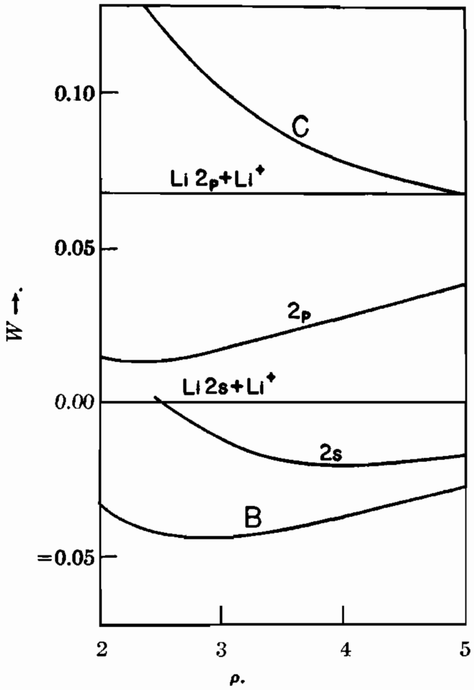

Fig. 7.—Energy curves for the lithium molecule-ion, with consideration of the s-p separation.

Although the s-p separation is nearly twice as large as the bond energy, there occurs extensive hybridization of the bond orbitals: at the equilibrium internuclear distance the bond orbitals are composed nearly equally of ψ_s and ψ_p, the ratio b/a being 0.92 (Fig. 8). This hybridization increases the bond energy by more than 100%, from 0.54 e. v. for a pure s bond (Fig. 7) to 1.19 e. v. The contribution of ψ_p and the value of the bond energy are of course smaller than they would be for zero s-p separation ($b/a = 1.9$ and $D = 2.16$ e. v. at $r = 3.0$ Å.). It may be pointed out that the ratio $b/a = 1$ corresponds to a bond angle of 180° for two equivalent orbitals.

James also carried out a treatment of the lithium molecule-ion with use of $2s$ orbitals and explicit consideration of the four K electrons, obtaining the energy value -0.304 e. v. at $r = 2.98$ Å. (this being not necessarily the minimum point of the curve). Our curve for an s bond similarly gives a very small energy value, -0.22 e. v., at this value of r. The calculations described above indicate that the principal source of inaccuracy in these treatments is the assumption that the bonds are s bonds, and that the consideration of s-p hybridization makes a great improvement.

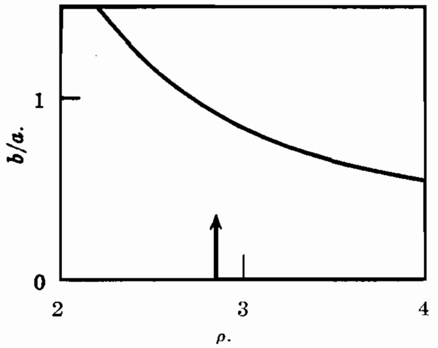

Fig. 8.—The ratio of coefficients of p and s orbitals for the normal state of the lithium molecule-ion.

A Test of the Validity of Simple Methods of Discussing Resonance.—In the quantum mechanical treatment of chemical problems, especially those involving the resonance of molecules among several valence-bond structures, many simplifying assumptions are made in order that the solution of the equations involved may become practicable. An important one of these assumptions, that the orthogonality integral $\Delta_{\text{I II}} = \int \psi_{\text{I}}\psi_{\text{II}}d\tau$ for two wave functions corresponding to two structures I and II can be neglected and the secular equation written in the form

$$\begin{vmatrix} H_{\text{I I}} - W & H_{\text{I II}} \\ H_{\text{I II}} & H_{\text{II II}} - W \end{vmatrix} = 0 \qquad (1)$$

rather than

$$\begin{vmatrix} H_{\text{I I}} - W & H_{\text{I II}} - \Delta_{\text{I II}} W \\ H_{\text{I II}} - \Delta_{\text{I II}} W & H_{\text{II II}} - W \end{vmatrix} = 0 \qquad (2)$$

can be tested for the system just discussed, the lithium molecule-ion. The functions I and II are the s-bond and p-bond functions, respectively. The curves B and C of Fig. 2 represent

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[8] H. M. James, *J. Chem. Phys.*, **3**, 9 (1935). No experimentally determined values for r_e and D_e have been reported.

the two roots of Equation 2 for zero *s-p* separation and the curves B and C of Fig. 7 the roots of Equation 2 with 1.84 e. v. *s-p* separation. To test the extent to which neglect of $\Delta_{\text{I II}}$ can be compensated by suitable choice of values of the energy exchange integral $H_{\text{I II}}$, we may evaluate $H_{\text{I II}}$ as a function of ρ by substituting for $H_{\text{I I}}$ and $H_{\text{II II}}$ in Equation 1 their values as given by curves 2*s* and 2*p*, respectively, of Fig. 2 and choosing values of $H_{\text{I II}}$ which cause curve *B* of this figure to represent the low root of the equation. The expression for $H_{\text{I II}}$ found in this way can then be used to evaluate the low root of Equation 1 for the case of 1.84 e. v. *s-p* separation. It is found that over the range 2.5 to 3.5 for ρ curve C as calculated in this way differs from the curve given by Equation 2 by less than 0.05 e. v. (4% of the bond energy). This provides some justification for the use of Equation 1 in place of Equation 2 for rough calculations in which the magnitude of the exchange integral is determined empirically.

We are indebted to Dr. S. Weinbaum and Mrs. M. R. Lassettre for assistance with the calculations described in this report.

Summary

Theoretical energy curves for one-electron bonds between two atoms are calculated for bond orbitals formed by hybridization of 2*s* and 2*p* orbitals, 3*s* and 3*p* orbitals, and 3*s*, 3*p*, and 3*d* orbitals, the same radial part being used for the orbitals in a set. It is found that for *s-p* hybridization the bond energy is closely proportional to S^2, with S the magnitude of the angular part of the bond orbital in the bond direction. This relation is less satisfactorily approximated in the case of *s-p-d* hybridization.

It is shown that the energy of a normal covalent bond A-B between unlike atoms is probably represented more closely by the geometric mean of the bond energies for A-A and B-B than by their arithmetic mean.

The energy of the one-electron bond in the lithium molecule ion is calculated with consideration of the *s-p* separation to be 1.19 e. v., and the hybrid bond orbital involved is shown to involve about equal contributions from the 2*s* and 2*p* orbitals of the lithium atom.

PASADENA, CALIF. RECEIVED JUNE 1, 1937

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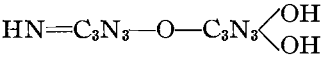
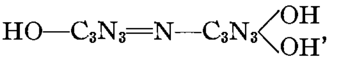
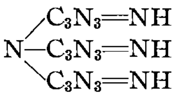
THE STRUCTURE OF CYAMELURIC ACID, HYDROMELONIC ACID, AND RELATED SUBSTANCES

By LINUS PAULING AND J. H. STURDIVANT

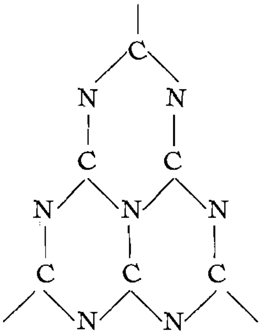
GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY*

Communicated October 20, 1937

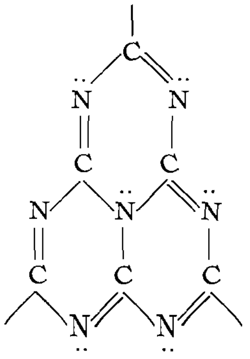
Over a century ago, in 1835, Leopold Gmelin[1] prepared the substance tripotassium hydromelonate by heating potassium ferrocyanide with sulfur; he also made other salts of hydromelonic acid, and carried out analyses, which, however, were not sufficiently accurate to lead to correct formulas. He recognized the similarity of the substances to the group of nitrogen compounds discovered and named by Justus Liebig,[2] including melon, melam, melamine, etc., and assigned names to them on this basis. Liebig[3] then prepared tripotassium hydromelonate by other methods, including, for example, the reaction of fused potassium thiocyanate with antimony trichloride, and in 1855, after much labor, he succeeded[4] in assigning to the acid essentially its correct formula, $H_3C_9N_{13}$ (using the incorrect atomic weight 6 for carbon, he wrote $C_{18}N_{13}H_3$). By decomposing hydromelonates with alkali, Henneberg[5] in 1850 prepared salts of another tribasic acid, cyameluric acid, $H_3O_3C_6N_7$, as well as the acid itself.[6] For this substance structural formulas such as  $HN{=}C_3N_3{-}O{-}C_3N_3\begin{matrix}\diagup OH\\ \diagdown OH\end{matrix}$ and  $HO{-}C_3N_3{=}N{-}C_3N_3\begin{matrix}\diagup OH\\ \diagdown OH\end{matrix}$, involving the cyanuric nucleus C_3N_3, were suggested long ago and the similar formula  $N\begin{matrix}\diagup C_3N_3{=}NH\\ {-}C_3N_3{=}NH\\ \diagdown C_3N_3{=}NH\end{matrix}$ was proposed for hydromelonic acid; formulas based on the hexamethylenetetramine nucleus have also been proposed.[7] These formulas, however, do not provide a satisfactory representation of the properties of the substances. We have been led to the belief that the substances contain a nucleus C_6N_7 (the "cyameluric nucleus"), which bears to the cyanuric nucleus a relation somewhat similar to that between the condensed aromatic hydrocarbons and benzene.

Four years ago Professor E. C. Franklin gave us for x-ray examination[8] a few small crystals of the substance $Na_3C_6N_9 \cdot 3H_2O$, the preliminary study of which indicated the presence of an anion $C_3N_3(NCN)_3^{\equiv}$ similar in structure to cyanuric triazide,[9] $C_3N_3(N_3)_3$. The corresponding acid $H_3C_6N_9$ can accordingly be considered to be a derivative of cyanuric acid; it may be called either cyanuric tricyanamide, $C_3N_3(NCNH)_3$, or tricyanomelamine,[10] $C_3N_3(NHCN)_3$. The strength of the acid is to be attributed to resonance between the valence-bond structures corresponding to these representations.

This formulation of the tribasic acid $H_3C_6N_9$ suggested to us the similar formulation of hydromelonic acid as $C_6N_7(NCNH)_3$, which would thus be related to cyameluric acid, $C_6N_7(OH)_3$, as cyanuric tricyanamide is to cyanuric acid, $C_3N_3(OH)_3$. Of the possible structures for the trivalent cyameluric nucleus C_6N_7 which occurred to us there is one which is so reasonable and which accounts so satisfactorily for the properties of the radical that there remains little doubt as to its correctness. This structure involves a coplanar arrangement of three fused rings,



The electronic structure corresponds to resonance not only between the two valence-bond structures



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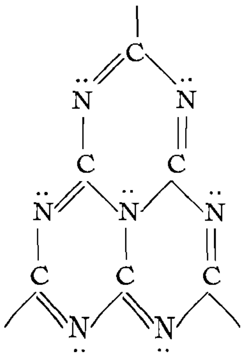
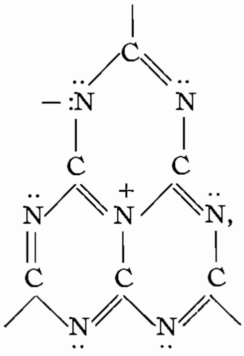


II

(corresponding to the Kekulé structures of benzene), but also among the eighteen structures of the type



III to XX

each of which, with six double bonds but with separated electric charges, should make a somewhat smaller contribution than structure I or II (probably about one-half or two-thirds as large). On this basis each of the six outermost C-N bonds in the nucleus would have 50% double-bond character, each of the six remaining peripheral bonds about 36% and each of the three central bonds about 28%. The corresponding values for the C-N distances predicted by use of the resonance curve and table of covalent radii,[11] with consideration also of the effect of electric charges,[12] are 1.33 Å, 1.35 Å and 1.32 Å, respectively; the C_3N_3 rings in the fused nucleus are thus nearly regular, and have nearly the same dimensions as expected for the cyanuric nucleus, 1.33 Å,[13] corresponding to 50% double-bond character.

The large number of important structures among which resonance can take place should make the cyameluric nucleus remarkably stable. This has been verified by a quantum mechanical calculation of the resonance energy by the molecular-orbital method, the valence-bond method in its simple form being inapplicable. Representing the C-N exchange integral by β, and assuming the greater electronegativity of nitrogen (relative to carbon) to correspond to a difference 2β in Coulomb energy,[14] we find for the cyameluric nucleus the resonance energy 7.4336β, relative to structure I or II. With β = 20,000 cal./mole (approximately the C-C value in benzene), this corresponds to stabilization by 150,000 cal./mole, or 25,000 cal./mole per double bond. (For the cyanuric nucleus a similar treatment gives 4.129β for the resonance energy, stabilizing the molecule by 27,500 cal./mole per double bond.) This large resonance energy completely removes the unsaturation expected for a non-resonating molecule with six double bonds, and accounts for the extraordinary stability observed for cyameluric acid and hydromelonic acid and their derivatives.

Except for the changes due to the increased molecular weight, the properties of derivatives of the cyameluric nucleus should resemble those of the corresponding derivatives of the cyanuric nucleus very closely. In table 2 there are given values of the conjugation energy of various groups with both the cyanuric nucleus and the cyameluric nucleus, calculated by subtracting the energy of the radicals C_3N_3 or C_6N_7 and 3R from that of the molecule $C_3N_3R_3$ or $C_6N_7R_3$ (table 1), and dividing by three. It is seen that these conjugation energies are closely similar for the two nuclei, the cyameluric nucleus being about 8% more effective in conjugation than the cyanuric nucleus.

TABLE 1

ENERGY VALUES CALCULATED BY THE MOLECULAR-ORBITAL METHOD

R	ENERGY OF R[a]	$C_3N_3R_3$	$C_6N_7R_3$
Amino, $-NH_2$	4.0000β	29.8272β	49.2900β
Cyanamide, $-NCNH$	9.4641β	45.9625β	65.3925β
Azide, $-NNN$	10.8284β	49.9208β	69.3274β
Hydroxyl, $-OH$	8.0000β	41.1513β	60.5323β

Energy of C_3N_3 radical, 16.1290β; of C_6N_7 radical, 35.4336β.

[a] In this calculation the values $q_C = 0$, $q_N = 2\beta$ and $q_O = 4\beta$ were used for the Coulomb energies of the p_z orbitals of carbon, nitrogen and oxygen, respectively.

TABLE 2

CONJUGATION ENERGIES OF GROUPS WITH THE CYANURIC AND CYAMELURIC NUCLEI

GROUP	CONJUGATION ENERGY PER GROUP		RATIO
	WITH CYANURIC NUCLEUS	WITH CYAMELURIC NUCLEUS	
Amino	0.5661β	0.6188β	0.915
Cyanamide	0.4804β	0.5222β	0.920
Azide	0.4355β	0.4695β	0.928
Hydroxyl	0.3408β	0.3662β	0.931

We accordingly believe that a series of cyameluric derivatives analogous to the cyanuric derivatives can be prepared. Of these only a few have so far been reported. Cyameluric acid, $C_6N_7(OH)_3$, is the analog of cyanuric acid, $C_3N_3(OH)_3$; and hydromelonic acid, $C_6N_7(NCNH)_3$, is the analog of cyanuric tricyanamide, $C_3N_3(NCNH)_3$. So far as we are aware, substances which might safely be identified as the cyameluric analogs of cyanuric trichloride, $C_3N_3Cl_3$, cyanuric tricyanide, $C_3N_3(CN)_3$, melamine, $C_3N_3(NH_2)_3$, hexamethylmelamine, $C_3N_3[N(CH_3)_2]_3$, and the many other known derivatives of cyanuric acid have not been described in the literature. The preparation and study of some of these substances are being carried on in these Laboratories.

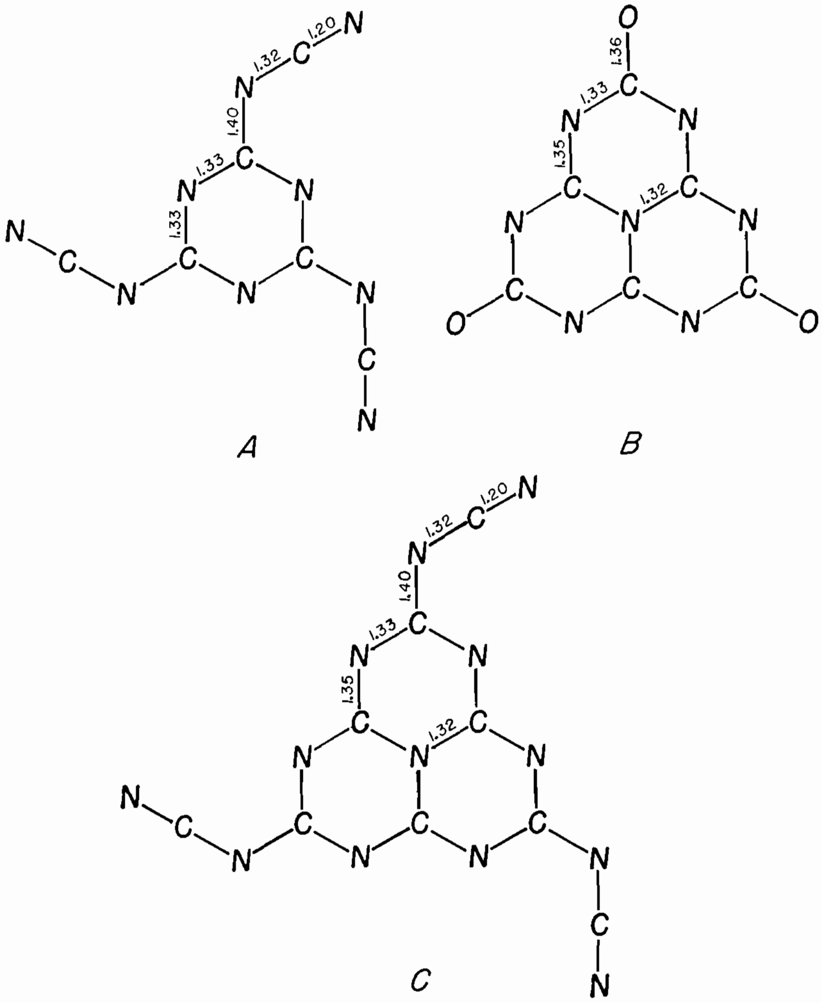


FIGURE 1

The structures of (*A*) the cyanuric tricyanamide ion, $C_6H_9^{\equiv}$, (*B*) the cyamelurate ion, $C_6N_7O_3^{\equiv}$ and (*C*) the cyameluric tricyanamide (hydromelonate) ion, $C_9N_{13}^{\equiv}$. Predicted values of interatomic distances are shown. The molecules are coplanar, with all bond angles (except in the linear cyanamide groups) close to 120°.

The configurations of the cyanuric tricyanamide ion, the cyamelurate ion and the cyameluric tricyanamide ion are shown in figure 1.

We are indebted for the gift of crystals of trisodium cyanuric tricyanamide to the late Professor E. C. Franklin. We wish to thank Dr. J. Sherman for assistance with the laborious quantum mechanical calculations.

*Contribution No. 628.

[1] L. Gmelin, *Ann. Pharmacie,* **15,** 252 (1835).

[2] J. Liebig, *Ibid.*, **10,** 1 (1834).

[3] J. Liebig, *Ann. Chem. Pharm.*, **50,** 337 (1844).

[4] J. Liebig, *Ibid.*, **95,** 257 (1855).

[5] W. Henneberg, *Ibid.*, **73,** 228 (1850).

[6] Henneberg assigned to the cyamelurates two alternative formulas, one including an extra atom of hydrogen. Analyses leading to the choice of the correct formula were later made by Liebig (Ref. 4).

[7] E. C. Franklin, "Nitrogen System of Compounds," Reinhold Publishing Corp., 1935.

[8] We learned later that crystals of the substance were also given by Professor Franklin to Dr. J. L. Hoard, who is continuing their study at Cornell University. The substance was originally identified (E. C. Franklin, *Jour. Am. Chem. Soc.*, **44,** 497 (1922)) as $NaC_2N_3 \cdot H_2O$, the sodium salt of dicyanimide. Our x-ray investigation led us to adopt the trimeric formula, which was also adopted by Professor Franklin (Ref. 4).

[9] E. W. Hughes, *Jour. Chem. Phys.*, **3,** 1 (1935); I. E. Knaggs, *Proc. Roy. Soc.*, **A150,** 576 (1935). The hexagonal unit of structure of $Na_3C_6N_9 \cdot 3H_2O$, containing two molecules, has $a_0 = 10.25$ Å and $c_0 = 6.60$ Å, whereas the corresponding dimensions for cyanuric triazide are $a_0 = 8.73$ Å, $c_0 = 5.96$ Å.

[10] Several organic tricyanomelamines have been prepared recently by J. Biechler, *Compt. Rend.*, **203,** 568 (1936).

[11] L. Pauling and L. O. Brockway, *Jour. Am. Chem. Soc.*, **59,** 1223 (1937).

[12] N. Elliott, *Ibid.*, **59,** 1380 (1937).

[13] There is evidence from electron diffraction studies of pyrazine and pyridine that this value should be increased by 0.01 or 0.02 Å because of the electronegativity of nitrogen (V. Schomaker and L. Pauling, paper to be published in *Jour. Am. Chem. Soc.*).

[14] G. W. Wheland and L. Pauling, *Ibid.*, **57,** 2086 (1935).

Reprinted from the Journal of the Chemical Society, 1948.

The Modern Theory of Valency.

THE LIVERSIDGE LECTURE, DELIVERED BEFORE THE CHEMICAL SOCIETY IN THE ROYAL INSTITUTION ON JUNE 3RD, 1948.

By LINUS PAULING.

NEARLY 100 years ago, in 1852, it was stated for the first time, by E. Frankland, that atoms have a definite combining power, which determines the formulas of compounds. Then in 1858 Archibald S. Couper introduced the idea of the valency bond and drew the first structural formulas, and August Kekulé showed that carbon is quadrivalent. This simple valency-bond theory permitted great progress to be made in structural organic chemistry, but structural inorganic chemistry remained largely undeveloped until the present century. With the discovery of the electron and the elucidation of the electronic structure of atoms, it became possible for Gilbert Newton Lewis in 1916 to identify the covalent bond with a pair of electrons shared by two atoms and counting as part of the outer shell of each, and thus to lay the basis for the development of the modern theory of valency, to which Sidgwick, Robinson, and many other chemists have contributed.

The modern theory of valency is not simple—it is not possible to assign in an unambiguous way definite valencies to the various atoms in a molecule or crystal. It is instead necessary to dissociate the concept of valency into several new concepts—ionic valency, covalency, metallic valency, oxidation number—that are capable of more precise treatment; and even these more precise concepts in general involve an approximation, the complete description of the bonds between the atoms in a molecule or crystal being given only by a detailed discussion of its electronic structure. Nevertheless, these concepts, of ionic valency, covalency, etc., have been found to be so useful as to justify our considering them as constituting the modern theory of valency.

Ionic Valency.

It is customary to describe a crystal of cæsium fluoride as a regular arrangement of ions Cs^+ and F^-, held together in a stable equilibrium between the Coulomb forces of electrostatic attraction and the characteristic repulsive forces of closed shells of electrons. The loss of an electron by an atom of cæsium and its gain by an atom of fluorine may be said to be due to the striving of the atoms to achieve the stable electronic structure of the neighbouring noble gases, xenon and neon, respectively. The crystal barium oxide may be similarly described as an arrangement of ions Ba^{++} and O^{--}, with the same noble-gas structures. These considerations lead to the assignment of the ionic valencies + 1, + 2, + 3 to elements of the first, second, and third, and − 1, − 2, − 3 to elements of the seventh, sixth, and fifth periods of the periodic table. In addition, there are ions, existing in aqueous solution, which do not correspond to noble-gas structures, such as the ferrous ion and the ferric ion. The existence of these ions is usually attributed to the relative ease of removing two or three of the outer electrons of the atoms of the transition elements.

This concept of ionic valency, useful as it is, must be considered only as an approximation to the truth. In a gaseous molecule CsF the electronic structure is not so well described by a wave function corresponding to a cæsium cation and a fluoride anion held together by electrostatic attraction as by a wave function describing a hybrid of this structure and a covalent structure, in which one pair of electrons is shared in the normal way between a cæsium atom and a fluorine atom. The difference in electronegativity, 3·3, of cæsium and fluorine permits the amount of covalent character of the cæsium–fluorine bond in this molecule to be estimated as 9%. It is only to this degree of approximation, then, that the bond in the cæsium fluoride molecule can be described as an ionic bond. In the cæsium fluoride crystal each cæsium atom is surrounded octahedrally by six fluorine atoms. If each of these bonds had 9% covalent character, the total covalency of cæsium and of fluorine would be 0·54, and the crystal could be described as involving, for each atom, a single bond, about 50% covalent and 50% ionic, resonating among the six positions connecting the atom with its six ligates.

This description would assign to the cæsium atom in the cæsium fluoride crystal a resultant charge $+\frac{1}{2}$, and to the fluorine atom a charge $-\frac{1}{2}$. It has seemed to me likely that in general all of the atoms in the complexes that constitute stable chemical substances have resultant electrical charges smaller than those shown by these most electropositive and electronegative atoms in their compounds with one another, and I have accordingly formulated the *postulate of the essential electrical neutrality of atoms* : namely, that the electronic structure of substances is such as to cause each atom to have essentially zero resultant electrical charge, the amount of leeway being not greater than about $\pm \frac{1}{2}$, and these resultant charges are possessed mainly by the most electropositive and electronegative atoms, and are distributed in such a way as to correspond to electrostatic stability.

According to this postulate the description of the barium oxide crystal as consisting of an arrangement of ions Ba^{++} and O^{--} would be a poorer approximation to reality than its description as a regular arrangement of atoms Ba and O, with each atom forming two covalent bonds, which resonate among the positions to the six surrounding atoms. These bonds have enough ionic character to give a small positive charge to each barium atom and a small negative charge to each oxygen atom.

I doubt whether the ferrous ion and ferric ion, and similar ions of the transition elements, exist in chemical substances. I think instead that the atoms of iron in all ferrous and ferric compounds form covalent bonds in such a way as to remain essentially neutral. The postulate of neutrality of all atoms permits one to understand why the transition elements tend to form hydrated ions that carry two or three positive charges, rather than a smaller or larger number, and thus accounts for the observed bivalency and tervalency of these elements.* Let us consider a hexahydrated ion $M(OH_2)_6^{v+}$. The transition metals have electronegativity values lying between 1·5 and 2·0, corresponding to bonds with oxygen having between 37% and 57% of covalent character. The sizes of these atoms are such as to permit them to co-ordinate six water molecules about them, and the six bonds with the oxygen atoms of the water molecules would accordingly transfer a negative charge of between 2·2 and 3·4 units to the metal atom. This would neutralise the positive charge of the metal atom if two or three electrons were to be removed from it. For example, a ferric ion Fe^{+++} could have its charge exactly neutralised by forming bonds with 50% covalent character with the oxygen atoms of six water molecules co-ordinated about it. The charge of $+ \frac{1}{2}$ would not, moreover, remain on the oxygen atoms of these water molecules, but would be transferred to the hydrogen atoms, since each O–H bond has enough ionic character (32%, as indicated by its electric dipole moment) to transfer $+ \frac{1}{4}$ charge to itself. Thus the total positive charge of the complex ion $Fe(OH_2)_6^{+++}$ is distributed over the twelve hydrogen atoms on its periphery, this distribution being that which is favoured by the electrostatic forces. It is seen from this example that the bivalency and tervalency shown by the transition elements is not the result of the ease of removal of two or three electrons from the atoms, but is rather a consequence of the electronegativity of these elements relative to the non-metallic elements, together with the tendency of atoms to remain electrically neutral.

Covalency.

A covalent bond between two atoms requires two electrons and two orbitals, one for each atom.† The factors determining the properties of the covalent bonds formed by an atom are primarily the number and nature of the orbitals (hybridised bond orbitals) available to the atom, and the number of electrons that it can use in bond formation without losing its electrical neutrality. The opportunities for stabilisation through resonance of covalent bonds among alternative positions are also important.

For elements adjacent to the noble gases the principal orbitals used in bond formation are those formed by hybridisation of the *s* and *p* orbitals. For the transition elements there are nine stable orbitals to be taken into consideration, which in general are hybrids of five *d* orbitals, one *s* orbital, and three *p* orbitals. An especially important set of six bond orbitals, directed toward the corners of a regular octahedron, are the d^2sp^3 orbitals, which are involved in most of the Werner octahedral complexes formed by the transition elements.

I feel that it is necessary to clarify the interpretation of the magnetic criterion for bond character.‡ It has been customary to describe the results of the application of this criterion by saying that the bonds in a complex are either essentially covalent or essentially ionic. For example, the bonds in the cobaltic hexammoniate complex, $Co(NH_3)_6^{+++}$, are said to be shown to be essentially covalent by the diamagnetism of the substance, and the bonds in the hexahydrated cobaltic ion, $Co(OH_2)_6^{+++}$, are said to be shown to be essentially ionic by the possession by this complex of a magnetic moment of about 5·3 Bohr magnetons. The diamagnetism of the first substance does in fact show that the six outer electrons of the cobalt atom not involved in the formation of single bonds with ammonia are forced in pairs into three of the 3*d* orbitals, showing that the remaining two of the 3*d* orbitals are used in bond formation.

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* See Pauling, Victor Henri Memorial Volume.

† Heitler and London, *Z. Physik*, **1927**, **44**, 455.

‡ Pauling, *J. Amer. Chem. Soc.*, **1931**, **53**, 1367.

With the sp^3 orbitals, these two orbitals permit the formation of six d^2sp^3 octahedral hybrid orbitals, which would permit the formation of a normal covalent bond between cobalt and each of the six nitrogen atoms. However, the six bonds that are formed by a cobalt atom with the nitrogen atoms have only about 50% covalent character, the amount required to neutralise the charge of a cobaltic ion. This amount of covalent character could be achieved with the use of only three orbitals, resonating among the six positions, and accordingly it is not necessary to have use of the two $3d$ orbitals in order to form six bonds with 50% covalent character. With the other complex, the hexahydrated cobaltic ion, the six outer electrons of the cobalt atom occupy all five of the $3d$ orbitals, leaving the four sp^3 hybrid orbitals for bond formation. By resonating among the six positions, these four orbitals could permit the formation of six bonds with as much as $\frac{2}{3}$ covalent character, and hence could provide the amount, 50%, required to make the central atom electrically neutral.

It now seems to me that there are two ways in which the bonds in the first complex differ from those in the second, and two mechanisms for providing the extra energy required to force the six outer electrons of the cobalt atom from five $3d$ orbitals into three $3d$ orbitals, with the accompanying decrease in stability indicated by Hund's rule of maximum multiplicity for electrons in a sub-shell of oribitals. In the first place, the d^2sp^3 orbitals have a larger bond strength than the sp^3 orbitals, 3 instead of 2, and the bonds that they form should accordingly be 50% stronger. Secondly, a greater amount of resonance stabilisation through ionic–covalent resonance is to be expected for six bonds if an orbital is at hand for each of them, permitting the resonance to be unsynchronised, than if there are only four orbitals available for the six bonds, requiring some synchronisation of the covalent phases of the resonating bonds. We conclude accordingly that the magnetic criterion distinguishes, not between essentially covalent bonds and essentially ionic bonds, but between strong covalent bonds, using good hybrid bond orbitals and with the possibility of unsynchronised ionic–covalent resonance, and weak covalent bonds, using poor bond orbitals, and with the necessity for synchronisation of the covalent phases of the bonds. In a complex of the first sort the stability of the complex is due in larger part to the bonds themselves and in smaller part to the atomic electrons, and in a complex of the second sort the situation is reversed.

It is interesting to note that as many as all nine of the d^5sp^3 hybrid bond orbitals may be involved in bond formation in complexes formed by the transition elements.* In the ferrocyanide ion, $Fe(CN)_6^{----}$, the distance between the iron atom and the carbon atoms shows that the bonds have a large amount of double-bond character. This could be achieved by using the nine outer orbitals of the iron atom and the appropriate electrons in the formation of three double bonds and three single bonds with the six surrounding carbon atoms. If these bonds were all normal covalent bonds the iron atom would have a resultant charge -1; but carbon is slightly more electronegative than iron, which permits this charge to be drained off into the carbon atoms, and from them to the nitrogen atoms, in such a way that the entire charge 4– of the ion is distributed over the six nitrogen atoms. The complex is thus stabilised not only through the formation of these covalent bonds, in a way compatible with the postulate of electrical neutrality of the atoms, but also by the resonance energy of the single and double bonds among the alternative positions.

The interesting fact that the ferrocyanide ion is less easily oxidised to the ferricyanide ion than is the hydrated ferrous ion to the hydrated ferric ion can now be explained. The ferricyanide ion, with one odd electron occupying one of the nine orbitals of the iron atom, contains only two double bonds between iron and carbon, resonating with four single bonds. However, there is a smaller amount of resonance energy associated with the resonance of two double bonds among six positions than of three double bonds among six positions (there being, respectively, 15 and 20 ways of arranging the bonds), and accordingly this ion is not stabilised so greatly by resonance as is the ferrocyanide ion. The same argument explains the stability of the ions $Mn(CN)_6^{-----}$ and $Co(CN)_6^{---}$, which are similar in electronic structure to the ferrocyanide ion.

The stability of sexivalent chromium, in the chromate ion and related ions, can also be understood. The chromic complexes, involving tervalent chromium, make use of d^2sp^3 bond orbitals, the three remaining outer electrons of the chromium atom being in three of the $3d$ orbitals, with parallel spins. The resonance energy of these three atomic electrons in a quartet state helps to stabilise the chromic compounds. However, if all of the nine outer orbitals of the chromium atom were available for bond formation, stable compounds might also be expected

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* Pauling, " The Nature of the Chemical Bond ", Cornell University Press, Ithaca, N.Y., Second Edition, 1940, p. 255.

to be formed. In the chromate ion, CrO_4^{--}, each of the oxygen atoms might use one of its σ orbitals and two of its π orbitals (relative to the axis connecting it with the chromium atom) for the formation of covalent bonds with that atom, the outer σ orbital not being suitable to bond formation, and being occupied by an unshared pair. The total of twelve bonds formed by the chromium atom (four triple bonds with the four oxygen atoms) would, with 50% covalent character per bond, lead to zero charge for the chromium atom, placing the charge $-\frac{1}{2}$ on each oxygen atom. The resonance of the bonds between covalent and ionic aspects (that is, between single, double, and triple bonds with oxygen) could not take place in a completely unsynchronised way, because chromium has only nine orbitals available; but the availability of as many as nine orbitals would lead to a large amount of resonance stabilisation.

The complex might be best described by saying that each oxygen atom could form a double bond with the chromium atom with the use of either one of its two π orbitals and the accompanying pair of electrons, extra stability being achieved through the resonance between the two kinds of double bonds.

Metallic Valency.

In most substances the phenomenon of quantum mechanical resonance of valency bonds among alternative positions is important for the stability and physical and chemical properties of the substances, but not directly for the valency of the elements. Thus the quadrivalency of carbon is not affected by the Kekulé resonance in benzene or the conjugation resonance in the polyenes, which instead affect principally the distribution of the four covalencies of each carbon atom among the bonds to its neighbours. The hydrocarbon free radicals constitute an exceptional case, in which the stabilising effect of the resonance of the odd electron among various carbon atoms is sufficiently great to cause one covalency—not, however, rigorously associated with one carbon atom—to become ineffective.

In recent years it has become clear that the structure of metals and alloys may be described in terms of covalent bonds that resonate among the alternative interatomic positions in the metals, and that this resonance is of greater importance for metals than for substances of any other class, including the aromatic hydrocarbons. Moreover, the phenomenon of metallic resonance of the valency bonds must be given explicit consideration in the discussion of metallic valency: it is necessary in deducing the metallic valency from the number of available electrons and bond orbitals to assign to one orbital a special rôle in the metallic resonance.

A few years ago, while examining the consequences of the concept that in a metal, in which each atom is surrounded by a large number of neighbours, the valency bonds that it is permitted to form by its numbers of outer electrons and bond orbitals resonate among the positions connecting it with its ligates, I concluded from the examination of the magnetic properties and mechanical properties of the transition elements that the nine outer orbitals may be divided into three classes: *viz.*, a class of stable bond orbitals, consisting of 5·78 orbitals per atom; a class of stable atomic orbitals, essentially *d* in character, consisting of 2·44 orbitals per atom; and the remaining 0·78 orbital per atom, with no apparent use, which was then designated as the unstable orbital.* It has now become evident that the characteristic nature of metals is determined by the unsynchronised resonance of individual valency bonds in the metal, and that the existence of this resonance depends upon the possession by each atom in the metal, or by a large number of the atoms, of an extra orbital, in addition to those normally occupied by unshared electrons or bonding electrons. The number 0·78 may be interpreted as showing that about three quarters of the metal atoms in the structures to which this number applies possess this extra orbital, the *metallic orbital.*

The significance of the metallic orbital to metallic valency may be illustrated by the example of the element tin. Tin has fourteen electrons outside of its completed krypton shell. These fourteen electrons might be introduced into the nine outer orbitals by placing pairs of electrons in five of the orbitals (presumably largely *d* and *s* in character, in order that the atomic energy might be minimised by the introduction of two electrons in each of these more stable 4*d* and 5*s* orbitals, rather than the less stable 5*p* orbitals), leaving the four remaining electrons to occupy four bond orbitals. This quadrivalent tin atom could then form covalent bonds, which might resonate among alternative positions in the crystal, but only by a process of synchronised resonance, similar to that between the Kekulé structures in benzene. The amount of resonance energy that could be achieved by this synchronous resonance might not be great enough to overcome the repulsive energy between non-bonded atoms, and thus to permit the increase in the co-ordination number of each tin atom above the covalency four. This is, in fact, true—

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* Pauling, *Physical Rev.*, 1938, **54**, 899; *J. Amer. Chem. Soc.*, 1947, **69**, 542.

quadrivalent tin forms the essentially non-metallic crystalline modification of the element called grey tin, in which each tin atom is bonded by single covalent bonds to four atoms that surround it tetrahedrally, in the same way that the carbon atom expresses its quadrivalency in diamond. On the other hand, if the fourteen outer electrons of the tin atom are introduced into eight of the nine orbitals, by placing six pairs in six orbitals (essentially hybrids of the three $4d$ orbitals and the single $5s$ orbital) and the two remaining electrons in two orbitals, the resulting bivalent tin can form a crystal in which each atom has co-ordination number larger than the covalence 2; in particular, it can have co-ordination number 6, which is observed in the metallic form of tin, white tin. The bonds present in this metallic tin do not need to resonate among the various positions synchronously, because the presence of an additional orbital, the metallic orbital, permits a tin atom to assume the covalency 3, by accepting an additional electron from a neighbouring tin atom, which would itself be reduced to covalency 1. This metallic resonance thus leads to the presence in the white tin crystal of neutral bicovalent tin atoms, tercovalent tin atoms with a negative electrical charge, and unicovalent tin atoms with a positive electrical charge. The amount of stabilisation by this resonance and the extra atomic energy resulting from changing one electron from a p orbital to the more stable s orbital are great enough to give to the crystal essentially the same stability as that of grey tin, in which each atom forms a larger number of covalent bonds. Approximate calculations of the resonance energy indicate that the energy of the system is minimised when the metallic crystal contains about 50% neutral atoms, 25% negatively charged atoms, and 25% positively charged atoms. The electrical conductivity of metals may be described as resulting from the motion of these negative and positive charges through the crystal.

In this way the conclusion is reached that the metallic valency of the transition metals is not the number of unpaired electrons obtained by distributing the outer electrons among the nine stable outer orbitals (valency 4 for germanium, 5 for gallium, 6 for zinc, 7 for copper, and 8 for nickel), but is, rather, a number 2 less than this, obtained by distributing the electrons among eight orbitals, and leaving the ninth for use as the metallic orbital (valency 2 for germanium, 3 for gallium, 4 for zinc, 5 for copper, and 6 for nickel). Thus metallic zinc in the elementary state seems to be quadrivalent; each zinc atom uses three of its covalencies in forming half-bonds with six ligates, and the remaining single covalency in forming one-sixth bonds with six somewhat more distant ligates.

Variability in metallic valency is also made possible by the resonance of atoms among two or more valence states. In white tin the element has valency approximately 2·5, corresponding to a resonance state between bicovalent tin, with a metallic orbital, and quadricovalent tin, without a metallic orbital, in the ratio 3 to 1; and copper seems similarly in the elementary state to have metallic valency 5·5.

The close relation between metallic valency and the valency operative in ordinary compounds between metals and non-metallic elements may be illustrated by chromium. This element occurs in two metallic forms, in which its valency is shown by the observed interatomic distances to be, respectively, 6 and 3. These two forms of the metal are accordingly analogous to the chromate ion and other ordinary compounds of sexivalent chromium, on the one hand, and, on the other, to the hexahydrated chromic ion and other chromic compounds. The stability of the two metallic forms may also be attributed to the same effects, described above, as for ordinary compounds of sexivalent chromium and tervalent chromium: namely, for sexivalent chromium the stabilising bond energy and resonance energy result from use of all six electrons and all available orbitals in forming bonds, and for tervalent chromium, with a decreased amount of bond energy and resonance energy, the extra atomic stability results from the presence of three unpaired electrons with parallel spin in stable atomic orbitals.

Oxidation Number.

One important use of the concept of valency is in the discussion of oxidation–reduction reactions. The assignment of positive and negative valencies to the elements in their various compounds and the consideration that in the processes usually classified as oxidation–reduction reactions electrons are transferred from the atoms of one element to those of another, causing an increase and decrease, respectively, in their positive valencies, have been found to be a useful part of chemical theory. With the development of a sound understanding of the electronic structure of molecules it has been recognised that this transfer of electrons to or from a single atom in a complex is not complete, and that the positive and negative valencies customarily used in the discussion of these reactions may be assigned in an arbitrary manner.

The special nature of these valencies has been indicated by designating them by the name oxidation number, and their values, agreeing for the elements in most substances with the values used by chemists of past generations, may be taken to be given by rules such as the following : *

1. The oxidation number of a monatomic ion in an essentially ionic substance is equal to its electrical charge.
2. The oxidation number of atoms in an elementary substance is zero.
3. In a covalent compound of known structure, the oxidation number of each atom is the charge remaining on the atom when each shared electron pair is assigned completely to the more electronegative of the two atoms sharing it. A pair shared by two atoms of the same element is split between them.
4. The oxidation number of an element in a compound of uncertain structure may be calculated from a reasonable assignment of oxidation numbers to the other elements in the compound.

Thus in the hexahydrated ferric ion hydrogen and oxygen are assigned their normal oxidation numbers + 1 and − 2, respectively, and the total charge of the complex ion, + 3, is assigned to the iron atom as its oxidation number. The same oxidation number would result from assigning the bonding electron pairs with hydrogen and iron to the oxygen atom, which is more electronegative than either hydrogen or iron. The fact that the electrical charge of the hexahydrated ferric ion is distributed among the twelve hydrogen atoms rather than being resident on the iron atom emphasises the artificiality of this assignment of oxidation numbers; but the fact that it is the iron atom which undergoes a significant change in electronic structure (the replacement of an unshared and unpaired electron by an unshared electron pair) when the hexahydrated ferric ion is reduced to the hexahydrated ferrous ion, the approximation to electrical neutrality being achieved by small changes in the amounts of partial ionic character of the bonds from iron to oxygen and from oxygen to hydrogen, validates the selection of iron as the element that undergoes the change in valency (oxidation number) during this process.

The rules that are given above permit the reasonable assignment of oxidation numbers to the elements in most substances, but occasionally are found to be insufficient or ambiguous. Thus in our description of the electronic structure of the ferrocyanide ion it has been said that the iron atom forms three single bonds and three double bonds with the surrounding carbon atoms, all of its electrons outside of the completed argon shell being used in bonding. Carbon is more electronegative than iron, and the application of Rule 3 would lead to the assignment of oxidation number + 8 to iron in the ferrocyanide ion. This is, however, unreasonable; the more reasonable oxidation number + 2 results from assigning to the iron atom two of the four electrons involved in each of the double bonds with carbon, and to the carbon atom two of the electrons involved in each double bond and each single bond. This procedure might be justified by showing that the carbon atom is more electronegative than iron with respect to the electrons used in the σ bonds, and less electronegative with respect to the electrons used in the π half of the double bonds.

Now that the general concept of valency has been divided into several concepts capable of more precise formulation we may ask whether the word valency, without qualification, need ever be used. I think that it may be used as a synonym for one of the more precise concepts when its meaning is clear from the context. Thus in the classification of the compounds of iron we may include the ferrocyanides among the compounds of bivalent iron. We might say that in the ferrocyanide ion the iron atom is sexiligant (has co-ordination number 6), is enneacovalent, and has oxidation number + 2. In the compound FeSi each silicon atom uses its four valencies in forming a single bond with one iron atom, three two-thirds bonds with iron atoms, and three one-third bonds with iron atoms, and each iron atom forms similar bonds with seven silicon atoms and in addition forms six one-third bonds with iron atoms. Thus iron in this compound is sexicovalent, and may be assigned oxidation number + 4, if silicon is assumed to be more electronegative than iron—actually the elements are essentially equal in electronegativity, and the assignment of oxidation numbers + 4 and − 4 to silicon may be less reasonable than that of oxidation number 0 for each element.

The Future of the Theory of Valency.

The theory of valency is equivalent to the theory of structural chemistry. This theory has now passed through the first stage of its modern development, that of the formal assignment of structures to chemical substances, and is entering upon its second stage, the development of a system permitting the prediction of the approximate thermodynamic stabilities corresponding

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* See Pauling, " General Chemistry ", W. H. Freeman and Co., San Francisco, Calif., 1947, Chap. 10.

to alternative structures. I believe that, despite the complexity of the problem, it will become possible to make reliable (but not precise) predictions of the free energy of substances, even before they have been synthesised, and that in this way the theory of valency will come to have far greater value than at present. A start has already been made on this programme—the discussion of the stabilising influence of the resonance corresponding to partial ionic character of single covalent bonds and of resonance of valence bonds among alternative positions in a molecule or crystal has aided in the systematisation of inorganic chemistry and of organic chemistry. The postulate of the electrical neutrality of atoms, discussed above, has provided us with a general explanation of the tendency of the transition elements to assume the valencies 2, 3, and 6. Professor Ingold has pointed out to me that this postulate also explains why it is that the cations stable in solution are in general complexes in which the outer layers of atoms consist of hydrogen atoms attached to electronegative atoms, so that the partial ionic character of the bonds leads to the production of a resultant positive charge on the peripheral hydrogen atoms, the charge of the cation thus being distributed in an electrostatically favourable manner. This explains the stability of the complexes with water and ammonia, as compared with complexes with dimethyl ether, trimethylamine, and phosphine. In a similar way the outermost atoms in the anionic complexes tend to be oxygen atoms, or atoms of another strongly electronegative element. The use of structural arguments to explain the relative stabilities of substances has also been illustrated in the discussion of the relative ease of oxidation of the ferrocyanide ion and the hexahydrated ferrous ion.

The progress that has been made during the last few decades has been the result of the development of the theory of quantum mechanics, and of the application of experimental methods of determining the structure of molecules and crystals, especially the methods of *X*-ray diffraction by crystals and of the diffraction of electrons by gas molecules. Much valuable information has been provided by the techniques of molecular spectroscopy, and by the measurement of electric and magnetic dipole moments. We may be assured that the continued application of these techniques will provide us with much more knowledge, and that in addition other methods of experimental investigation will be found. Perhaps microwave spectroscopy and the more complex electrical and magnetic phenomena (Kerr effect, magnetic birefringence, etc.) will be found to be very useful—and we may hope that powerful methods of investigation that are not yet known will be discovered. If scientific progress continues, the next generation may have a theory of valency that is sufficiently precise and powerful to permit chemistry to be classed along with physics as an exact science.

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INTERATOMIC DISTANCES AND BOND CHARACTER IN THE OXYGEN ACIDS AND RELATED SUBSTANCES

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In a complex such as the sulfate ion the sulfur–oxygen bond assumes multiple-bond character through resonance involving one sigma bond and two pi bonds. An empirical equation has been formulated connecting interatomic distances and bond number for resonance of this sort. On application of this equation it is found that in many complexes the amounts of multiple-bond character are such as to cause all atoms to conform rather closely to the principle of electroneutrality.

A number of years ago there was developed in our laboratories[1] an interpretation of observed interatomic distances in the oxygen acids and related substances in terms of the partial double-bond character of the bonds. For example, the Si–O distance 1.60 Å. observed in the silicate group in silica and many silicate crystals, which is 0.23 Å. less than the sum of the single-bond radii, was interpreted as indicating that the silicon atom forms with each of the four adjacent oxygen atoms a bond that is essentially a double bond, making use to some extent of the 3*d* orbitals of silicon, as well as the 3*s* and 3*p* orbitals. This interpretation is not completely satisfactory, in that bonds of this sort, even with a reasonable amount of ionic character for the σ bond (about 40%), would correspond to a negative charge on the silicon atom, which however would be expected to have a positive charge.

Schomaker and Stevenson[2] have introduced a revised set of single-bond covalent radii for the first-row elements, and an equation by means of which the effect of partial ionic character of a bond on the interatomic distance may be computed; the use of their system leads to a smaller difference between the observed interatomic distances and those calculated for single bonds with the normal amount of ionic character, as given by the difference in electronegativities of the bonded atoms. Pitzer[3] has recently stated that he does not believe that these bonds have any multiple-bond character whatever; he suggested that the observed short distances are due entirely to the Schomaker–Stevenson shortening plus a bond-lengthening effect that operates in bonds between second-row atoms (such as the Si–Si bond) because of a great repulsion of inner shells. The question of the nature of the bonds has been discussed also by Wells[4] and Moffitt.[5]

A few years ago[6,7] I proposed an electroneutrality principle—the postulate that the electron distribution in stable molecules and crystals is such that the electrical charge that is associated with each atom is close to zero, and in all cases less than ±1, in electronic units. In a molecule involving single bonds we expect a transfer of charge from atom to atom as a result of the partial ionic character of the bonds. For the Si–O bond, for example, the difference in electronegativity of the two atoms corresponds to a partial ionic character of the σ bond amounting to roughly 50%, as found by use of the empirical function based on dipole-moment data.[8] The partial ionic character of four Si–O single bonds would thus confer on the silicon atom a charge of approximately +2, which is incompatible with the electroneutrality principle. A reasonable way to neutralize this large positive charge is through the formation of π bonds between oxygen and silicon, with use of the extra outer electron pairs of the oxygen atom. If each Si–O bond were to have about 50% π-bond character enough negative charge would be transferred to the silicon atom to give it the resultant charge zero, and thus to cause silica and the silicates to satisfy the electroneutrality principle.

I have found that the assumption that in molecules and crystals in which there are atoms with extra electron pairs the bonds have somewhat less π-bond character than necessary to neutralize the charges on the atoms due to the σ bonds, as calculated from differences in electronegativity of the bonded atoms, leads to calculated interatomic distances, electric dipole moments, and bond angles in good general agreement with experiment. Use is made in this calculation of a new equation that is proposed for representing the shortening effect of π-bond character when two pairs of π electrons are involved, and also of a revised relation between the partial ionic character and the electronegativity difference.

Interatomic Distances for π-Bond Resonance

In calculating the interatomic distance with use of the amount of π-bond character we need an equation different from the original equation representing resonance between single bonds and double bonds. The original equation[9]

$$R = R_1 - (R_1 - R_2)\,3n'/(2n' + 1) \qquad (1)$$

in which n' is the amount of double-bond character, leads with $R_1 - R_2$ given the value 0.21 Å. to satisfactory agreement with the observed carbon–carbon interatomic distances for graphite and benzene in relation to those of ethane and ethylene. The curve corresponding to this equation is shown in Fig. 1. It falls below the curve $R = R_1 - 0.706 \log n$, in which n is the bond number, by about

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(1) See L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, Chap. 7.

(2) V. Schomaker and D. P. Stevenson, *J. Am. Chem. Soc.*, **63**, 37 (1941).

(3) K. S. Pitzer, *ibid.*, **70**, 2140 (1948).

(4) A. F. Wells, *J. Chem. Soc.*, **1949**, 55.

(5) W. E. Moffitt, *Proc. Roy. Soc. (London)*, **A200**, 409 (1950)

(6) L. Pauling, Victor Henri Memorial Volume, Liège, Maison Desser, 1948.

(7) L. Pauling, *J. Chem. Soc.*, 1461 (1948).

(8) Reference 1, Sec. 12.

(9) Reference 1, Chap. 5.

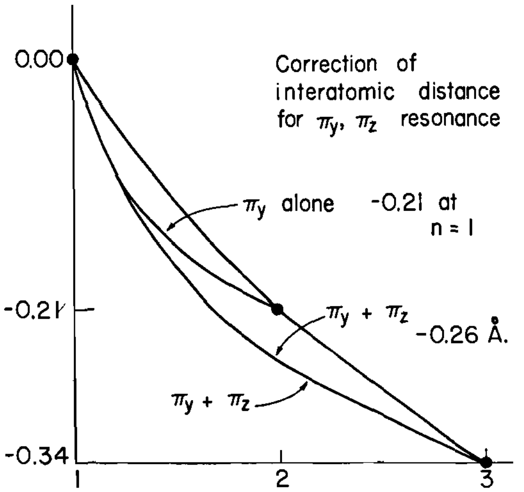

Fig. 1.—Curves representing the dependence of interatomic distance on amount of π-bond character for resonance with a single π electron pair, and with two π electron pairs. The uppermost curve represents the function $R = R_1 - 0.706 \log n$, in which n is the bond number; it corresponds to the dependence of interatomic distance on bond number without correction for resonance shortening. The numbers 1, 2, 3 as abscissas are bond numbers, which are 1 greater than n_π.

0.03 Å. in the neighborhood of 50% double-bond character, because of the stabilizing effect of resonance.[10] In case that two pairs of π electrons, corresponding to the wave functions p_y and p_z (with the x axis taken in the direction of the bond), are involved, a larger amount of resonance energy would be expected for the same amount of π character than in case that only one pair of π electrons is involved. It is found by solution of the appropriate secular equation that the resonance energy for 50% π-bond character when equally divided between π_y and π_z is about twice as great as the resonance energy for 50% π-bond character of a single type; we would accordingly predict that the interatomic distance would be about 0.03 Å. less for the former case than for the latter case.

In the following discussion use is made of an equation that has been formulated by the method given earlier in a discussion of the equation for resonance between a single bond and a double bond[11] and of the interatomic distances in the carbon monoxide molecule and carbon dioxide molecule.[12] The potential function for the bond is assumed to have the form

$$V(R) = \frac{1}{2}\alpha_1 k_1(R - R_1)^2 + \frac{1}{2}\alpha_2 k_2(R - R_2)^2 + \frac{1}{2}\alpha_3 k_3(R - R_3)^2 \quad (2)$$

in which α_1, α_2, α_3 represent the extents to which the single-bond structure, the double-bond structure, involving either the π_y or the π_z electron pair, and the triple-bond structure, involving both of these electron pairs, contribute to the state of the molecule, the k's are their force constants, and the R's their interatomic distances. For single, double, and triple bonds the k's may be taken in the ratio 1:3:6. The equilibrium value of R is found by equating the derivative $\mathrm{d}V/\mathrm{d}R$ to zero and solving for R, which leads, with introduction of the empirical values 0.21 Å. for $R_1 - R_2$ and 0.34 Å. for $R_1 - R_3$, and by taking the values of α_1, α_2, and α_3 as $\left(1 - \frac{1}{2}n_\pi\right)^2$, $n_\pi\left(1 - \frac{1}{2}n_\pi\right)$, and $\frac{1}{4}n_\pi{}^2$, corresponding to independent resonance of the π_y and π_z electron pairs, to the result

$$R = R_1 - \frac{0.63n_\pi + 0.195n^2{}_\pi}{1 + 2n_\pi + \frac{1}{4}n^2{}_\pi} \quad (3)$$

Here n_π is the total amount of π-bond character.

The curve corresponding to this equation is also shown in Fig. 1. It is seen that it lies below the curve representing resonance between a single bond and a π_y (or π_z) double bond by the amount 0.026 Å. at $n_\pi = 0.5$, and by 0.045 Å. at the point for a pure double bond, $n_\pi = 1.0$, these differences representing the effect of the extra resonance stabilization when two π electron pairs are involved. Values corresponding to the curve are given in Table I.

TABLE I

BOND SHORTENING BY π-BOND RESONANCE

n_π[a]	$-\Delta R$	n_π	$-\Delta R$
0.0	0.000	0.8	0.227
.1	.054	0.9	.241
.2	.095	1.0	.255
.3	.127	1.2	.276
.4	.154	1.4	.294
.5	.176	1.6	.310
.6	.195	1.8	.325
.7	212	2.0	.340

[a] Here n_π is the amount of π character (the sum of π_y and π_z, which are equal), and $-\Delta R$ is the bond shortening, in Å.

For calculating the interatomic distance for a single bond, R_1, involving an atom of nitrogen, oxygen, or fluorine (or two such atoms), we use the equation of Schomaker and Stevenson; namely

$$R_1 = R_A + R_B - 0.09|x_A - x_B| \quad (4)$$

The radii 0.74 Å. for nitrogen, 0.74 Å. for oxygen, and 0.72 Å. for fluorine are to be used with this equation.

The question may be raised as to the extent to which the Schomaker–Stevenson correction includes recognition of the double-bond effect. Equation 4 applies to trimethylamine and dimethyl ether, in which there is no double-bond formation expected because the more electropositive atom in the C–N and C–O bonds, the carbon atom, is given a negative charge by the partial ionic character of its bonds to hydrogen that is larger in magnitude than the positive charge conferred on it by the C–N or C–O bond, and hence does not have a free π orbital to accept an electron from the nitrogen or oxygen atom. We conclude that separate consideration must be given to the effect of the formation of π bonds by atoms of second-row elements with use of $3d$ orbitals. The correction for this effect is made by application of Equation 1 or Equation 3.

The Partial Ionic Character of σ Bonds

A number of years ago an equation was proposed[13] for calculating the partial ionic character of a σ bond between two atoms A and B from their electronegativity difference $x_A - x_B$

$$\text{partial ionic character} = 1 - e^{-a(x_A - x_B)^2} \quad (5)$$

This equation, with $a = 0.25$, was based on the observed electric dipole moments of HCl, HBr, and HI. Since then the value of the dipole moment of HF has been determined; it is 1.98 D, which corresponds to 47% ionic character, whereas Equation 5 with $a = 0.25$ gives 59%. It seems justified to formulate an empirical function, based on the values 5, 11, 17, and 47% for the hydrogen halides HI, HBr, HCl, and HF, as calculated from their

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[10] L. Pauling, *J. Am. Chem. Soc.*, **69**, 542 (1947).

[11] Reference 1, Sect. 22.

[12] Reference 1, Sect. 25.

[13] Reference 1, Chap. 2.

electric dipole moments and internuclear distances. The values given in Table II were obtained by making uniform slight adjustments, by not over ±0.03, in the curve of Equation 5 with $a = 0.18$, so as to conform to the values for the hydrogen halides. Several authors have pointed out that other structural features (unshared electron pairs, asymmetry of electron distribution for pure covalent bond between unlike atoms) contribute to the dipole moment, but lack of knowledge of the magnitude of their contributions prevents us from making corrections to the values given in Table II.

TABLE II

PARTIAL IONIC CHARACTER OF BONDS IN RELATION TO ELECTRONEGATIVITY DIFFERENCE

Δx^a	I^a	Δx	I	Δx	I
0.0	0	0.9	17	1.8	44
.1	1	1.0	20	1.9	47
.2	2	1.1	23	2.0	51
.3	3	1.2	26	2.2	58
.4	5	1.3	29	2.4	64
.5	7	1.4	32	2.6	70
.6	9	1.5	35	2.8	75
.7	11	1.6	38	3.0	80
.8	14	1.7	41	3.2	83

[a] I is the per cent. partial ionic character, and Δx is the electronegativity difference $x_A - x_B$.

The Extent of π-Bond Formation

In a molecule such as SiF_4, in which the central atom forms several bonds with a large amount of ionic character (58%), it is to be expected that a compensatory mechanism, the formation of π bonds, would operate to reduce the charge on this atom; but it also seems likely that this mechanism would not reduce the charge to zero, but rather would leave it at an intermediate value. An experimental determination of the charge distribution for this molecule is not easily made. The consideration of values of electric dipole moments and interatomic distances for many substances has indicated that the extent to which π bonds are formed is dependent on the row-numbers of the atoms involved and on the number of bonds formed by the central atom. Let us consider a molecule MX_n, in which each atom X is attached to the central atom M by a σ bond and $n_\pi \pi$ bonds. Let the electronegativity difference of M and X be such as to transfer the charge ϵ from each X to M. The charge distribution is then $M^{n(\epsilon - n_\pi)}X^{-(\epsilon - n_\pi)}$. We assume that the energy E of the molecule contains a quadratic term in the charge of each atom: $\frac{1}{2}k(\epsilon - n_\pi)^2$ for each atom X and $\frac{1}{2}kn^2(\epsilon - n_\pi)^2$ for M. This term represents the electroneutrality principle: it operates to minimize the charges on the atoms. The value of k depends, of course, on the nature of the atom; for simplicity, we shall neglect this dependence. We also assume that E contains a similar term $\frac{1}{2}k'n_\pi^2$ for each bond, representing the resistance of the π electron pairs of X to being drawn into π bonds. The expression for E is thus

$$E = \frac{1}{2}kn^2(\epsilon - n_\pi)^2 + \frac{1}{2}kn(\epsilon - n_\pi)^2 + \frac{1}{2}k'nn_\pi^2 \quad (6)$$

The energy has a minimum value relative to the structural parameters. Hence we place

$$\partial E/\partial n_\pi = -k(n^2 + n)(\epsilon - n\pi) + k'nn_\pi = 0 \quad (7)$$

which leads to

$$\frac{n_\pi}{\epsilon} = \frac{n + 1}{k'/k + n + 1} \quad (8)$$

This equation gives the calculated extent of neutralization of the charge due to the σ bonds through π-bond formation, as a function of the number of X atoms in the molecule, n, and the ratio k'/k of the two force constants, the electroneutrality constant k and the π-electron constant k'. With $k'/k = 1.5$, for example, the values 0.77 for $n = 4$ and 0.57 for $n = 1$ are obtained.

Dipole-moment and interatomic-distance data indicate that Equation 8 can be used generally for compounds MX_n by giving k'/k the values $0.0555 \times 3^{(a+b)}$, in which a and b are the row-numbers of atoms M and X, respectively: 1 for O and F, 2 for Si, P, S, Cl, and so on. Table III contains values of n/ϵ_π calculated in this way.

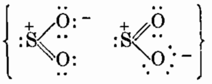
TABLE III

PERCENTAGE OF NEUTRALIZATION OF BOND MOMENT BY π-BOND FORMATION FOR MOLECULES MX_n

$a + b =$	3	4	5	6	7
$n = 1$	57	31	13	5	2
2	67	40	18	7	2
3	73	47	23	9	3
4	77	53	27	11	4

Sulfur Dioxide and Other Oxides

For sulfur dioxide, with resonating Lewis structure



a charge $-\frac{1}{2}$ is placed on each oxygen atom and +1 on the sulfur atom. In addition, the electronegativity difference 1.0 leads to 20% ionic character for each σ bond. The charge distribution without π-bond formation would be $S^{+1.40}O_2^{-0.70}$. From Table III ($a + b = 3$, $n = 2$) we obtain 67% as the amount of neutralization of charge through π-bond formation, which gives $n_\pi = 0.47$ and the charge distribution $S^{+0.46}O_2^{-0.23}$.

This charge distribution, with the known structural parameters[14] S–O = 1.433 Å. and ∠ O–S–O = 119.5°, leads to 1.61 D as the calculated value of the dipole moment. This value agrees exactly with the experimental value.

For S–O the single-bond distance is 1.69 Å., and the π-bond correction (for $n_\pi = 0.97$, the sum of the π-bond character given by the Lewis structure, 0.50, and that induced by the charge distribution, 0.47) is 0.25 Å. Hence the predicted S–O distance is 1.44 Å., in satisfactory agreement with the experimental value 1.433 Å.

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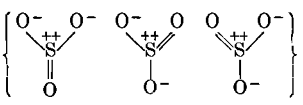
[14] B. P. Dailey, S. Golden, and E. B. Wilson, Jr., *Phys. Rev.*, **72**, 871 (1947).

For sulfur trioxide, with resonating Lewis structure



and 0.20 ionic character of the σ bonds, the charge distribution before π-bond neutralization is $S^{+2.60}O_3^{-0.87}$. Table III gives 73% neutralization, which leads to $n_\pi = 0.97$ (including 0.33 for the Lewis double bond). The predicted S–O distance is hence 1.44 Å., which agrees satisfactorily with the observed value, 1.43 ± 0.02 Å.

For dimethyl sulfone, $(CH_3)_2SO_2$, the predicted amount of π-bond character is 0.67 × 1.10 = 0.80, which leads to S–O = 1.46 Å., slightly larger than the experimental value, 1.43 ± 0.02 Å. In dimethyl sulfoxide, $(CH_3)_2SO$, the predicted value of n_π is 0.57 × 1.20 = 0.68, and the predicted value of S–O, 1.48Å., agrees with the observed value, 1.47 Å.

An interesting example is provided by the trimer of sulfur trioxide. In this molecule the three sulfur atoms are joined together into a six-membered ring by bridging oxygen atoms, and each sulfur atom also has attached to it two unshared oxygen atoms, in addition to the two bridging oxygen atoms, the four oxygen atoms being arranged tetrahedrally about it. The sulfur–oxygen distance is 1.60 Å. for the bridging oxygen atoms, and 1.40 Å. for the others. The Lewis structure, with 20% ionic character of σ bonds, gives the charge distribution $S^{+2.80}O_3^{-0.40}O_6^{-1.20}$. We make use of the value for $n = 4$ of Table III, 77%, which leads to 0.15 and 0.92 for n_π, and hence to 1.61 Å. and 1.44 A. for the two kinds of S–O bonds, in reasonably good agreement with experiment.

Molecules of the oxides of phosphorus P_4O_6 and P_4O_{10} also contain bridging oxygen atoms. The predicted amounts of π-bond character, 0.73 × 0.32 = 0.23 and 0.77 × 0.32 = 0.25, respectively, lead with use of the single-bond distance 1.71 Å. and Equation 1 to the predicted value 1.61 Å. for P–O in P_4O_6 and 1.60 Å. in P_4O_{10}. The observed values, 1.65 ± 0.02 Å. in P_4O_6 and 1.62 + 0.02 Å. in P_4O_{10}, are slightly larger.

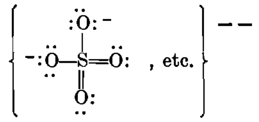
For the oxygen atoms in P_4O_{10} that are bonded to only one phosphorus atom the predicted amount of π-bond character, 1.02, leads to 1.45 Å. for the P=O distance. This is in only rough agreement with the observed distance, 1.39 ± 0.02 Å.

Salts of Oxygen Acids

The discussion of interatomic distances in salts of oxygen acids of the second-row elements is presented in Table IV. In the first row of this table, below the names of the salts, there are given values of the electronegativity difference $x_A - x_B$, in the second row the sum of the single-bond radii, in the third row the Schomaker–Stevenson correction, and in the fourth row the single-bond interatomic distance. The next row contains the fractional amount of ionic character of the σ bond, as given by the electronegativity difference with use of Table II. The next row contains the amount of positive charge placed on the central atom, per bond, by the single-bond formula; that is, it is equal to the oxidation number of the central atom diminished by 4 and divided by 4. The sum of these two quantities, given in the following row, is the amount of charge placed on the central atom by one bond of the single-bond structure. This number multiplied by 0.77, from Table III, in the next row, represents the amount of π-bond character. The following row gives the change in interatomic distance corresponding to this amount of π-bond character, as calculated with Equation 3, and the row below it the predicted interatomic distance, according to our assumptions. Finally, in the last row there are given values of the observed interatomic distances in crystals of salts of these acids. It is seen that the agreement with experiment is good.

The charges on the oxygen atoms due to partial ionic character of the bonds to the metal atoms in the silicates and other salts should be taken into consideration in making this calculation. These charges lead to further decreases in the Si–O, P–O, S–O, and Cl–O distances, of amount depending on the nature of the metal and the structure of the crystals. Because of uncertainties in the system of equations used in this paper, this refinement in the calculation has not been carried out.

It is interesting that the amount of π-bond character in these oxygen complexes varies from about $^1/_3$ to about $^2/_3$, and that for the sulfate ion it corresponds closely to the resonance formula



in which the central atom is shown with zero formal charge.

TABLE IV

INTERATOMIC DISTANCES IN SALTS OF OXYGEN ACIDS

Salt	Silicate	Phosphate	Sulfate	Perchlorate
Electronegativity difference	1.7	1.4	1.0	0.5
Sum of radii	1.91	1.84	1.78	1.73
$-0.09\,\lvert x_A - x_B\rvert$	−0.15	−0.13	−0.09	−0.05
Single-bond distance	1.76	1.71	1.69	1.68
Ionic character of σ bond	0.41	0.32	0.20	0.07
Formal charge per bond	.00	.25	.50	.75
Sum	.41	.57	.70	.82
Amount of π-bond character	.32	.44	.54	.63
Correction for π-bond	−0.13	−0.16	−0.18	−0.20
Predicted distance	1.63	1.55	1.51	1.48
Observed distance	1.62[a]	1.55[b]	1.50[c]	1.49[d]

[a] Average of reported values for zircon, andalusite, sillimanite, staurolite, topaz, titanite, thortveitite, muscovite, apophyllite, hardystonite, analcite, carnegieite, sodalite, danburite, scapolite, and cristobalite; mean deviation 0.02 Å. [b] Average for BPO_4 (1.54 Å.) and KH_2PO_4 (1.56 Å.). [c] For K_2SO_4 and other sulfates. [d] For $Mg(ClO_4)\cdot 6H_2O$.

It may be emphasized that bonds corresponding to a completed sp^3 octet for the second-row atom are to be distinguished from those involving orbitals beyond the octet. It is the octet bonds—the Lewis structures—that are of primary importance in determining the bond angles and general configuration of the complex, with the additional π bonds, involving *d* orbitals, effective mainly in changing the interatomic distances and the charge distribution.

It might be possible to formulate an empirical system of quadratic energy terms, like those in Equation 6, that would reproduce many properties of molecules in a satisfactory way. Efforts to this end have not yet been successful; even the simple treatment of Equation 6 fails when it is applied to molecules in which atoms of two or more kinds are attached to a central atom, and a similar treatment of the charge distribution (electric dipole moment) in molecules in which polar bonds interact with one another through induction has been found to be only partially satisfactory. The practical difficulties attending the quantum-mechanical treatment of the electronic structure of molecules are so great that the main hope for future progress in the treatment of molecular structure may well lie in the development of a quantitative empirical theory of this sort.

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Five Equivalent *d* Orbitals

Powell[2] has recently pointed out that in some textbooks the erroneous statement is made that there is no way of choosing the five *d* orbitals of a subshell so that they are equivalent, and, after mentioning that Kimball[3] had discussed five equivalent *d* orbitals long ago, he has shown that there are in fact two sets of five equivalent *d* orbitals, and has given expressions for them in terms of the conventional set, in which one differs in shape from the other four.

In this paper we amplify Powell's discussion, which is in some respects misleading. For example, Powell made the following statement: "Unlike the familiar four-lobed cubic *d* orbital, the pyramidal *d* orbital has only rather inconspicuous lobes of opposite sign. Each orbital is not quite cylindrically symmetrical about its own axis of maximum probability." In fact, the pyramidal *d* orbital that he discusses in detail is far from cylindrically symmetrical about its own axis of maximum probability, and the other pyramidal *d* orbital is also far from cylindrically symmetrical. In the equatorial plane about the axis of maximum probability the functions of Powell's first set (which we shall call II) vary from −0.3706 in two opposite directions to −1.7247 in the orthogonal directions. Each of these functions has almost the same value (strength) in the latter directions as in the principal directions, for which its value is 2.0950. The functions of the other set (which we call I) vary in this plane from −0.7247 to −1.4696, their value in the principal direction being 2.1943.

In the early discussions of hybrid orbitals[4,5] it was pointed out that the maximum strength (the maximum value in the bond direction) of a bond orbital formed from completed subshells of orbitals is associated with cylindrical symmetry of the orbital. In order to simplify the analysis of *spd* hybridization Hultgren[5] decided to discuss only orbitals with cylindrical symmetry. He pointed out that no more than three *d* orbitals with cylindrical symmetry can be formed in a set of five *d* orbitals, and that each of these three is equivalent to the function d_{z^2} (see Table 1), except in orientation.

The conventional set of five *d* orbitals, given in Table 1, is chosen such that the symmetry elements of the orthorhombic point group (the minimum symmetry of a general *d* orbital) lie along the *x*, *y*, and *z* axes.

Table 1. The Usual Set of *d* Orbitals

$$d_{z^2} = \frac{\sqrt{5}}{2}(3\cos^2\theta - 1)$$

$$d_{xz} = \sqrt{15}\sin\theta\cos\theta\cos\phi$$

$$d_{yz} = \sqrt{15}\sin\theta\cos\theta\sin\phi$$

$$d_{x^2-y^2} = \frac{\sqrt{15}}{2}\sin^2\theta\cos 2\phi$$

$$d_{xy} = \frac{\sqrt{15}}{2}\sin^2\theta\sin 2\phi$$

All possible shapes of a *d* orbital can be expressed as a linear function of $d_z{}^2$ and $d_x{}^2{}_{-y}{}^2$, with the coefficient *a* ranging from 1 to $\sqrt{3/2}$

$$d = ad_{z^2} + (1 - a^2)^{1/2}d_{x^2-y^2} \quad \sqrt{3/2} = 0.866025 \leq a \leq 1$$

It is convenient to introduce the shape parameter $\xi = 4(1 - a^2)$. The function $d_z{}^2$ corresponds to $\xi = 0$ and the function $d_x{}^2{}_{-y}{}^2$ to $\xi = 1$.

Values of the general *d* function in the ±*x*, ±*y*, and ±*z* directions are shown in Figure 1 as a function of *a*. The functions in each region differ from those in the other two regions by at most a phase factor, −1, and a rotation, which serves to permute the variables *x*, *y*, and *z*.

The sets of five equivalent *d* orbitals discussed by Kimball and by Powell have symmetry axes lying along five equivalent directions in space, related by a

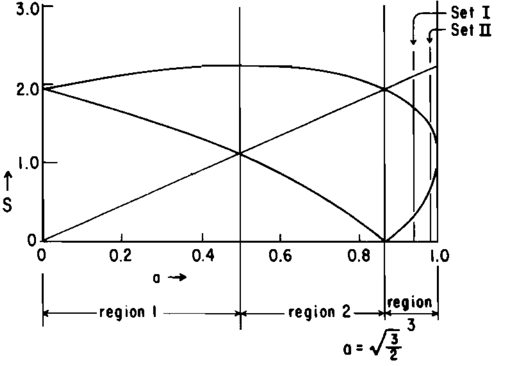

Figure 1. Diagram showing the values of *d* orbitals in the directions of the three principal axes, as a function of the shape parameter *a*.

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[1] Present address: Chemistry Department, Stanford University, Stanford, California 94305.

[2] Powell, R. E., J. Chem. Educ., 45, 45 (1968).

[3] Kimball, G. E., *J. Chem. Phys.*, 8, 188 (1940).

[4] Pauling, Linus, *J. Am. Chem. Soc.*, 53, 1367 (1931).

[5] Hultgren, R., *Phys. Rev.*, 40, 891 (1932).

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Table 2. Set I of Pyramidal *d* Orbitals

$$\left.\begin{matrix} d_0(2) \\ d_{1/5}(2) \\ d_{2/5}(2) \\ d_{3/5}(2) \\ d_{4/5}(2) \end{matrix}\right] = \begin{bmatrix} -\sqrt{\frac{1}{5}} & \sqrt{\frac{2}{5}} & 0 & \sqrt{\frac{2}{5}} & 0 \\ -\sqrt{\frac{1}{5}} & \sqrt{\frac{2}{5}}\cos\frac{2\pi}{5} & -\sqrt{\frac{2}{5}}\sin\frac{2\pi}{5} & -\sqrt{\frac{2}{5}}\cos\frac{\pi}{3} & -\sqrt{\frac{2}{5}}\sin\frac{\pi}{5} \\ -\sqrt{\frac{1}{5}} & -\sqrt{\frac{2}{5}}\cos\frac{\pi}{5} & -\sqrt{\frac{2}{5}}\sin\frac{\pi}{5} & \sqrt{\frac{2}{5}}\cos\frac{2\pi}{5} & \sqrt{\frac{2}{5}}\sin\frac{2\pi}{5} \\ -\sqrt{\frac{1}{5}} & -\sqrt{\frac{2}{5}}\cos\frac{\pi}{5} & \sqrt{\frac{2}{5}}\sin\frac{\pi}{5} & \sqrt{\frac{2}{5}}\cos\frac{2\pi}{5} & -\sqrt{\frac{2}{5}}\sin\frac{2\pi}{5} \\ -\sqrt{\frac{1}{5}} & \sqrt{\frac{2}{5}}\cos\frac{2\pi}{5} & \sqrt{\frac{2}{5}}\sin\frac{2\pi}{5} & -\sqrt{\frac{2}{5}}\cos\frac{\pi}{5} & \sqrt{\frac{2}{5}}\sin\frac{\pi}{5} \end{bmatrix} \begin{matrix} d_{z^2} \\ d_{xz} \\ d_{yz} \\ d_{x^2-y^2} \\ d_{xy} \end{matrix}$$

Table 3. Set II of Pyramidal *d* Orbitals

$$\left.\begin{matrix} d_0(1) \\ d_{1/5}(1) \\ d_{2/5}(1) \\ d_{3/5}(1) \\ d_{4/5}(1) \end{matrix}\right] = \begin{bmatrix} \sqrt{\frac{1}{5}} & \sqrt{\frac{2}{5}} & 0 & \sqrt{\frac{2}{5}} & 0 \\ -\sqrt{\frac{1}{5}} & \sqrt{\frac{2}{5}}\cos\frac{2\pi}{5} & \sqrt{\frac{2}{5}}\sin\frac{2\pi}{5} & -\sqrt{\frac{2}{5}}\cos\frac{\pi}{5} & \sqrt{\frac{2}{5}}\sin\frac{\pi}{5} \\ \sqrt{\frac{1}{5}} & \sqrt{\frac{2}{5}}\cos\frac{\pi}{5} & \sqrt{\frac{2}{5}}\sin\frac{\pi}{5} & \sqrt{\frac{2}{5}}\cos\frac{2\pi}{5} & -\sqrt{\frac{2}{5}}\sin\frac{2\pi}{5} \\ \sqrt{\frac{1}{5}} & -\sqrt{\frac{2}{5}}\cos\frac{\pi}{5} & -\sqrt{\frac{2}{5}}\sin\frac{\pi}{5} & \sqrt{\frac{2}{5}}\cos\frac{2\pi}{5} & \sqrt{\frac{2}{5}}\sin\frac{2\pi}{5} \\ \sqrt{\frac{1}{5}} & \sqrt{\frac{2}{5}}\cos\frac{2\pi}{5} & -\sqrt{\frac{2}{5}}\sin\frac{2\pi}{5} & -\sqrt{\frac{2}{5}}\cos\frac{\pi}{5} & -\sqrt{\frac{2}{5}}\sin\frac{\pi}{5} \end{bmatrix} \begin{matrix} d_{z^2} \\ d_{xz} \\ d_{yz} \\ d_{x^2-y^2} \\ d_{xy} \end{matrix}$$

fivefold symmetry axis. The five directions may be described as the body diagonals of a pentagonal antiprism. The functions themselves are represented in terms of the conventional functions, normalized to 4π, in Tables 2 and 3. The values of the functions along their principal axes are given in Table 4.

It is seen that the maximum bond strength for set I (Powell's second set) is greater than that for set II (Powell's first set), and also that there is for each of the two kinds of functions great deviation from cylindrical symmetry. The values of the functions in the planes of symmetry are shown in Figures 2 and 3. Comparison with the corresponding cross sections for $d_z{}^2$ and $d_{x^2-y^2}$ shows that the functions I are qualitatively similar to $d_z{}^2$, and the functions II are more similar to $d_{x^2-y^2}$. The values for the two functions are indicated in Figure 1.

The symmetry axis with maximum strength for each function of set I is 69° 1.35′ from the fivefold axis of the pentagonal antiprism, corresponding to the ratio 0.38341 of half height to radius of the antiprism, with the corresponding values for set II of 41° 47.65′ and 1.1186.

The functions I accordingly correspond to an oblate antiprism and II to a prolate antiprism. There is a simple explanation for the difference in orientation of the principal axes. The theorem that the sum of the squares of the values of the functions for a complete set (a subshell) is constant requires that the shape parameters vary in a satisfactory way with change in orientation of the principal axes. For the prolate set (II) the maximum value in the plane orthogonal to the principal axis of the function lies in the basal plane of the antiprism, and thus serves to increase the electron

Table 4. Properties of Some *d* Orbitals

	$d_{x^2+y^2}$	Set I (Oblate)	Set II (Prolate)	d_{z^2}
S_z	0	2.1943	2.0950	2.23607
S_x	1.93649	−0.7247	−0.3706	−1.11803
S_y	−1.93649	−1.4696	−1.7244	−1.11803
a	0	0.9813	0.9369	1
ξ	1	0.1482	0.4889	0

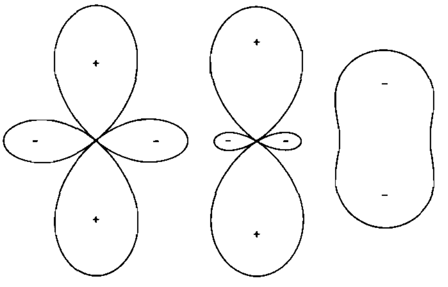


Figure 2. The principal cross sections of a *d* orbital of the oblate set of five equivalent *d* orbitals (set I).

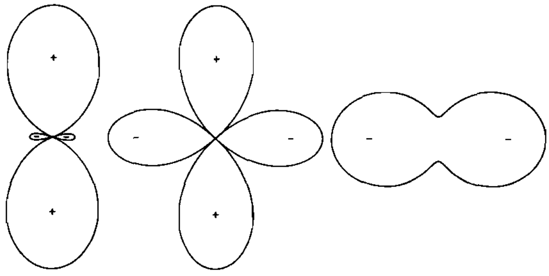


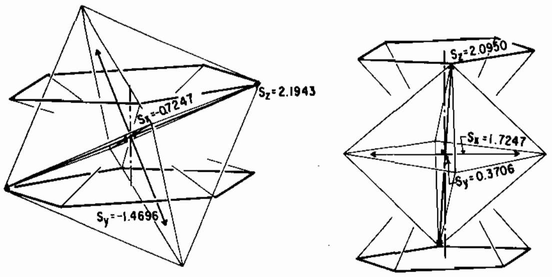
Figure 3. The principal cross sections of a *d* orbital of the prolate set of five equivalent *d* orbitals (set II).

density in the equatorial region. For the oblate set (I) the electron density in the equatorial region is larger because of the larger contribution of the principal lobes of the function. The maximum value of the function in the plane perpendicular to the principal symmetry axis of the function for this set extends more in the direction of the fivefold axis of the antiprism, and thus serves to fill in this region (see Fig. 4).

Our attention was attracted to the considerable deviation from axial symmetry of the Powell orbital through our application of a theorem about the values of the function along the principal axes. This theorem is that for any d orbital the sum of the squares of the values along the six principal directions is equal to 15. (In our discussion all functions are normalized to 4π.) This theorem is proved in the following way. Hultgren[5] has shown that the most general d orbital, D, can be written as a linear combination of d_{z^2} and $d_{x^2-y^2}$

$$D = a_1 d_{z^2} + a_2 d_{x^2-y^2}$$

with $a_1^2 + a_2^2 = 1$. In our evaluation of the function $D^2(x, y, z)$ in the $\pm x$, $\pm y$, and $\pm z$ directions the terms involving products of variables will vanish, because of the orthorhombic symmetry $m\ m\ m$, and may be omitted. The use of braces, { }, indicates that this has been done.



OBLATE SET I

PROLATE SET II

Figure 4. The oblate and prolate pentagonol antiprisms, the axes of which give the direction of the principal axes of the two sets of five equivalent d orbitals.

$$\{D^2\} = \frac{15}{4r^4}\left[\frac{a_1^2}{3}(9z^4 - 6r^2z^2 + r^4) + a_2^2(x^4 + y^4) - \frac{a_1 a_2}{\sqrt{3}} r^2(x^2 - y^2)\right]$$

$$\{2D^2(x, 0, 0) + 2D^2(0, y, 0) + 2D^2(0, 0, z)\}$$
$$= \left[\frac{(2)(15)}{3} + \frac{15}{3}\right] a_1^2 + 15a_2^2$$
$$= 15(a_1^2 + a_2^2) = 15$$

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Chemistry

Bond angles in transition-metal tricarbonyl compounds: A test of the theory of hybrid bond orbitals*

(enneacovalence/cobalt tricarbonyls/iron tricarbonyls/manganese tricarbonyls/chromium tricarbonyls)

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ABSTRACT The theory of hybrid bond orbitals is used to calculate equations giving the value of the bond angle OC—M—CO in relation to the bond number of the metal-carbonyl bond for tricarbonyl groups in which the transition-metal atom is enneacovalent or octacovalent and the group has approximate trigonal symmetry. For cobalt and iron and their congeners the average experimental values lie within about 1° of the theoretical values for enneacovalence, which are 101.9° for $Co(CO)_3$ and 94.5° for $Fe(CO)_3$. This agreement provides strong support for the theory. For $Mn(CO)_3$ and $Cr(CO)_3$ the experimental values indicate the average covalence to be about 8.4 and 7.7, respectively, in agreement with considerations based on the electroneutrality principle.

According to the simple theory of hybrid bond orbitals, in which only the angular dependence of the orbitals is taken into account, the strongest *spd* single bonds can be formed at angles 73.15° and 133.62° (1–4). The favored angles between a double bond and a single bond or between a pair of double bonds can be found from these angles by assuming the axis of a double bond to lie midway between the axes of the two single bonds that by bending constitute the double bond. These considerations have been used in the calculation for comparison with experimental values of bond angles in some molecules, such as those involving the $Mn(CO)_5$ group and the $Co(CO)_4$ group, in which the transition-metal atom can form a single bond with another ligand, in addition to the eight bonds to the carbonyl groups (4). Many compounds of the transition metals are known in which the metal atom is attached to three carbonyl groups and forms between three and six bonds with other ligands, the bond number of the metal-carbonyl bonds decreasing from 2 to 1, with 2 corresponding to the structure M =C=O: and 1 to the structure M^-—C≡O:$^+$. The existence of a large number of experimental values of tricarbonyl bond angles permits a significant test to be made of the theory of hybrid *spd* bond orbitals.

Calculation of tricarbonyl bond angles

There is no way of arranging nine bonds about an atom such that all bond angles equal 73.15° or 133.62°. There are three arrangements that approximate this goal, the McClure arrangement (3, 5), the tetragonal antiprism with cap (3), and the trigonal prism with three lateral caps (3). For these structures the smaller bond angles usually lie in the range from 67° to 80° and the larger in the range from 120° to 140°. The prediction of bond angles is made somewhat uncertain because of this effect of the geometry of space. In the following discussion, except where noted, the axes of the bond orbitals are placed at the angle 73.15° with one another.

I consider groups $M(CO)_3$ with a threefold axis. Three single bonds can be formed with bond angles all equal to 73.15°. In the three best arrangements of nine bonds the coordination polyhedrons have nearly equilateral triangles as most of their faces, and for these triangular faces, which would be appropriate to the $M(CO)_3$ group, the average bond angle is 72.2°. The difference between this value and the ideal value 73.15° suggests that the predicted values are uncertain by a degree or two.

To make a calculation for three double bonds we need three more orbitals. These may be the three equatorial bonds of the trigonal prism with three caps; that is, with $\theta = 90°$ and $\phi = 60°$, 180°, and 300° (the three other orbitals have $\theta = 43.47°$ and $\phi = 0°$, 120°, and 240°). The axis for each of the three double bonds is placed midway between an equatorial orbital and one of the other orbitals. The double-bond axes lie at $\theta = 63.73°$, which corresponds to 101.85° for the bond angle for doubly bonded carbonyls in the $M(CO)_3$ group (bond number $n = 2$).

There is some uncertainty in the calculation of the bond angle for resonance of two single bonds and one double bond among the three positions ($n = 1.33$) or of one single bond and two double bonds ($n = 1.67$). For $n = 1.5$, however, there is no uncertainty; symmetry requirements fix the bond angle at 90°. The three calculated points are shown in Fig. 1, together with a curve through them. This curve is given by the equation:

$$\text{Tricarbonyl bond angle } (v = 9) = 73.15° + 38.7°(n - 1) - 10°(n - 1)^2 \quad [1]$$

in which v is covalence.

For octacovalence a different equation is needed. From symmetry considerations we see that the OC—M—CO bond angle for $M(CO)_3$ with three double bonds is the tetrahedral angle 109.47°. The upper curve in Fig. 1 has been drawn as a straight line passing through the points for $n = 1$ and $n = 2$:

$$\text{Tricarbonyl bond angle } (v = 8) = 73.15° + 36.3°(n - 1). \quad [2]$$

The cobalt tricarbonyl group

The neutral cobalt atom has nine electrons in its valence shell and accordingly can form nine single bonds, with use of the sp^3d^5 orbitals, without transfer of electrons. Its electronegativity, 1.9, permits the formation of bonds with elements with electronegativity as great as 2.5 without violating the principle that the charge on the atom be within one unit of zero; hence bonds with hydrogen, boron, carbon, silicon, phosphorus, sulfur, arsenic, and some other atoms must predominate. Cobalt forms a double bond with each terminal carbonyl, and in the $Co(CO)_3$

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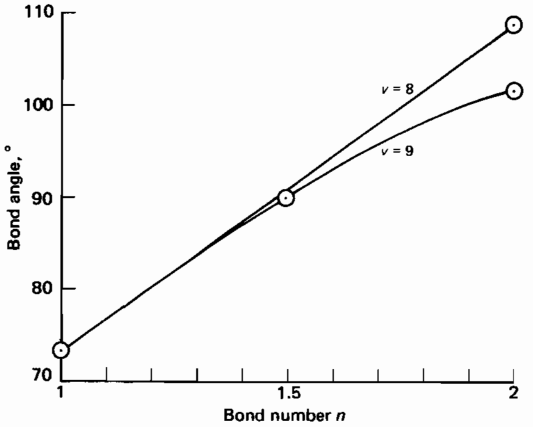

FIG. 1. Theoretical curves of OC—M—CO bond angle in $M(CO)_3$ groups with approximate trigonal symmetry, with transition metal M enneacovalent ($v = 9$) or octacovalent ($v = 8$), as functions of the bond number n from $n = 1$ (single bond from metal to carbonyl) to $n = 2$ (double bond).

group it forms three bonds with other atoms. For example, in $\{(OC)_3Co\}_3C—C\{Co(CO)_3\}_3$ there are two Co_3C tetrahedra connected by the C—C bond, and each cobalt atom forms two single bonds (length 245.7 pm) with other cobalt atoms and one (length 196 pm) with a carbon atom (6). Observed values of the average OC—Co—CO bond angles in molecules in which the cobalt atom forms three single bonds with other atoms are given in Table 1. The average value is 101.0°, with mean deviation 1.1°. The agreement with 101.9° is accordingly good.

It is not required by the theory that each of the angles be close to 101.9°, but rather only that the average for the three have this value. The smallest calculated value for the angle between two double bonds is 87.1°, corresponding to four orbitals directed toward the corners of a 73.15° rhomb. The value for a 73.15° square is 90°. Observed individual values for the $Co(CO)_3$ group lie between 93° and 110°.

The iron tricarbonyl group

With eight outer electrons in the formally neutral atom, iron needs to acquire an electron to achieve covalence. Often the ninth electron is obtained from a carbonyl group forming a dative single covalent bond, $Fe^-—CO^+$. The $Fe(CO)_3$ group then involves five of the nine bonds formed by the iron atom, the bond number of the iron-carbonyl bonds being 1.67, and the iron atom forms four other bonds. If the added electron comes from some other source, such as a quadricovalent nitrogen atom, the iron-carbonyl bonds are double bonds and the iron atom of the tricarbonyl iron group forms only three other bonds.

Table 1. Values of OC—Co—CO bond angles in the cobalt tricarbonyl group

Compound [R = $Co(CO)_3$]	Average angle, °	Ref.
$C_5H_5(CO)Fe(CO)_2R$	102.5	7
$C_9H_7(CO)Fe(CO)_2R$	101.8	8
$C_7H_8(CO)Co(CO)_2R$	102.5	9
$R_3C—CR_3$	98.5	6
$R_3C—C_2(R_2)—C{\equiv}C—CR_3$	99.9, 100.1	10, 11
$R_3C—C{\equiv}C—CR_3$	99.8	12
$C_6F_6R_2$	100.5	13
R_3CCH_3	100.5	14
$R_3(CO)BH_2N(C_2H_5)_3$	103.0	15
Average	101.0	

Table 2. Values of OC—Fe—CO bond angles in the iron tricarbonyl group

Compound [R = $Fe(CO)_3$]	Average angle, °	Ref.
$C_{10}H_{12}R_2$	93.6	16
$(C_{12}H_{12}O)R_2$	95.2	17
$C_7H_8R_2$	95.0	18
$C_8H_{10}R_2$	95.2	19
$(C_9H_{12}O)R_2$	94.2	20
C_6F_8R	95.1	21
CR_5	94.3	22
C_4H_4R	95.5	23
$(C_6H_5)_2C_2R_3$	95.0	24
36 others, average	95.8	
Average for 45 compounds	95.6	

The transfer of an electron to the iron atom is compatible with the electroneutrality principle. The electronegativity of iron is 1.8, leading to 12% ionic character of the iron-carbon bonds and to the satisfactory value +0.04 for the resultant charge on an iron atom that has accepted an electron and is forming nine bonds with carbon atoms.

With one dative bond from carbonyl and $n = 1.67$, the average bond angle for $Fe(CO)_3$ is predicted from Eq. 1 to have the value 94.5°. Most of the numerous experimental values lie within about 2° of this value, and their average, 95.6°, with mean deviation 1.2° (Table 2), is in acceptable agreement with it.

The manganese tricarbonyl group

Enneacovalence of manganese is achieved by the transfer of two electrons to the manganese atom. For the manganese tricarbonyl group this transfer can result from two dative single bonds and one double bond to carbonyl groups, leaving the manganese atom with electrons and orbitals for forming five single bonds with other atoms. An example is cyclopentadienyltricarbonyl manganese (25), which in this approximation is described as having single bonds to each of the five carbon atoms of the ring. It is necessary, however, to consider whether or not the formal transfer of two electrons to the manganese atom is compatible with the electroneutrality principle. The electronegativity of manganese in compounds such as $MnCl_2$ has been reported to be 1.5. It is likely, however, that for enneacovalent or octacovalent manganese the correct value is about 1.7, obtained by interpolation between neighboring elements. With this value the Mn—C bonds have 15% ionic character, which leads to charges −0.65, +0.20, and +1.05, respectively, on the manganese atom with 9, 8, and 7 bonds to carbon atoms. These three structures are accordingly allowed, with the second one favored. They permit the $Mn(CO)_3$ group to form bonds with 5, 3, and 1 of the carbon atoms of the cyclopentadienyl ring, respectively.

The stability of a structure increases with increase in the number of bonds. This effect favors the structure with $v = 9$, and probably overcomes its less satisfactory agreement with electroneutrality (charge −0.65) and makes it roughly equivalent to the structure $v = 8$. (The structure with $v = 7$ may be ignored as unfavorable in having both a smaller number of bonds and a large charge.) The experimental value (Table 3) of the OC—Mn—CO angle for compounds in which the

Table 3. Values of OC—Mn—CO bond angles in the manganese tricarbonyl group

Compound [R = $Mn(CO)_3$]	Average angle, °	Ref.
C_5H_5R	92.0	25
C_6H_7R	92.8	26
$C_{10}H_8R_2$	92.2	27
Average	92.3	

manganese atom forms bonds with five carbon atoms is 92.3°, which corresponds to bond number $n = 1.55$ for the manganese–carbonyl bonds, and hence to resonance between the structures with $v = 9$ and 8 in the ratio 33% to 67%.

There is also some contribution of structures in which two M—C bonds are broken, with formation of a ring double bond and an unshared electron pair on the metal atom, with no electron transfer. These structures increase the bond number of the carbon–carbon bonds and decrease that of the metal–carbon bonds.

The chromium tricarbonyl group

Chromium in the chromium tricarbonyl group can be made enneacovalent by three dative carbonyl single bonds. It can then form single bonds with six other atoms, such as the six carbon atoms of the benzene ring in benzenechromium tricarbonyl (28). With electronegativity 1.6 for chromium, the calculated charges on the chromium atom for $v = 9$, 8, 7, and 6 are −1.38, −0.56, +0.26, and +1.08, respectively. They would be −1.02, −0.24, +0.54, and +1.32 if the electronegativity were 1.5, which is possible because of uncertainty in the value. The average observed value of the OC—Cr—CO bond angle is 88.5°, with mean deviation 0.9° (Table 4). This value corresponds to bond number 1.43 for the chromium–carbonyl bonds, and hence indicates that the structure with $v = 8$ contributes about 70% and that with $v = 7$ about 30% to the normal states of these molecules.

Tricarbonyls of the heavier transition metals

The observed values of the bond angles of the carbonyls of the heavier transition metals in general agree with the values discussed in the preceding sections. For example, the group $Ir(CO)_3$, in the compound $Ir_2Co_2(CO)_{12}$ (36), in which the iridium atom forms three double bonds with carbonyl groups and three single bonds with two cobalt atoms and one iridium atom, has the average value 100° for the OC—Ir—CO bond angle, in satisfactory agreement with the theoretical value 101.9° and the average observed value for OC—Co—CO, 101.0°. For $Ru(CO)_3$ and $Os(CO)_3$ the expected value of about 94.5° is close to the observed values; examples are 94.7° for cyclooctatetraenedirutheniumhexacarbonyl (37), 94.8° for 1,2,3,6-*tetrahapto*-5-cyanocyclooctadienylrutheniumtricarbonyl (38), 92.2° for bis-(μ-acetato)diosmiumhexacarbonyl (39), and 94.3° for di-μ-cyclononaallyldiosmiumhexacarbonyl (40). For $Tc(CO)_3$ and $Re(CO)_3$ the expected value is about 92.3° (Table 3); an observed value is 91.1° for trimethylsilyl-π-cyclopentadienylrheniumtricarbonyl (41). The expected value for $Mo(CO)_3$ and $W(CO)_3$ is about 88.5° (Table 4). Representative observed values are 86.6° for guaiazulenedimolybdenumhexacarbonyl (42), 88.5° for trimethylbenzenemolybdenumtricarbonyl (43), and 87.0° for hexamethylbenzenemolybdenumtricarbonyl (43).

Table 4. Values of OC—Cr—CO bond angles in the chromium tricarbonyl group

Compound [R = $Cr(CO)_3$]	Average angle, °	Ref.
C_6H_6R	89.6	28
$C_6(CH_3)_6R$	88.0	29
$C_{12}H_{10}R_2$	88.3	30
$C_{10}H_8R$	89.3	31
$C_{14}H_{10}R$	89.2	32
$C_{14}H_{10}R$	88.3	33
$C_6H_5COOCH_3R$	88.3	34
$C_6H_5OCH_3R$	89.3	35
10 others, average	88.2	
Average for 18 compounds	88.5	

Ligands other than carbonyl

The foregoing considerations apply also to other ligands, such as the phosphines, that can form either a dative single bond or a non-dative double bond with a transition-metal atom. An example is π-cyclopentadienyldicarbonyltriphenylphosphinemanganese (44), in which the manganese atom forms five single bonds with the carbon atoms of the ring and other bonds with the two carbonyl groups and the phosphine group. The observed bond angles OC—Mn—CO = 92.4° and OC—Mn—$P(C_6H_5)_3$ = 92.7° and 90.5° have an average of 91.9°, in good agreement with the average for the $Mn(CO)_3$ group, 92.3° (Table 3). The approximate equality of the OC—Mn—CO angle and the two OC—Mn—$P(C_6H_5)_3$ angles indicates approximate equality of carbonyl and phosphine in the ratio of the tendency to form a dative single bond and a non-dative double bond.

Conclusion

The excellent agreement between the observed bond angles for the groups $Co(CO)_3$ and $Fe(CO)_3$ with approximate trigonal symmetry and other bonds (three and four, respectively) to carbon atoms with the values derived from the theory of sp^3d^5 enneacovalence provides strong support for this theory. For $Mn(CO)_3$ and $Cr(CO)_3$ the number of additional bonds, five and six, respectively, agrees with enneacovalence, but the observed bond angles indicate that octacovalent and heptacovalent structures also are important, reducing the average covalence to about 8.4 for manganese and 7.7 for chromium. These values are compatible with the requirements of the principle of electroneutrality.

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Reprinted from *The Nature of the Chemical Bond and the Structure of Molecules and Crystals: An Introduction to Modern Structural Chemistry, 1st edn.*, by Linus Pauling, Cornell University Press, Ithaca, NY, Chapter 12, pp. 403–411 (1939).

CHAPTER XII

A SUMMARIZING DISCUSSION OF RESONANCE AND ITS SIGNIFICANCE FOR CHEMISTRY

56. THE NATURE OF RESONANCE

Now that we have considered some of the ways in which the idea of resonance has brought clarity and unity into modern structural chemistry, has led to the solution of many problems of valence theory, and has assisted in the correlation of the chemical properties of substances with the information obtained about the structure of their molecules by physical methods, we may well inquire again into the nature of the phenomenon of resonance.[1]

The goal of the structural investigation of a system is the description of the system in terms of simpler entities. This description may be divided into two parts, the first relating to the material particles or bodies of which the system is considered to be composed, and the second to the ways in which these particles or bodies are interrelated; that is, to their interactions and interconnections. In describing a system it is usually convenient to resolve it first into the next simpler parts, rather than into its ultimate constituents, and then to carry the resolution farther and farther in steps. We are thoroughly accustomed to this way of describing the material constitution of substances. The use of the concept of resonance permits the extension of the procedure to include the discussion not only of the next simpler constituent bodies but also of their interactions. Thus the material description of the benzene molecule as containing carbon and hydrogen atoms, which themselves contain electrons and nuclei, is amplified with use of the resonance concept in the following way: the structure of the normal benzene molecule corresponds to resonance

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[1] An interesting discussion of resonance is given in the introduction of "The Organic Chemistry of Nitrogen," N. V. Sidgwick, T. W. J. Taylor, and W. Baker, Oxford, **1937**. The concept of resonance is extensively used in this book, which gives a modern and thorough treatment of an important branch of organic chemistry.

between the two Kekulé structures, with smaller contributions by other valence-bond structures, and the molecule is stabilized and its other properties are changed somewhat by this resonance from those expected for either Kekulé structure alone; each Kekulé structure consists of a certain distribution of single and double bonds, with essentially the properties associated with these bonds in other molecules; each bond represents a type of interaction between atoms which can be discussed in terms of the resonance between structures differing in the interchange of electrons between atomic orbitals.

It was pointed out in Chapter I that the selection of the primary structures for the discussion of any particular case of quantum-mechanical resonance is arbitrary, but that this arbitrariness (which has an analogue in the classical resonance phenomenon) does not impair the value of the concept of resonance.

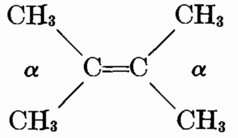
57. THE RELATION BETWEEN RESONANCE AND TAUTOMERISM

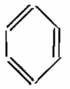
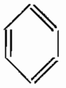
There is no sharp distinction which can be made between tautomerism and resonance; but it is convenient in practice to make a distinction between the two which is applicable to all except the border-line cases.

Tautomers are defined as isomers which are readily interconvertible. It is clear that the distinction between tautomerism and ordinary isomerism is very vague indeed, and that it depends on the interpretation of the adverb "readily." It is customary to designate as tautomers those isomers whose half-lives (with respect to interconversion) are under ordinary circumstances less than the times required for laboratory operations to be carried out (some minutes or hours), so that the separation of the isomers from the equilibrium mixtures is difficult. The distinction between tautomers and ordinary isomers has no molecular significance whatever, since it is dependent on the accidental ordinary rate of human activity.

It is possible, on the other hand, to define tautomerism and electronic resonance in a way which gives structural significance to them individually.

Let us consider as a definite example a benzene molecule, which may have different substituent groups in the 1, 2, · · · , 6 positions. The nuclei of the molecule vibrate relative to one another in a way which is determined by the electronic energy function for nuclear configurations.[1] For most molecules this electronic energy function is such that there is one most stable nuclear configuration, about which the nuclei carry out small vibrations, with amplitudes of about 0.1 Å. If the molecule can be assigned a single valence-bond structure, the nature of this equilibrium configuration can be predicted by the rules of stereochemistry. Thus for tetramethylethylene the expected configuration is



with the angle α equal to about 110° (close to the tetrahedral angle 109°28′). This has been verified experimentally. In benzene, however, there is resonance between the two valence-bond structures  (I) and  (II). This resonance is so rapid that its frequency (the resonance energy divided by Planck's constant *h*) is a thousand-fold greater than the frequency of nuclear vibration, so that resonance between the Kekulé structures occurs in the time required for the nuclei to move an inappreciable distance (0.0001 Å). Hence the effective electronic energy function determining the nuclear configuration is not that for either Kekulé structure, but instead that corresponding to the Kekulé resonance. Since the predicted stable configurations for the two Kekulé structures do not differ greatly, there is an intermediate configuration which is the stable equilibrium configuration for the actual resonating molecule. This is the hexagonal coplanar configuration with 120° bond angles.

Now the magnitude of the resonance integral, which determines the resonance energy and the resonance frequency, depends on the nature of the structures involved. In benzene it is large (about 36 kcal./mole); but it might have been much smaller. Let us consider what the benzene molecule would be like if the value of the resonance integral were very small, so that the resonance frequency were less than the frequency of nuclear

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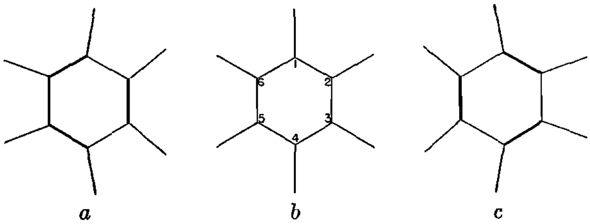
[1] "Introduction to Quantum Mechanics," Chap. X.

oscillation. For each nuclear configuration there would be more or less electronic resonance of the Kekulé type. We may discuss three nuclear configurations, *a*, *b*, and *c*.



In *a* and *c* the bond angles to the substituent groups approach 110° and 125° in alternate pairs, corresponding to the tetrahedral model for alternating single and double bonds in the ring, and in *b* the bond angles are all 120°. Now for configuration *a* the valence-bond structure I is stable, whereas structure II is unstable because of the strain involved in the bond angles. Since the resonance integral is assumed to be small in value, this energy difference would cause structure II to be unimportant. The normal electronic state of the molecule would be represented for this nuclear configuration essentially by Kekulé structure I alone, with only a negligible amount of resonance with structure II.

Similarly for configuration *c* structure II alone would be of significance.

The intermediate configuration *b* would involve complete resonance between I and II. Since the resonance energy is assumed to be very small, and this configuration corresponds to bond-angle strain for both I and II, the configuration would be less stable than *a* or *c*.

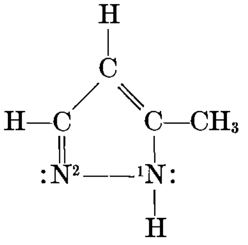
This hypothetical benzene molecule would accordingly oscillate for some time about the configuration *a*, with essentially the valence-bond structure I; it might then pass through the configuration *b*, with resonance to structure II becoming complete, and then oscillate for some time about configuration *c*, with essentially the valence-bond structure II.

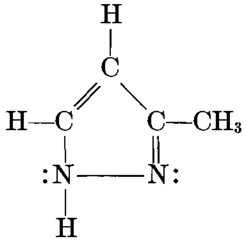
The chemical properties of this hypothetical benzene would be just those expected for the valence-bond structures I and II, and, indeed, the substance would be correctly described as a mixture of these two isomers or tautomers.

It is evident that we may define tautomerism and resonance in the following reasonable way: *When the magnitudes of the electronic resonance integral (or integrals) and of the other factors* *determining the electronic energy function of a molecule are such that there are two or more well-defined stable nuclear equilibrium configurations, we refer to the molecule as capable of existing in tautomeric forms; when there is only one well-defined stable nuclear equilibrium configuration, and the electronic state is not satisfactorily represented by a single valence-bond structure, we refer to the molecule as a resonating molecule.*

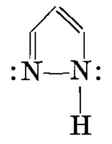
This may be expressed somewhat more loosely by saying that, whereas a tautomeric substance is a mixture of two types of molecules, differing in configuration, in general the molecules of a substance showing electronic resonance are all alike in configuration and structure.

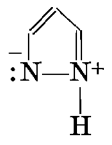
Each of the tautomeric forms of a substance may show electronic resonance; tautomerism and resonance are not mutually exclusive. Let us discuss 5-methylpyrazole as an example. This substance exists in two tautomeric forms, A and B, differing in the position of the N-hydrogen atom.

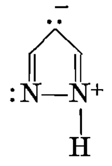

A


B

Each of these tautomers in its normal state is represented not by the conventional valence-bond structure shown above, but by a resonance hybrid of this structure and others. For tautomer A, with the hydrogen atom attached to the nitrogen atom 1, the principal resonance is between structures A I and A II, with A I the more important; smaller contributions are made also by other structures such as A III. Similar resonance occurs for tautomer B. Thus for both tautomers the principal resonance

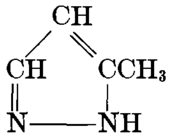
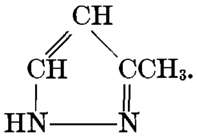

A I


A II


A III

is between valence-bond structures I  and II 

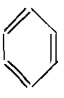
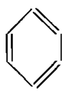
with I the more important for A and II for B; but it is not correct (according to our conventional nomenclature regarding electronic resonance) to say that methylpyrazole resonates between the structures

 and 

58. THE REALITY OF THE CONSTITUENT STRUCTURES OF A RESONATING SYSTEM

It is often asked whether or not the constituent structures of a resonating system, such as the Kekulé structures for the benzene molecule, are to be considered as having reality. There is one sense in which this question may be answered in the affirmative; but the answer is definitely negative if the usual chemical significance is attributed to the structures. *A substance showing resonance between two or more valence-bond structures does not contain molecules with the configurations and properties usually associated with these structures.* The constituent structures of the resonance hybrid do not have reality in this sense.

The question may also be discussed in a different way. The stable equilibrium configuration of the nuclei of a benzene molecule is not that appropriate to either of the two Kekulé structures, but is the intermediate hexagonal configuration. The valence-bond structures I and II are hence to be interpreted as being

 I  II

somewhat different from those for non-resonating molecules; they mean that the electronic motion is that corresponding to alternating single and double bonds, but with the equilibrium internuclear distances constant (1.39 Å), rather than alternating between 1.54 Å and 1.34 Å. The electronic wave function for the normal benzene molecule can be composed of terms corresponding to the Kekulé structures I and II, plus some additional terms; hence, according to the fundamental ideas of quantum mechanics, *if it were possible to carry out an experimental test of the electronic structure which would identify structure I or structure II, each structure would be found for the molecule to the extent determined by the wave function.* The difficulty for benzene and for other molecules showing electronic resonance is to devise an experimental test which could be carried out quickly enough and which would distinguish among the structures under discussion. In benzene the frequency of Kekulé resonance is only a little less than the frequency of the bonding resonance of electron pairs, so that the time required for the experiment is closely limited.

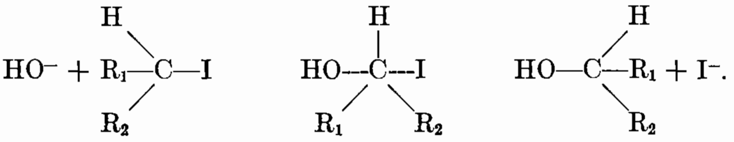
Most methods of testing bond type involve the motion of nuclei. The chemical method, such as substitution at positions adjacent to a hydroxyl group in testing for double-bond character, as used in the Mills-Nixon studies, is one of these. This method gives only the resultant bond type over the period required for the reaction to take place. Since this period is much longer than that of ordinary electronic resonance, the chemical method cannot be used in general to test for the constituent structures of a resonating molecule. Only in case that the resonance frequency is very small (less than the frequencies of nuclear vibration) can the usual methods be applied to test for the constituent structures; and in this case the boundary between resonance and tautomerism is approached or passed.

59. THE FUTURE DEVELOPMENT AND APPLICATION OF THE CONCEPT OF RESONANCE

When we compare our present knowledge of structural chemistry with that of ten years ago and become cognizant of the extent to which clarity has been brought into this field of knowledge by the extensive application of the concept of resonance we are tempted to speculate about the future development of this concept and the nature of the further applications of it which may be made.

The applications of the idea of resonance which have been made during the last decade are in the main qualitative in nature. This represents only the first step, which should be followed by more refined treatments with quantitative significance. Some rough quantitative considerations, such as those regarding interatomic distances, the partial ionic character of bonds, and the energy of resonance of molecules among several valence-bond structures, have been described in the preceding chapters of this book; these, however, deal with only small portions of the broad field of structural chemistry. The ultimate goal, a theory permitting the quantitative prediction of the structure and properties of molecules, is still very far away.

In this book the discussion has been restricted to the structure of the normal states of molecules, with little reference to the great part of chemistry dealing with the mechanisms and rates of chemical reactions. It seems probable that the concept of resonance can be applied very effectively in this field. The "activated complexes" which represent intermediate stages in chemical reactions are, almost without exception, unstable molecules which resonate among several valence-bond structures. Thus, according to the theory of Lewis, Olson, and Polanyi, Walden inversion occurs in the hydrolysis of an alkyl halide by the following mechanism:



The activated complex can be described as involving resonance of the fourth bond of carbon between the hydroxyl and iodine ions. Some very interesting rough quantum-mechanical calculations bearing on the theory of chemical reactions have been made of Eyring and Polanyi and their collaborators. It is to be hoped that the quantitative treatments can be made more precise and more reliable; but before this can be done effectively there must take place the extensive development of the qualitative theory of chemical reactions, probably in terms of resonance.

So far only a start has been made (mainly by G. E. K. Branch and G. Schwarzenbach) on the problem of correlating the acidity or basicity of a substance with its resonating electronic structure. It should be possible to develop the theory of molecular structure to such an extent as to permit the reliable prediction of the behavior of substances with respect to this property and other physical and chemical properties.

The color of organic dyes is obviously closely connected with resonance.[1] Recent experimental work, especially that of Schwarzenbach and Michaelis, shows more and more clearly how close this connection is; and, although there exists now no real theory of color, we may look forward to seeing the development of one on the basis of resonance, probably during the next decade.

Among the most interesting problems of science are those of the structure and properties of substances of biological importance. I have little doubt that in this field resonance and the hydrogen bond are of great significance, and that these two structural features will be found to play an important part in such physiological phenomena as the contraction of muscle and the transmission of impulses along nerves and in the brain. A conjugated system provides the only way of transmitting an effect from one end to another of a long molecule; and the hydrogen bond is the only strong and directed intermolecular interaction which can come into operation quickly. It will be many years before our understanding of molecular structure becomes great enough to encompass in detail such substances as the proteins, with highly specific properties (such as those shown by antibodies) which must be attributed to their possession of well-defined and complex molecular structures; but the attack on these substances by the methods of modern structural chemistry can be begun now, and it is my belief that this attack will ultimately be successful.

[1] C. R. Bury, *J.A.C.S.* 57, 2115 (1935); L. Pauling, Chapter 22 of Gilman's "Organic Chemistry," John Wiley and Sons, New York, 1938.

Chapter 2

IONIC BONDING, PARTIAL IONIC CHARACTER, AND ELECTRONEGATIVITY

Contents

[Reprint from the Journal of the American Chemical Society, 49, 765 (1927).]

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

THE SIZES OF IONS AND THE STRUCTURE OF IONIC CRYSTALS

BY LINUS PAULING[1]

RECEIVED JANUARY 25, 1927 PUBLISHED MARCH 9, 1927

The Wave-Mechanics Picture of the Atom

In recent years the old quantum theory, associated principally with the names of Bohr and Sommerfeld, encountered a large number of difficulties, all of which vanished before the new quantum mechanics of Heisenberg.[2] Because of its abstruse and difficultly interpretable mathematical foundation, Heisenberg's quantum mechanics cannot be easily applied to the relatively complicated problems of the structures and properties of many-electron atoms and of molecules; in particular is this true for chemical problems, which usually do not permit simple dynamical formulation in terms of nuclei and electrons, but instead require to be treated with the aid of atomic and molecular models. Accordingly, it is especially gratifying that Schrödinger's interpretation of his wave mechanics[3] provides a simple and satisfactory atomic model, more closely related to the chemist's atom than to that of the old quantum theory.

In Schrödinger's wave mechanics (which has been shown[4] to be mathematically identical with Heisenberg's quantum mechanics), a conservative Newtonian dynamical system is represented by a wave function or amplitude function ψ, which satisfies the partial differential equation

$$\Delta^2\psi + (8\pi^2/h^2)(W - V)\psi = 0 \tag{1}$$

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[1] Fellow of the John Simon Guggenheim Memorial Foundation.

[2] Heisenberg, *Z. Physik*, **33**, 879 (1925). Born and Jordan, *ibid.*, **34**, 858 (1925). Born, Heisenberg and Jordan, *ibid.*, **35**, 557 (1926); etc. Heisenberg based his theory on the thesis that it should not contain reference to quantities which are in principle unobservable. It is of interest that G. N. Lewis, in 1923, suggested this idea, writing.... "we should look for no effects which depend upon the momentary position of any electron in its orbit" ("Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., New York, **1923**, p. 52).

[3] Schrödinger, *Ann. Physik*, **79**, 361, 489; **80**, 437; **81**, 109 (1926); *Phys. Rev.*, **28**, 1049 (1926).

[4] Schrödinger, *Ann. Physik*, **79**, 734 (1926). Eckart, *Phys. Rev.*, **28**, 711 (1926).

In this equation W and V are the energy constant and the potential energy, respectively; the indicated partial differential operations involve coördinates whose line element is

$$ds^2 = 2Tdt^2 \tag{2}$$

in which T is the kinetic energy expressed as a function of the velocities; ψ must be continuous, single-valued, and bounded throughout the entire region traversed by the coördinates. Only certain functions (called eigenfunctions) satisfy these requirements in any given problem. In the case of the hydrogen atom these functions, Ψ_{nlm}, are known;[3,4,5] the one corresponding to the lowest quantum state is

$$\Psi_{100} = -\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \cdot \epsilon^{-\frac{\xi}{2}} \tag{3}$$

with

$$\xi = 2\frac{Z}{a_0}r \tag{4}$$

and

$$a_0 = \frac{h^2}{4\pi^2 me^2} = 0.532 \text{ Å}.$$

Schrödinger has interpreted the quantity $\psi\tilde{\psi}$ ($\tilde{\psi}$ being the conjugate complex of ψ) as giving the probability of the occurrence of the corresponding microscopic state of the system. For the hydrogen atom $\Psi\tilde{\Psi}$ accordingly gives the *electron density* about the nucleus. This may be considered as an actual stationary distribution of the individual electron throughout space, following Schrödinger, or as a time average of all the positions assumed by a point electron. The electron density ρ for the lowest quantum state of a hydrogen-like atom is, then,

$$\rho = \Psi_{100}^2 = \frac{1}{\pi}\left(\frac{Z}{a_0}\right)^3 \epsilon^{-\xi} \tag{5}$$

In Fig. 1 there are represented the eigenfunction Ψ_{100}, the electron density ρ, and the electron distribution function $D = 4\pi r^2\rho$ for the hydrogen atom as functions of r.

This model of the hydrogen atom accordingly consists of a nucleus embedded in a ball of negative electricity—the electron distributed through space. The atom is spherically symmetrical. The electron density is greatest at the nucleus, and decreases exponentially as r, the distance from the nucleus, increases. It remains finite, however, for all finite values of r, so that the atom extends to infinity; the greater part of the atom, however, is near the nucleus—within 1 or 2 Å.

A similar model for many-electron atoms has been developed,[6] by considering each electron to be hydrogen-like, but under the influence of an effective nuclear charge $(Z-S_S)e$, in which S_S is called the size-screening constant. It is found that atoms and ions containing only S electrons (with the quantum number l equal to zero) and completed sub-groups of

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[5] Waller, *Z. Physik*, **38**, 635 (1926).

[6] Pauling, paper submitted to *Proc. Roy. Soc.*

electrons are spherically symmetrical. In Fig. 2 is shown the electron distribution D as a function of r for the sodium ion and the chloride ion. The chloride ion may be described in the following words: the nucleus is embedded in a small ball of electricity, consisting of the two K electrons, with a trace of the L and M electrons; surrounding this are two concentric shells, containing essentially the eight L and the eight M electrons. In general, an atom or ion consists of the nucleus in the K electron ball, and surrounded by more or less sharply demarcated shells, one for each succeeding value of the principal quantum number n.

Since every atom extends to an unlimited distance, it is evident that no single characteristic size can be assigned to it. Instead, the apparent atomic radius will depend upon the physical property concerned, and will differ for different properties. In this paper we shall derive a set of ionic radii for use in crystals composed of ions which exert only a small deforming force on each other. The application of these radii in the interpretation of the observed crystal structures will be shown, and an attempt made to account for the formation and stability of the various structures.

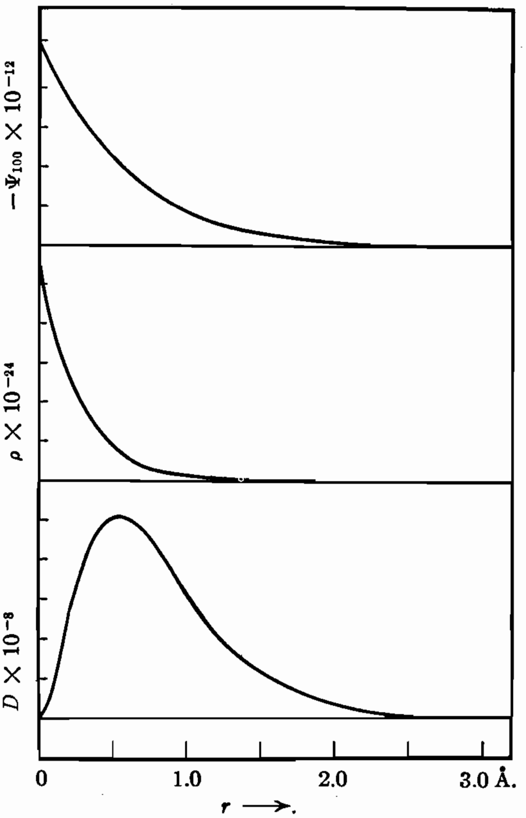

Fig. 1.—The eigenfunction Ψ_{100}, the electron density $\rho = \Psi_{100}^2$, and the electron distribution function $D = 4\pi r^2\rho$ for the lowest state of the hydrogen atom, as functions of r.

The Forces in Crystals

Hitherto it has been generally assumed that the repulsive forces between atoms arise from the interaction of the quadrupole (and higher) moments of the atoms, that is, from their departure from spherical symmetry.[7]

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[7] For example, (a) Born and Landé, *Sitzber. preuss. Akad. Wiss.*, **1918**, 1048. (b) Born, *Verh. d. Deutsch. phys. Ges.*, **20**, 230 (1918). (c) Landé, *Z. Physik*, **1**, 191 (1920); (d) **2**, 83, 87, 80 (1920). (e) Smekal, *ibid.*, **1**, 309 (1920). (f) Rella, *ibid.*, **3**,

This assumption is no longer valid; in its place the wave mechanics provides the simple explanation that the repulsive forces arise from the interpenetration of the atoms. As a simple example, we may consider the hydrogen ion and the chloride ion; according to the wave mechanics the potential energy of these two ions at a distance R apart, assuming that no deformation occurs, is[6]

$$\Phi_{\mathrm{HCl}} = -\frac{e^2}{R} + \frac{e^2}{18R}e^{-\xi}(\xi^5 + 2\xi^4 + 12\xi^3 + 48\xi^2 + 120\xi + 144) \qquad (6)$$

in which $\xi = (2/3)[(Z - S_S)/a_0]R$. The first term is the Coulomb potential energy of the two ions, and the second term arises from the penetration of the hydrogen ion in the chloride ion, and the resultant repulsion of the two similarly charged nuclei.[8]

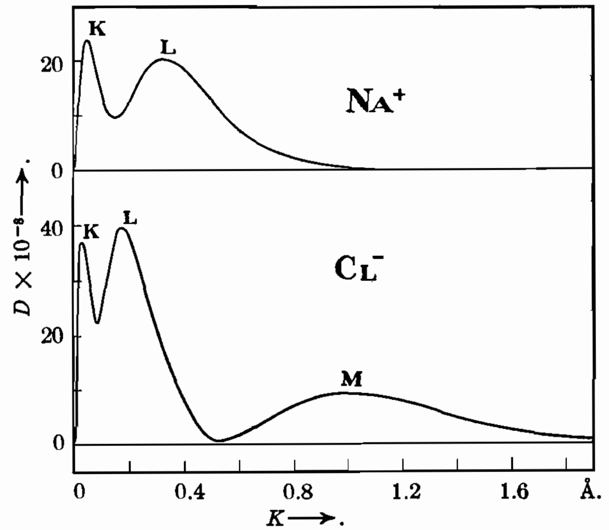

Fig. 2.—The electron distribution $D = 4\pi r^2\rho$ as a function of r for the sodium ion and the chloride ion.

157 (1920). The idea that the repulsive forces arise from the interaction of "cubical" ions (with electrons at cube corners) has been made the basis of a very extensive discussion [by Fajans and Herzfeld, *ibid.*, **2**, 309 (1920). Grimm, *Z. physik. Chem.*, **98**, 353 (1921); **101**, 403 (1922); **102**, 113, 141, 504 (1922); **119**, 254 (1926); **122**, 177 (1926); etc.] in which the sizes of these hypothetical cubes are estimated from experimental data for a large number of ions, and the attempt is made to bring these sizes into agreement with the Bohr atomic model, and to explain with them the physical properties of substances. Since, accepting the wave mechanics, we now believe that most ions are spherically symmetrical, and that the repulsive forces have an entirely different origin, no physical significance can be attributed to these cubical ion sizes. It is worthy of mention that the cubical ion sizes derived are in general about one-half of our univalent crystal radii; so that discussions involving their relative values are still valid.

[8] The expression for the potential energy of a potassium ion and a chloride ion, for example, is similar to that of Equation 6, but is still more complicated.

The potential energy of an ionic crystal (ions of valence z) may be written $\Phi = -\alpha(e^2z^2)/R + \varphi(R)$, the first term representing the Coulomb energy, and the second the potential of the repulsive forces. Equation 6 suggests a simple form for $\varphi(R)$, namely

$$\varphi(R) = \beta_m R^m e^{-\gamma R} \tag{7}$$

It has been customary, however, to use the expression

$$\varphi(R) = \beta_n R^{-n} \tag{8}$$

widely applied by Born and his co-workers. The constants β_m and γ (for a given choice of m) or β_n and n may be determined from the experimental measurements of the size of the unit of structure in crystals and of their compressibility, which provide values of $d\varphi/dR$ and $d^2\varphi/dR^2$ for $R = R_0$, the equilibrium distance. For many calculations only these two derivatives are significant, so that it is immaterial which form of $\varphi(R)$ is used; examples of such calculations will be given later. For others the value of $\varphi(R_0)$ itself is needed, which depends on the particular empirical equation used. For example, the values obtained for the crystal energy Φ by the use of Equation 8 and by the use of Equation 7 (with $m = 0$) differ by about 1%, or around 2000 cal. per mole for crystals such as sodium chloride.

The Sizes of Ions in Crystals

As a first approximation, each electron in a many-electron atom can be considered to have the distribution in space of a hydrogen-like electron under the action of the effective nuclear charge $(Z-S_S)e$, in which S_S represents the screening effect of inner electrons. In the course of a previous investigation,[6] values of S_S for a large number of ions were derived.

TABLE I

THE SIZE-SCREENING CONSTANT

Structure	Z_e	Sub-group	S_{S0}	ΔS_S
He	2	K	0.188	0
Ne	10	L_{11}	2.84	0
		L_{21} L_{22}	4.52	
Ar	18	M_{11}	9.15	0.07
		M_{21} M_{22}	10.87	
Kr	36	N_{11}	23.91	.25
		N_{21} N_2	26.83	
Xe	54	O_{11}	38.68	.49
		O_{21} O_{22}	41.80	
[Cu+]	28	M_{11}	10.9	.03
		M_{21} M_{22}	13.15	
		M_{32} M_{33}	17.7	
[Ag+]	46	N_{11}	27.9	.31
		N_{21} N_{22}	30.3	
		N_{32} N_{33}	35.1	
[Au+]	78	O_{11}	54.2	.67
		O_{21} O_{22}	57.0	
		O_{32} O_{33}	62.7	

For an ion of nuclear charge Ze, the size-screening constant for a given electron is

$$S_S = S_{S_0} + (Z - Z_0)\Delta S_S \qquad (9)$$

Values of S_{S_0}, ΔS_S and Z_0 for the outer electrons for various ionic structures are given in Table I.

The size of an atom or ion is determined by the distribution of the outermost electrons, which are for neon the L_{21} L_{22}, for argon the M_{21} M_{22}, etc. Moreover, for similar ions the electron distribution is similar, but equivalent radii are in the inverse ratio of the corresponding effective nuclear charges. With this principle we shall obtain radii for ions, which we shall define in such a way as to fulfil the following condition: the sum of the radii of two ions equals the inter-ionic distance in a normal crystal composed of these ions with the sodium chloride structure.[9] As a starting point we shall use the following experimental inter-ionic distances, for crystals with the sodium chloride structure:[10] Na^+-F^-, 2.31; K^+-Cl^-, 3.14; Rb^+-Br^-, 3.43; Cs^+-I^-, 3.85 Å. The Cs^+-I^- distance is obtained by subtracting 2.7% from the experimental distance in the crystal with the cesium chloride structure; the justification for this will be given later. In addition we shall assume for Li^+ the radius 0.60 Å., obtained later from the experimental distance in lithium oxide. From these values all of our radii will be derived. By dividing these distances between the two ions concerned, with the use of the screening constants given in Table I, the radii for the alkali ions and the halogen ions given in Table II are obtained. For other ions with similar structures radii are also calculated by assuming them inversely proportional to the effective nuclear charge. These radii, given in parentheses in Table II are, however, not to be directly applied in the consideration of inter-ionic distances in crystals, for they are the radii which the ions would have *if they were univalent;* they provide, however, a measure of the relative sizes of ions of a given structure, that is, of their extension in space. The actual crystal has the following potential energy.

$$\Phi = -\alpha (z^2e^2)/R + \beta/R^n \qquad (10)$$

For equilibrium, at $R = R_s$, we have the condition

$$(d\Phi/dR)_{R=R_s} = \alpha(z^2e^2)/R_s^2 - n\beta/R_s^{n+1} = 0 \qquad (11)$$

or

$$R_s^{n-1} = n\beta/\alpha e^2z^2$$

If the ions were univalent, but otherwise unchanged, the potential energy would be $\Phi_1 = -\alpha e^2/R + \beta/R^n$, and for equilibrium, with $R = R_1$

$$R_1^{n-1} = (n\beta)/(\alpha e^2) \qquad (12)$$

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[9] A normal crystal is one in which contact (that is, strong repulsion) occurs only between adjacent anions and cations, and in which there is only so much deformation as that shown by the alkali halides.

[10] The crystal structure data are taken from Wyckoff, "International Critical Tables," except where otherwise noted. Inter-atomic distances referred to Goldschmidt are from Goldschmidt, *Skrifter Det. Norske Videnskaps-Akad. Oslo I. Matem.-Naturvid. Klasse,* **1926,** No. 2.

TABLE II

CRYSTAL RADII AND UNIVALENT CRYSTAL RADII OF IONS

			H^- 2.08 (2.08)	He (0.93)	Li^+ 0.60 (.60)	Be^{++} 0.31 (.44)	B^{+3} 0.20 (.35)	C^{+4} 0.15 (.29)	N^{+5} 0.11 (.25)	O^{+6} 0.09 (.22)	F^{+7} 0.07 (.19)
C^{-4} 2.60 (4.14)	N^{-3} 1.71 (2.47)	$O^{=}$ 1.40 (1.76)	F^- 1.36 (1.36)	Ne (1.12)	Na^+ 0.95 (.95)	Mg^{++} 0.65 (.82)	Al^{+3} 0.50 (.72)	Si^{+4} 0.41 (.65)	P^{+5} 0.34 (.59)	S^{+6} 0.29 (.53)	Cl^{+7} 0.26 (.49)
Si^{-4} 2.71 (3.84)	P^{-3} 2.12 (2.79)	$S^{=}$ 1.84 (2.19)	Cl^- 1.81 (1.81)	Ar (1.54)	K^+ 1.33 (1.33)	Ca^{++} 0.99 (1.18)	Sc^{+3} 0.81 (1.06)	Ti^{+4} 0.68 (.96)	V^{+5} 0.59 (.88)	Cr^{+6} 0.52 (.81)	Mn^{+7} 0.46 (.75)
					Cu^+ 0.96 (.96)	Zn^{++} 0.74 (.88)	Ga^{+3} 0.62 (.81)	Ge^{+4} 0.53 (.76)	As^{+5} 0.47 (.71)	Se^{+6} 0.42 (.66)	Br^{+7} 0.39 (.62)
Ge^{-4} 2.72 (3.71)	As^{-3} 2.22 (2.85)	$Se^{=}$ 1.98 (2.32)	Br^- 1.95 (1.95)	Kr (1.69)	Rb^+ 1.48 (1.48)	Sr^{++} 1.13 (1.32)	Y^{+3} 0.93 (1.20)	Zr^{+4} 0.80 (1.09)	Nb^{+5} 0.70 (1.00)	Mo^{+6} 0.62 (.93)	
					Ag^+ 1.26 (1.26)	Cd^{++} 0.97 (1.14)	In^{+3} 0.81 (1.04)	Sn^{+4} 0.71 (.96)	Sb^{+5} 0.62 (.89)	Te^{+6} 0.56 (.82)	I^{+7} 0.50 (.77)
Sn^{-4} 2.94 (3.70)	Sb^{-3} 2.45 (2.95)	$Te^{=}$ 2.21 (2.50)	I^- 2.16 (2.16)	Xe (1.90)	Cs^+ 1.69 (1.69)	Ba^{++} 1.35 (1.53)	La^{+3} 1.15 (1.39)	Ce^{+4} 1.01 (1.27)			
					Au^+ 1.37 (1.37)	Hg^{++} 1.10 (1.25)	Tl^{+3} 0.95 (1.15)	Pb^{+4} 0.84 (1.06)	Bi^{+5} 0.74 (.98)		

From Equations 11 and 12 there is obtained

$$R_s = R_1 z^{-\frac{2}{n-1}} \qquad (13)$$

From this equation we can calculate the actual crystal radius R_s (for use in normal sodium chloride type crystals) from R_1, the univalent crystal radius. A knowledge of the repulsion exponent n is needed, however. This can be derived from the experimental measurement of the compressibility of crystals. Born[11] and Herzfeld,[12] give the values in Table III, obtained in this way.

TABLE III

THE REPULSION EXPONENT FOR CRYSTALS

Crystal	n (Born)	n (Herzfeld)	n
NaCl	7.84	9.1	8
NaBr	8.61	9.5	8.5
NaI	8.45	..	9.5
KF	..	7.9	8
KCl	8.86	9.7	9
KBr	9.78	10.0	9.5
KI	9.31	10.5	10.5
RbBr	..	10.0	10
RbI	..	11.0	11

We shall use the following values of N for ions with the structures indicated: He, 5; Ne, 7; Ar, Cu^+, 9; Kr, Ag^+, 10; Xe, Au^+, 12. Averages of these values for the two ions concerned, given in the last column of Table III, are seen to correspond satisfactorily with the experimental results. There is no experimental verification of the values of n assumed for the eighteen-shell ions. The radii calculated with these values of n from the univalent radii R_1 by means of Equation 13 are included in Table II.[13]

At first it seems that the radius of the cuprous ion would be greater than that calculated by assuming it to be similar to argon, potassium ion, etc., and using the appropriate screening constant (for M_{32} M_{33}); for there are ten M_{32} M_{33} electrons, and only six M_{21} M_{22}. However, the M_{32} M_{33} eigenfunction has its maximum nearer the nucleus than has the M_{21} M_{22} eigenfunction, and the electron density per electron is smaller in the outer part of the atom (corresponding in the old quantum theory to smaller orbital eccentricity). This effect is such that in the outer part of the atom the density of ten M_{32} M_{33} electrons is very nearly equal to that of six M_{21} M_{22} electrons. Accordingly, radii for cuprous ion and similar ions

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[11] Born, *Enz. math. Wiss.*, [V] **25**, p. 735.

[12] Herzfeld, "Handbuch der Physik," **1926**, vol. 22, p. 454.

[13] The same results would be obtained by the use of any other function for $\varphi(R)$, instead of the Born expression; for the calculation depends mainly on the first and second derivatives, which are found experimentally.

may be calculated just as though they had the argon structure, but using the M_{32} M_{33} screening constant. Similarly, the silver and the aurous ions may be treated as though they had the krypton and the xenon structure, respectively.

The radii found in this way are given in Table II, the univalent radii being also included, in parentheses. The dependence of the univalent crystal radius and the crystal radius on the atomic number is shown graphically in Fig. 3.[14] The effect of the valence in causing the crystal radius to deviate from the regular dependence on the atomic number shown by the univalent crystal radius is clearly evident.

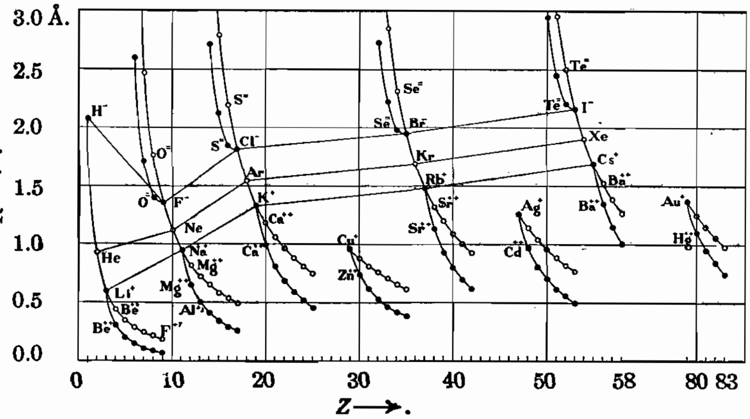

Fig. 3.—The crystal radius (solid circles) and the univalent crystal radius (open circles) for a number of ions.

In deriving theoretical values for inter-ionic distances in ionic crystals the sum of the univalent crystal radii for the two ions should be taken, and corrected by means of Equation 13, with z given a value dependent on the ratio of the Coulomb energy of the crystal to that of a univalent sodium chloride type crystal. Thus, for fluorite the sum of the univalent crystal radii of calcium ion and fluoride ion would be used, corrected by Equation 13 with z placed equal to $\sqrt{2}$, for the Coulomb energy of the fluorite crystal (per ion) is just twice that of the univalent sodium chloride structure. This procedure leads to the result 1.34 Å. (the experimental distance is 1.36 Å.). However, usually it is permissible to use the sodium chloride crystal radius for each ion, that is, to put $z = 2$ for the calcium

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[14] It is to be expected that the relative values of the univalent crystal radius would be of significance with respect to physical properties involving atomic sizes. That this is true for the viscosity of the rare gases is seen from the radii evaluated by Herzfeld (Ref. 12, p. 436) from viscosity data: He, 0.94 (0.93); Ne, 1.18 (1.12); Ar, 1.49 (1.54); Kr, 1.62 (1.69); Xe, 1.77 (1.90). (The values in parentheses are the univalent crystal radii.)

ion and $z = 1$ for the fluoride ion, without introducing a large error; the result 1.35 Å. is obtained in this way for fluorite.[15]

Comparison with Experiment

Empirical Crystal Radii.—A set of crystal radii, derived empirically by Wasastjerna[16] with the aid of mole refraction values, is at present generally accepted[17] as giving satisfactorily the "sizes" of ions in crystals. Wasastjerna's radii are given in Table IV.

TABLE IV

IONIC RADII (WASASTJERNA)

$O^=$	1.32 Å.	F^-	1.33 Å.	Na^+	1.01 Å.	Mg^{++}	0.75 Å.
$S^=$	1.69	Cl^-	1.72	K^+	1.30	Ca^{++}	1.02
		Br^-	1.92	Rb^+	1.50	Sr^{++}	1.20
		I^-	2.19	Cs^+	1.75	Ba^{++}	1.40

A method for obtaining radii for the alkali and halide ions in agreement with Wasastjerna's was given earlier by Landé,[7c] who assumed the iodide ions in lithium iodide to be in mutual contact. Wasastjerna also pointed out that in some crystals observed inter-atomic distances are explicable with his radii by assuming the anions to be in contact. Bragg and Brown[18] have shown that in a number of oxides the oxygen-oxygen distance is about 2.7 Å., in accordance with a radius of about 1.35 Å.

The radii in Table II are in reasonable agreement with Wasastjerna's, and accordingly also account satisfactorily for the empirical data.

In the past, ionic radii have often been compared with observed inter-atomic distances without much regard to the nature of the crystal from which they were derived. Recently several investigators[19] have concluded that in many crystals the bond between atoms does not consist of the electrostatic attraction of only slightly deformed ions. Goldschmidt in particular has divided crystals into two classes, ionic and atomic crystals, and has shown that ionic radii (using Wasastjerna's set) do not account for the observed inter-atomic distances in atomic crystals. In the following pages our crystal radii will be compared with the experimental dis-

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[15] The forces between ions have been discussed by Lennard-Jones and his collaborators, who have given tables showing the repulsive forces as a function of the repulsion exponent n [Lennard-Jones and Dent, *Proc. Roy. Soc.*, **112A,** 230 (1926)]. In conjunction with Wasastjerna's radii, these tables have been used in the theoretical treatment of crystals such as calcite, $CaCO_3$, which, however, we consider not to be composed of monatomic ions. Thus, they assume C^{+4} and $O^=$ to be present in calcite [Lennard-Jones and Dent, *Proc. Roy. Soc.*, **113A,** 673, 690 (1927)], although the carbonate ion is generally believed by chemists to contain shared-electron bonds.

[16] Wasastjerna, *Soc. Sci. Fenn. Comm. Phys. Math.*, **38,** 1 (1923).

[17] For a general discussion see W. L. Bragg, *Phil. Mag.*, **2,** 258 (1926).

[18] Bragg and Brown, *Proc. Roy. Soc.*, **110A,** 34 (1926).

[19] (a) Huggins, *Phys. Rev.*, **21,** 379 (1923); (b) **27,** 286 (1926). (c) Grimm and Sommerfeld, *Z. Physik*, **36,** 36 (1926). (d) Goldschmidt, Ref. 10.

tances in ionic crystals.[20] It will be shown that the theoretical radii account satisfactorily for the experimental results not only for normal crystals, but also for those deviating from additivity (through mutual contact of the anions or through the action of double repulsion), and that furthermore they permit the theoretical prediction of the relative stabilities of the fluorite and the rutile (and anatase) structure, and of the sodium chloride and the sphalerite (and wurzite) structure.

The Alkali Halides.—In Table V are given the experimental inter-atomic distances for the alkali halides with the sodium chloride structure, together with the sum of the radii of Table II.

TABLE V

ALKALI HALIDES WITH THE SODIUM CHLORIDE STRUCTURE

	Li^+, Å.	Na^+, Å.	K^+, Å.	Rb^+, Å.	Cs^+, Å.
H^-, calcd.	2.68				
obs.	2.05				
F^-, calcd.	1.96	(2.31)	2.69	2.84	3.05
obs.	2.01	2.31	2.67	2.82[a]	3.01
Cl^-, calcd.	2.41	2.76	(3.14)	3.29	
obs.	2.57	2.81	3.14	3.29	
Br^-, calcd.	2.55	2.90	3.28	(3.43)	
obs.	2.75	2.97	3.29	3.43	
I^-, calcd.	2.76	3.11	3.49	3.64	
obs.	3.00	3.23	3.53	3.66	

[a] Goldschmidt.

The agreement is satisfactory, except in the cases where there are deviations from additivity. This fact is a verification of our treatment and of the correctness of our screening constants, for the arbitrary selection of only one ionic radius in a series of salts showing additivity in inter-atomic distances is permitted, and our screening constants fixed four radii independently.

The experimental values for the lithium halides are high. This is due to two different phenomena. In the case of the chloride, bromide and iodide the *anions are in mutual contact,* that is, the repulsive forces operative are those between the anions, and the anion radius alone determines the inter-atomic distances. The geometry of the sodium chloride structure requires that, for R_{M^+}/R_{X^-} less than 0.414, the anions come into contact (considering the ions as solid spheres). This requirement is fulfilled for the chloride, bromide and iodide of lithium. In Table VI are given radii

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[20] Huggins, who has particularly emphasized the fact that different atomic radii are required for different crystals, has recently [*Phys. Rev.*, **28**, 1086 (1926)] suggested a set of atomic radii based upon his ideas of the location of electrons in crystals. These radii are essentially for use with crystals in which the atoms are bonded by the sharing of electron pairs, such as diamond, sphalerite, etc.; but he also attempts to include the undoubtedly ionic fluorite and cesium chloride structures in this category.

of these halogen ions calculated from this assumption. The agreement with the calculated radii is satisfactory.

TABLE VI
HALIDE ION RADII IN THE LITHIUM HALIDES

	Obs., Å.	Calcd., Å.
Cl^-	1.82	1.81
Br^-	1.95	1.95
I^-	2.12	2.16

In the case of lithium fluoride the ratio R_{Li^+}/R_{F^-} is 0.44. In this crystal there is *double repulsion;* the repulsive forces between anion and anion and those between anion and cation are simultaneously operative. The inter-atomic distances are determined neither by the sum of the radii for the anion and cation nor by the radius of the anion alone, but are larger than those calculated by either method. Thus the lithium-fluoride distance is 0.05 Å. (2.5%) larger than the sum of the radii, and one-half the fluorine-fluorine distance is 0.06 Å. larger than the fluoride radius.

The sodium salts also show the effect of double repulsion, the increase of the observed distances over the calculated being greatest (2.7%) for the iodide, for which R_{Na^+}/R_{I^-} is 0.44.

The large effect of deformation of the hydride ion, whose mole refraction[6] (deformability) is 25, is shown by the contraction in lithium hydride.

The alkali halides with the cesium chloride structure also show satisfactory agreement, the observed values being about 2.5% larger than the sum of the theoretical radii.

TABLE VII
INTER-ATOMIC DISTANCES FOR CESIUM CHLORIDE TYPE CRYSTALS

	Obs., Å.	Calcd., Å.
CsCl	3.56	3.50
CsBr	3.72	3.64
CsI	3.96	3.85

The Alkaline-Earth Oxides, etc.—The observed and calculated inter-atomic distances for the alkaline-earth oxides, sulfides, selenides and tellurides are given in Table VIII. Except for the magnesium com-

TABLE VIII
ALKALINE-EARTH OXIDES, ETC., WITH THE SODIUM CHLORIDE STRUCTURE

	Mg^{++}, Å.	Ca^{++}, Å.	Sr^{++}, Å.	Ba^{++}, Å.
$O^=$, calcd.	2.05	2.39	2.53	2.75
obs.	2.10	2.40	2.55	2.75
$S^=$, calcd.	2.49	2.83	2.97	3.19
obs.	2.54	2.80[a]	2.94	3.18
$Se^=$, calcd.	2.63	2.97	3.11	3.33
obs.	2.72	2.96	3.12	3.31
$Te^=$, calcd.		3.20	3.34	
obs.		ca. 3.05[a]	ca. 3.24[a]	

[a] Goldschmidt.

pounds, the agreement is excellent, and provides a remarkable verification of our entire procedure, *for the experimental data were in no way involved in the derivation of the theoretical crystal radii.* In magnesium sulfide and selenide the anions are in contact; the radii deduced on this assumption, given in Table IX, are in satisfactory agreement with those calculated.

Table IX

The Radii of the Sulfide and Selenide Ions

	Obs., Å.	Calcd., Å.
$S^{=}$ (in MgS)	1.80	1.84
$Se^{=}$ (in MgSe)	1.93	1.98

The ratio $R_{Mg^{++}}/R_{O^{=}}$ is 0.46, so that in magnesium oxide the mutual repulsion of the oxide ions is beginning to have influence, and the interatomic distance is increased by 0.05 Å. (2.5%) through the effect of double repulsion.

Other Binary Compounds.—Scandium nitride and zirconium and titanium carbide do not conform with the theoretical radii. It is possible that these crystals do not consist essentially of Sc^{+3}, N^{-3}, Ti^{+4}, Zr^{+4} and C^{-4} ions, especially since zirconium and titanium nitride, ZrN and TiN, also form crystals with the sodium chloride structure; but possibly also the discrepancy can be attributed to deformation of the anions, which have very high mole refraction values.

Table X

Nitrides and Carbides with the Sodium Chloride Structure

	Obs., Å.	Calcd., Å.
ScN	2.22	2.52
TiC	2.15	3.28
ZrC	2.37	3.40

The Fluorite Structure.—In Table XI are given the observed interatomic distances in crystals with the fluorite structure. There is good

Table XI

Inter-Atomic Distances in Fluorite Type Crystals

		Obs., Å.	Calcd., Å.
CaF_2	Ca^{++}-F^{-}	2.36	2.35
SrF_2	Sr^{++}-F^{-}	2.54, 2.51[a]	2.49
BaF_2	Ba^{++}-F^{-}	2.69	2.71
$SrCl_2$	Sr^{++}-Cl^{-}	3.03	2.94
Li_2O	Li^{+}-$O^{=}$	2.00	(2.00)
Li_2S	Li^{+}-$S^{=}$	2.47	2.44
Na_2S	Na^{+}-$S^{=}$	2.83	2.79
ZrO_2	Zr^{+4}-$O^{=}$	2.20	2.20
CeO_2	Ce^{++}-$O^{=}$	2.34	2.36
Mg_2Si	Mg^{++}-Si^{-4}	2.77	3.35
Mg_2Sn	Mg^{++}-Sn^{-4}	2.94	3.59

[a] Goldschmidt.

agreement in the case of the alkaline-earth halides, except for strontium chloride. Here, however, the large observed value arises from the mutual contact of the chloride ions, which are only 2 × 1.75 Å. apart. The apparently low value 1.75 Å. for the chloride ion radius is due to the fact that in this crystal the Coulomb forces are stronger than in a sodium chloride type crystal, on account of the bivalent cation. We should actually use a theoretical chloride radius obtained by placing $z = \sqrt{2}$, which gives 1.67 Å. The observed value is larger than this, on account of double repulsion.

The agreement is also satisfactory for lithium and sodium sulfide. The oxide was used in calculating the lithium radius, 0.60 Å., for in this compound it is safe to assume that the anions are not in mutual contact. It is further highly pleasing to note that even in zirconium and cerium oxide, containing quadrivalent cations, our theoretical radii are substantiated by the experimental inter-atomic distances; for this makes it probable that even in these crystals the ions are not greatly deformed.

The disagreement found for the compounds magnesium silicide and magnesium stannide may be explained as the result of the deformation of the anions (mole refraction of Si^{-4}, 950; of Sn^{-4}, 228) or, on the other hand, the crystals may not have the ionic structure assumed.

The Rutile Structure.—A large number of compounds MX_2 crystallize with the tetragonal structure of rutile, TiO_2. In this structure the position of the ion X is fixed only by the determination of a variable parameter by means of the intensity of reflection of x-rays from various crystal planes. In accordance with the discussion in a following section, we shall assume the parameter to have the value which causes the distances between X and the three ions M surrounding it to be constant. With this requirement the inter-atomic distance R and the edges a and c of the unit of structure are related by the equation $R = (a/4\sqrt{2})[2 + (c/a)^2]$. In this way the inter-atomic distances in Table XII are obtained. In the case of magnesium fluoride the agreement is satisfactory.

TABLE XII

INTER-ATOMIC DISTANCES IN RUTILE TYPE CRYSTALS AND IN ANATASE

		Obs., Å.	Calcd., Å.
Rutile type MgF_2	Mg^{++}-F^-	1.99	2.01
TiO_2	Ti^{+4}-$O^=$	1.98	2.08
Anatase type TiO_2[a]	Ti^{+4}-$O^=$	1.94	2.08

[a] Vegard, *Phil. Mag.*, **1**, 1151 (1926). Ref. 19 b, p. 638.

Probably the high calculated inter-atomic distances in the oxides are due to our method of using the crystal radii. The substitution in Equation 13 of $z = 4$ for the cation and $z = 2$ for the anion, instead of $z = \sqrt{8}$ for each, would lead to high calculated values in case the anion is much smaller than the cation, as in the rutile type crystals and anatase.

Trivalent Oxides.—It is probable that the rhombohedral crystal corundum, Al_2O_3, consists of ions; that is, the bonds are probably electrostatic. The oxygen ions are arranged in layers parallel to the base (111); within each layer the distances between adjacent ions are 2.50 and 2.89 Å., the values being somewhat uncertain because of the difficulty in the accurate determination of the parameter. These values are probably compatible with the oxygen radius 1.40 Å., calculated for crystals with bivalent cations. The aluminum-oxygen distances are 1.85 and 1.99 Å., in satisfactory agreement with the calculated radius sum 1.90 Å.

Goldschmidt has classed also with the ionic crystals the C-modification of the sesqui-oxides, cubic crystals with 16 M_2O_3 in the unit of structure. The inter-atomic distances reported by him are 2.16–2.20 Å. for scandium oxide and 2.34–2.38 Å. for yttrium oxide, in good agreement with the radius sums 2.21 Å. for Sc^{+3}–$O^{=}$ and 2.33 Å. for Y^{+3}–$O^{=}$.

Eighteen-Shell Ions.—The crystals containing eighteen-shell ions (Table XIII) can be divided into two classes: the first, containing the oxygen or fluoride ion, agreeing reasonably well with the theoretical radii, and the second, containing more easily deformable anions, having smaller inter-atomic distances than the predicted ones. The action of the small cuprous ion on the easily deformable selenium ion (mole refraction, 26.8) is especially large. From these results the conclusion can be drawn that the deforming action of an eighteen-shell ion is much greater than that of an eight-shell ion of the same size and valence. This is to be explained as due to the large effective nuclear charge within the eighteen-shell ions, and it indicates that the deformation of an anion by a cation takes place to a great extent in the interior of the cation, within the outer electron shells.

TABLE XIII

CRYSTALS CONTAINING EIGHTEEN-SHELL IONS

Crystal	Type		Obs., Å.	Calcd., Å.	Δ
CdO	Sodium chloride	Cd^{++}-$O^{=}$	2.36	2.37	0.01
CdF_2	Fluorite	Cd^{++}-F^{-}	2.34	2.33	– .01
HgF	Fluorite	$Hg^{++}F^{-}$	2.43[a]	2.46	.03
ZnF_2	Rutile	Zn^{++}-F^{-}	2.04	2.10	.06
SnO_2	Rutile	Sn^{+4}-$O^{=}$	2.06	2.11	.05
PbO_2	Rutile	Pb^{+4}-$O^{=}$	2.16	2.24	.08
AgF	Sodium chloride	Ag^{+}-F^{-}	2.62[a]	2.63	.00
			(2.46[b]	2.62	.16)
AgCl	Sodium chloride	Ag^{+}-Cl^{-}	2.77	3.07	.30
AgBr	Sodium chloride	Ag^{+}-Br^{-}	2.88	3.21	.33
AgI	Sodium chloride	Ag^{+}-I^{-}	2.99[c]	3.42	.43
Cu_2Se	Fluorite	Cu^{+}-$Se^{=}$	2.49	2.94	.45
TlSb	Cesium chloride	Tl^{+3}-Sb^{-3}	3.33	3.41	.08

[a] From the density $\varphi = 5.852$ (Landolt-Börnstein).

[b] Ott, *Z. Krist.*, **63**, 222 (1926).

[c] From solid solutions with silver bromide, Goldschmidt.

Such an action is understandable with the wave-mechanics picture of interpenetrating ions.

It is doubtful that the compound TlSb is to be considered as composed of the ions Tl^{+3} and Sb^{-3}, for much deformation would be expected (the mole refraction of Sb^{-3} is 80), and the inter-atomic distance would then be very much less than the calculated one, instead of only 0.08 Å. less.

Other Crystal Radii.—In Table XIV are collected data from which reasonably accurate crystal radii for some ions not included in Table II may be derived. In all cases fluorides and oxides with the sodium chloride and fluorite structures have been considered to give the correct radius sums. The correction of 2.7% (Ref. 24) was made in selecting the thallous ion crystal radius. The radii derived from rutile type oxides have been

TABLE XIV

EMPIRICALLY DEDUCED CRYSTAL RADII

Crystal	Structure	Obs. distance, Å.	Ion	Effective radius, Å.	Selected radius, Å.
TlCl	Cesium chloride	3.33	Tl^+	1.52	1.44
TlBr	Cesium chloride	3.44		1.49	
TlI	Cesium chloride	3.64[a]		1.48	
MnO	Sodium chloride	2.20	Mn^{++}	0.80	0.80
MnS	Sodium chloride	2.61		.76	
MnF_2	Rutile	2.12[b]		.76	
FeO	Sodium chloride	2.15	Fe^{++}	.75	.75
FeF_2	Rutile	2.06		.71	
CoO	Sodium chloride	2.12	Co^{++}	.72	.72
CoF_2	Rutile	2.04		.68	
NiO	Sodium chloride	2.09	Ni^{++}	.69	.69
NiF_2	Rutile	2.02		.66	
PbF_2	Fluorite	2.57[a]	Pb^{++}	1.21	1.21
PbS	Sodium chloride	2.97[a]		1.13	
PbSe	Sodium chloride	3.03[a]		1.05	
PbTe	Sodium chloride	3.21[a]		1.00	
ThO_2	Fluorite	2.42	Th^{+4}	1.02	1.02
UO_2	Fluorite	2.37	U^{+4}	0.97	0.97
PrO_2	Fluorite	2.32[a]	Pr^{+4}	.92	.92
VO_2	Rutile	1.93	V^{+4}	.53	.59
MnO_2	Rutile	1.84	Mn^{+4}	.44	.50
NbO_2	Rutile	2.01	Nb^{+4}	.61	.67
MoO_2	Rutile	2.00	Mo^{+4}	.60	.66
RuO_2	Rutile	1.97	Ru^{+4}	.57	.63
TeO_2[c]	Rutile	2.21	Te^{+4}	.81	.81
WO_2	Rutile	2.00	W^{+4}	.60	.66
OsO_2	Rutile	1.99	Os^{+4}	.59	.65
IrO_2	Rutile	1.98	Ir^{+4}	.58	.64

[a] Goldschmidt.

[b] The data for rutile type crystals are given in Table XVI.

[c] Because of the anomalous axial ratio of TeO_2 (Table XVI), no attempt was made to correct the radius.

corrected by adding 0.06 Å., derived from the results for tin and lead oxides. Some of these ions, such as Pb^{++}, presumably contain only S electrons and completed sub-groups, and are hence spherically symmetrical. Others, however, deviate from spherical symmetry, so that perhaps one crystal radius alone cannot be assigned each ion.

The effect of deformation is shown in the sulfide, selenide and telluride of lead. Especially interesting is the decrease in the crystal radius in the series Mn^{++}, Fe^{++}, Co^{++}, Ni^{++}; there must then come an increase when the shell is completed, at Zn^{++}, with the radius 0.74 Å.

The Relative Stabilities of Different Ionic Arrangements

The Sodium Chloride and Cesium Chloride Structures.—The agreement found between the observed inter-atomic distances and our calculated ionic radii makes it probable that the crystals considered are built of only slightly deformed ions; it should, then, be possible, with the aid of this conception, to explain the stability of one structure, that of sodium chloride, in the case of most compounds, and of the other, that of cesium chloride, in a few cases, namely, the cesium and thallous halides.

Born[21] has shown that of a number of ionic structures which can be assumed by a binary compound, the sodium chloride arrangement has the lowest Coulomb energy, if it be assumed that the densities of the various forms are the same. He advanced this calculation in explanation of the prevalence of this arrangement in nature. The structures considered were chosen because of the simplicity of their mathematical treatment; no simple arrangement other than the sodium chloride arrangement is included among them, however, so that Born's result is not surprising. As a matter of fact, the Coulomb energy of the sodium chloride arrangement is *greater* than that of one other simple structure (the sphalerite arrangement), assuming the densities of the two forms to be the same. We would expect, however, that not the density, but rather the inter-atomic distance should remain constant for different ionic arrangements. The Coulomb energies of the sodium chloride and cesium chloride structures are[22]

$$\Phi^{(1)}_{\mathrm{NaCl}} = -\,(z^2e^2/R)\,1.7476 \tag{14}$$

$$\Phi^{(1)}_{\mathrm{CoCl}} = -\,(z^2e^2/R)\,1.7624 \tag{15}$$

in which R represents the smallest distance between oppositely charged ions in each case. If this distance were constant, then the Coulomb energy would be smaller for the cesium chloride arrangement, making it more stable than the other.

However, the energy of the repulsive forces must be taken into account; moreover, the possibility of a difference in R in the two structures must

[21] Born, *Z. Physik,* **7**, 124 (1921).

[22] Emersleben, *Physik. Z.,* **24**, 73, 97 (1923).

be considered. This has been done by Hund[23] who, using the repulsion expression of Equation 8, showed that the cesium chloride structure is stable if the exponent n is greater than 35, and the sodium chloride structure is stable if n is less than 35. This result accounts qualitatively for the observed facts, for from the compressibility data the cesium salts would be supposed to have large values of n; but quantitative agreement is not found.[24] There are a number of possible explanations of the discrepancy. It might be due to the use of the Born repulsive force expression; however, the use of Equation 7, with various reasonable values of m, does not remove the disagreement. The probable explanation is that through deformation of the ions the energy of a crystal is changed somewhat (perhaps by changing the effective charge of the ions slightly, if we consider the deformation to be the attraction of a small portion of the electrons of the anion to a position near the nucleus of the cation), so that the transition occurs at about $n = 12$. It is of interest to mention that this calculation indicates that the crystal energy as calculated by the Born method is accurate only to about 2%, or 4000 cal. per mole.

These considerations also explain the occurrence of cases of dimorphism involving the sodium chloride and cesium chloride structures. It would be expected that increase in thermal agitation of the ions would smooth out the repulsive forces, that is, would decrease the value of the exponent n. Hence the cesium chloride structure would be expected to be stable in the low temperature region, and the sodium chloride structure in the high-temperature region. This result may be tested by comparison with the data for the ammonium halides, if we assume the ammonium ion to approximate closely to spherical symmetry. The low-temperature form of all three salts, ammonium chloride, bromide and iodide, has the cesium chloride structure, and the high-temperature form the sodium chloride structure. Cesium chloride and bromide are also dimorphous, changing into another form (presumably with the sodium chloride structure) at temperatures of about 500°.

The Fluorite and Rutile Structures.—Compounds of the type MX_2 also have their choice of two ionic structures, but the factors influencing them

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[23] Hund, *Z. Physik*, **34**, 833 (1925).

[24] The calculation depends on the difference in the repulsion coefficient β in the two structures, for there are six anion-cation contacts in the sodium chloride structure, and eight in the cesium chloride structure. With $\beta_{NaCl} = 6\beta_0$ and $\beta_{CsCl} = 8\beta_0$, and with $n = 12$, it is found that the equilibrium inter-atomic distance for the cesium chloride structure is about 2.7% greater than that for the sodium chloride structure. For this reason the observed inter-atomic distance in cesium iodide was decreased by this amount in obtaining the initial values for the cesium and iodide crystal radii, which are defined to be valid for a crystal with the sodium chloride structure. It has also been inferred by Goldschmidt, from the observed inter-atomic distances for the two forms of the ammonium halides, that there is a decrease of about 3% in going from the cesium chloride to the sodium chloride arrangement.

in their choice are entirely different from those in the case just considered.[25] The Coulomb energy of the rutile arrangement is a function of two parameters, the axial ratio c/a, and a variable u determining the location of the X ions. We should expect with spherical ions that the parameter would have the value making the distance between the X ion (3, Fig. 4) and each of the surrounding M ions (A and B) constant, namely

$$u = (^1/_8)[(c/a)^2 + 2] \qquad (16)$$

This is verified experimentally, except for a small uncertainty; thus, for rutile u should have the value 0.302, corresponding to $c/a = 0.644$. Vegard[26] gives the experimental value 0.302, Greenwood[27] 0.300 and Huggins[28] 0.30 ± 0.01. Similar agreement is found for other crystals with this structure.

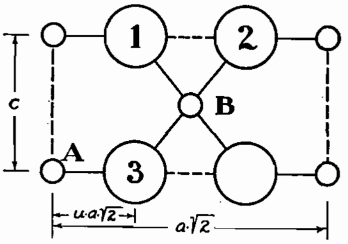

Fig. 4.—Location of titanium ions (small circles) and oxygen ions (large circles) in the plane (110) of rutile.

Bollnow[29] has evaluated the Coulomb energy of the rutile arrangement as a function of the axial ratio c/a, making the assumption that u is given by Equation 16. His results may be given by the equation

$$\Phi^{(1)}_{\text{Rutile}} = -(z^2e^2/R)\alpha \qquad (17)$$

for the Coulomb energy per $M^{+2z}X_2^{-z}$, in which R is the M–X distance, and α has the values given in Table XV. It will be seen that α has a maximum at $c/a = 0.721$, so that this axial ratio should be assumed by crystals composed of spherical ions, in the absence of disturbing influences. The observed values (Table XVI), except in three cases, lie between the limits 0.62 and 0.71, with an average of 0.67, which is lower than that calculated. The explanation of this (given by Bollnow) is that the X ions 1 and 2 (Fig. 4) are in contact, and so increase a and decrease c/a somewhat; thus the F^-–F^- distance in magnesium fluoride is only 2.57 Å.

TABLE XV

THE COULOMB CONSTANT FOR THE RUTILE STRUCTURE

c/a	u	α	c/a	u	α
0.400	0.27	4.38	0.694	0.310	4.810
.490	.28	4.64	.721	.315	4.816
.565	.29	4.75	.749	.320	4.809
.633	.300	4.783	.800	.330	4.789

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[25] It was shown by Hund (Ref. 23) that for small values of n (less than 6 or 9, depending upon the assumptions made) the rutile structure can become stable. However, our discussion makes it probable that the transition is actually due to the radius ratio.

[26] Vegard, *Phil. Mag.*, **1**, 1151 (1926).

[27] Greenwood, *ibid.*, **48**, 654 (1924).

[28] Huggins, *Phys. Rev.*, **27**, 638 (1926).

[29] Bollnow, *Z. Physik*, **33**, 741 (1925).

TABLE XVI

CRYSTALS WITH THE RUTILE STRUCTURE

Crystal	a, Å.	c, Å.	c/a	Crystal	a, Å.	c, Å.	c/a
MgF_2[a]	4.66	3.08	0.660	NbO_2[e]	4.77	2.96	.620
MnF_2[b,c]	4.88	3.29	.674	MoO_2[e]	4.86	2.79	.573
FeF_2[b]	4.67	3.30	.706	RuO_2[e]	4.51	3.11	.689
CoF_2[b,e]	4.70	3.19	.679	SnO_2[e]	4.75	3.19	.673
NiF_2[b,e]	4.68	3.10	.663	TeO_2[e]	4.79	3.77	.788
ZnF_2[b,e]	4.72	3.13	.663	WO_2[e]	4.86	2.77	.571
TiO_2[d]	4.58	2.95	.664	OsO_2[e]	4.51	3.19	.707
VO_2[e]	4.54	2.88	.634	IrO_2[e]	4.49	3.14	.700
MnO_2[e,d]	4.41	2.88	.653	PbO_2[e]	4.96	3.39	.683

[a] Buckley and Vernon, *Phil. Mag.*, **49**, 945 (1925).

[b] Ferrari, *Atti accad. Lincei*, [6] **3**, 224, 324 (1926).

[c] Van Arkel, *Rec. trav. chim.*, **45**, 437 (1926).

[d] Huggins, Ref. 20.

[e] Goldschmidt, Ref. 10.

and the $O^{=}$–$O^{=}$ distance in rutile itself only 2.53 Å. (These low radii arise from the fact that in these crystals, containing bivalent and quadrivalent cations, the Coulomb forces are larger than in sodium chloride type crystals.) The very low axial ratio 0.57 for the dioxides of molybdenum and tungsten and the high axial ratio 0.79 for tellurium dioxide probably are caused by the cations not having spherical symmetry. It will be noticed that the entire range from 0.57 to 0.79 involves a maximum change in the Coulomb energy of only about 1%.

We may accordingly write for α its value for $c/a = 0.67$, so that the Coulomb energy is

$$\Phi^{(1)}_{\text{Rutile}} = -(z^2e^2/R)\ 4.80 \tag{18}$$

For the fluorite arrangement the Coulomb energy is

$$\Phi^{(1)}_{\text{Fluorite}} = -(z^2e^2/R)\ 5.04 \tag{19}$$

Bollnow also evaluated the Coulomb energy of anatase, the other tetragonal form of titanium dioxide, by again making the assumption of a constant Ti^{+4}–$O^{=}$ distance in order to fix the value of the parameter. He found this energy to have a minimum value

$$\Phi^{(1)}_{\text{Anatase}} = -(z^2e^2/R)\ 4.80 \tag{20}$$

for an axial ratio 2.62, in satisfactory agreement with the observed value 2.51. With the assumption of a constant Ti^{+4}–$O^{=}$ distance the parameter in anatase should have the value 0.204, in agreement with the experimental values 0.204 (Vegard) and 0.20 ± 0.01 (Huggins).

The possibility of the existence of two forms of titanium dioxide, rutile and anatase, is evident from the identity of their Coulomb energies; taking the energy of the repulsive forces and of possible deformation into account, it is seen that the choice between the two structures would depend on the thermodynamic environment during crystallization. In the case of different compounds the choice might depend on the repulsion exponent *n;* it is interesting that no compounds other than titanium oxide have the anatase structure.

From Equation 19 we should conclude that all ionic crystals MX_2 would have the fluorite structure, on account of the much smaller Coulomb energy for this arrangement. For a compound $M^{+4}X_2^{=}$, with $R = 2$ Å., the free energy of the fluorite arrangement is 160,000 cal. per mole smaller than that of the rutile or anatase arrangement. This very large difference cannot be counteracted by the possible small differences in the repulsion coefficients β, as occurs in the case of the sodium chloride and cesium chloride structures, nor by the effect of deformation. The transition from the fluorite to the rutile structure actually arises from a geometrical effect, the mutual contact of the large anions, and the factor determining the form to be assumed is the ratio of the radius of the cation to that of the anion. From the geometry of the fluorite arrangement it is seen that for values of the ratio R_M/R_X greater than 0.732, contact occurs between anion and cation (considered as rigid spheres), but for smaller values of this ratio the repulsive forces balancing the Coulomb forces will arise from the anions[30] alone, and that the distance R in Equation 19 will not be $R_M + R_X$, but will correspond instead to $2R_X$, the geometrical relation being $R' = \sqrt{3}R_X$. On the other hand, there is still contact between anion and cation in the rutile arrangement, so that R in Equation 18 is given by $R = R_M + R_X$. Substituting these values of R' and R in Equations 19 and 18, and equating $\Phi^{(1)}_{\text{Fluorite}}$ and $\Phi^{(1)}_{\text{Rutile}}$, it is found that the transition radius ratio is

$$R_M/R_X = [(4.80/5.04)\sqrt{3}] - 1 = 0.65 \tag{21}$$

We have accordingly shown that *for values of the ratio of the crystal radius of the cation to that of the anion greater than 0.65 the fluorite structure is stable; for values less than 0.65 the rutile structure is stable.*

This theoretical result is completely substantiated by experiment. Goldschmidt,[31] from a study of crystal structure data, observed that the radius ratio is large for fluorite type crystals, and small for those of the rutile type, and concluded as an empirical rule that this ratio is the determining factor in the choice between these structures. Using Wasastjerna's radii he decided on 0.67 as the transition ratio. He also stated that this can be explained as due to anion contact for a radius ratio smaller than about 0.74. With our radii we are able to show an even more satisfactory verification of the theoretical limit. In Table XVII are given values of the radius ratio for a large number of compounds. It is seen that the max-

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[30] In this discussion the formula $M^{+2z}X_2^{-z}$ is assumed; for $M_2^{+z}X^{-2z}$ the words cation and anion must be interchanged.

[31] Goldschmidt, *Skrifter Det. Norske Videnskaps-Akad. Oslo I. Matem.-Naturvid. Klasse,* **1926,** No. 1.

TABLE XVII

THE RADIUS RATIO FOR FLUORITE TYPE AND RUTILE TYPE CRYSTALS

Fluorite type	R_M/R_X	Rutile type	R_M/R_X
Li_2S	3.07	PbO_2	0.59
Li_2O	2.33	MnF_2	.59
$K_2[SnCl_6]$[a]	2.24	TeO_2	.58
Cu_2Se	2.06	FeF_2	.55
Na_2S	1.94	ZnF_2	.54
$[Ni(NH_3)_6]Cl_2$	1.41	CoF_2	.53
$[N(CH_3)_4]_2[PtCl_6]$[b]	1.11	NiF_2	.51
BaF_2	0.98	SnO_2	.51
PbF_2	.86	TiO_2	.49
SrF_2	.83	MgF_2	.48
HgF_2	.81	NbO_2	.48
CaF_2	.73	MoO_2	.47
ThO_2	.73	WO_2	.47
CdF_2	.71	OsO_2	.46
CeO_2	.70	IrO_2	.46
UO_2	.69	RuO_2	.45
PrO_2	.66	VO_2	.42
$SrCl_2$	.63	MnO_2	.36

[a] The radii used for complex ions are: $[SnCl_6]^{=}$, 2.98 Å.; $[Ni(NH_3)_6]^{++}$, 2.55 Å. $[PtCl_6]^{=}$, 2.88; $[N(CH_3)_4]^{+}$, 2.60.

[b] Huggins, *Phys. Rev.*, **27**, 638 (1926).

imum value of the ratio for the rutile structure is 0.59, and the minimum value for the fluorite structure 0.63, in satisfactory agreement with the theoretical limit 0.65.[32]

Goldschmidt predicted from his empirical rule that calcium chloride would not have the fluorite structure, and he states that on investigation he has actually found it not to crystallize in the cubic system. Our theoretical deduction of the transition radius ratio allows us to predict that of the halides of magnesium, calcium, strontium and barium only calcium fluoride, strontium fluoride and chloride, and barium fluoride, chloride,

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[32] In this discussion, two mutually canceling simplifications have been made. For the transition value of the radius ratio the phenomenon of double repulsion causes the inter-atomic distances in fluorite type crystals to be increased somewhat, so that R' is equal to $\sqrt{3}R_X.\delta$, where δ has a value of about 1.05 (found experimentally in strontium chloride). Double repulsion is not operative in rutile type crystals, for which $R = R_M + R_X$. From these equations the transition ratio is found to be $(4.80/5.04)\sqrt{3}\delta - 1 = 0.73$, for $\delta = 1.05$; that is, it is increased 12%. But R_M and R_X in these equations are not the crystal radii, which we have used above, but are the univalent crystal radii multiplied by the constant of Equation 13 with z placed equal to $\sqrt{2}$, for $M^{++}X_2^{-}$. Hence the univalent crystal radius ratio should be used instead of the crystal radius ratio, which is about 17% smaller (for strontium chloride). Because of its simpler nature the treatment in the text has been presented; it is to be emphasized that the complete agreement with the theoretical transition ratio found in Table XVII is possibly to some extent accidental, for perturbing influences might cause the transition to occur for values a few per cent. higher or lower.

bromide and iodide would have the fluorite structure. Of these all but the last three are known to have this structure, and magnesium fluoride is known to have the rutile structure. The oxides, sulfides, selenides and tellurides of all the alkali metals satisfy the fluorite requirement; of these, lithium oxide and sulfide and sodium sulfide are known to have this structure. It will be of interest to carry on the experimental study of others of these compounds.

The Transition to the Sphalerite Structure.—The oxide, sulfide and selenide of beryllium have neither the sodium chloride nor the cesium chloride structure, but instead the sphalerite or the wurzite structure. The Coulomb energy for the sphalerite arrangement is

$$\Phi^{(1)}_{\text{Sphalerite}} = -(z^2e^2/R)\,1.640 \qquad (22)$$

in which R is the smallest anion-cation distance. The Coulomb energy of the closely similar wurzite arrangement has been found by Hund to be the same, within the limits of accuracy of his calculation. He found for the coefficient 1.641 ± 0.003. Comparing this equation with Equations 14 and 15, we should conclude that compounds with undeformed ions could not assume these structures. Accordingly the observed structures of the beryllium salts have previously been explained by saying that the very small beryllium ion has a large deforming action on the surrounding anions.

However, in the wave-mechanics atomic model, deformation occurs within the outer shell of the cation, and in this region the effective nuclear charge of the beryllium ion is only $4e$, instead of $10e$ for eight-shell cations and $20e$ for eighteen-shell cations. Hence we conclude that the deforming action of the beryllium ion is *less* than that of the magnesium, calcium, etc., ions. The explanation of the sodium chloride-sphalerite transition which we advance is the geometrical one used for the fluorite-rutile transition, and does not involve deformation. When the radius ratio R_M/R_X is less than $\sqrt{2}-1 = 0.414$, mutual contact between the anions occurs in the sodium chloride arrangement, so that R in Equation 14 has the value $R = \sqrt{2}R_X$. R in Equation 26 still has the value $R' = R_M + R_X$. Comparing $\Phi^{(1)}_{\text{NaCl}}$ and $\Phi^{(1)}_{\text{Sphalerite}}$, it is found that *for R_M/R_X greater than* $(1.640/1.7476)\sqrt{2}-1 = 0.33$ *the sodium chloride arrangement is stable, and for a value of the radius ratio less than 0.33 the sphalerite (or wurzite) arrangement is stable.*[33]

In Table XVIII are given values of the radius ratio for the salts of beryllium, magnesium and calcium (those of barium and strontium, with the sodium chloride structure, also obviously satisfy the radius ratio criterion). It is seen that all of the sodium chloride type crystals containing eight-shell cations have radius ratios greater than the limit 0.33, and the beryl-

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[33] The effect of double repulsion for the sodium chloride structure may raise this limit a few per cent.

TABLE XVIII

THE RADIUS RATIO FOR SODIUM CHLORIDE AND SPHALERITE OR WURZITE TYPE CRYSTALS

Sodium chloride structure		Sphalerite or wurzite structure	
	R_M/R_X		R_M/R_X
CaO	0.71	BeO	0.22
CaS	.54	BeS	.17
CaSe	.50	BeSe	.16
CaTe	.45	BeTe	.14
MgO	.47		
MgS	.35	ZnO	.53
MgSe	.33	ZnS	.40
		ZnSe	.38
CdO	.69	ZnTe	.34
		CdS	.53
		CdSe	.49
		CdTe	.44
		HgS	.60
		HgSe	.56
		HgTe	.50

lium salts with the sphalerite or wurzite structures have lower values of the radius ratio than this limit. Accordingly, the conclusion is drawn that the beryllium salts may be composed of ions, even though they have the sphalerite and wurzite structures.[34]

The prediction may be made that the still unstudied crystal magnesium telluride, with the radius ratio 0.29, has the sphalerite or wurzite structure rather than the sodium chloride structure.

TABLE XIX

INTER-ATOMIC DISTANCES FOR BERYLLIUM SALTS

	Structure	Obs., Å.	Calcd., Å.
BeO	Wurzite	1.65[a]	1.71
BeS	Sphalerite	2.10[a]	2.15
BeSe	Sphalerite	2.20[a]	2.29
BeTe	Sphalerite	2.40[a]	2.52

[a] Goldschmidt.

The observed inter-atomic distances (Table XIX) for the beryllium salts are somewhat smaller than those calculated. This indicates that there is more deformation in these crystals than in the sodium chloride type crystals, despite the smaller effective nuclear charge of the two-shell cation; and points to the existence of an increased tendency to deformation

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[34] It was concluded by Zachariasen [*Norsk geol. Tidsskrift,* **8,** 189 (1925); *Z. physik. Chem.,* **119,** 201 (1926)] from the intensities of reflection of x-rays that beryllium oxide does not contain Be^{++} and $O^{=}$ ions. However, it has since been shown by Claassen [*ibid.,* **124,** 139 (1926)] and Zachariasen himself [*Z. Physik,* **40,** 637 (1926)] that if the electron distribution of the ions is taken into account, the x-ray measurements are compatible with an ionic structure.

in structures in which the anion is surrounded tetrahedrally by cations; that is, in which an electron pair can be shared with each cation.

The radius ratios for sphalerite and wurzite type crystals with eighteen-shell cations do not conform to our criterion, so that some other influence must be operative. Without doubt this is deformation. Here again it is seen that the tetrahedral structure is particularly favorable to deformation, for the observed $Zn^{++}-O^{=}$ distance (1.93 Å.) is 0.21 Å. shorter than the theoretical one, while in cadmium oxide, with the sodium chloride structure, the difference is only 0.01 Å.

Extension to Complex Ions

Many complex ions, such as NH_4^+, $N(CH_3)_4^+$, $PtCl_6^=$, $Cr(H_2O)_8^{+++}$, etc., are roughly spherical in shape, so that they may be treated as a first approximation as spherical. Crystal radii can then be derived for them from measured inter-atomic distances although, in general, on account of the lack of complete spherical symmetry radii obtained for a given ion from crystals with different structures may show some variation. Moreover, our treatment of the relative stabilities of different structures may also be applied to complex ion crystals; thus the compounds K_2SnCl_6, $Ni(NH_3)_6Cl_2$ and $[N(CH_3)_4]_2PtCl_6$, for example, have the fluorite structure, with the monatomic ions replaced by complex ions and, as shown in Table XVII, their radius ratios fulfil the fluorite requirement. Doubtless in many cases, however, the crystal structure is determined by the shapes of the complex ions.

I wish to express my gratitude to the John Simon Guggenheim Memorial Foundation and to the California Institute of Technology for providing the opportunity for the prosecution of this work, and to Professor A. Sommerfeld for the interest he has taken in it.

Summary

Using an atomic model derived from the wave mechanics of Schrödinger, size-screening constants have been calculated for the electrons in many-electron atoms and ions. After a discussion of the forces between ions, and of the significance of ionic sizes, values of the univalent crystal radius and the crystal radius are derived for a large number of ions with the aid of these screening constants, using as a starting point the observed inter-atomic distances in crystals of sodium fluoride, potassium chloride, rubidium bromide, cesium iodide and lithium oxide. The crystal radius of an ion is defined so that the sum of two radii gives the equilibrium distance in a normal crystal with the sodium chloride structure. The univalent crystal radius is the crystal radius the ion would possess if it were univalent, but otherwise unchanged.

The crystal radii for eight-shell ions are in agreement with the observed inter-atomic distances for normal alkali halide crystals, showing that the

various screening constants are self-consistent. Excellent agreement with experiment is found also for the normal alkaline-earth oxides, sulfides selenides and tellurides with the sodium chloride structure, and for the normal alkaline-earth halides, alkali oxides and sulfides and quadrivalent oxides with the fluorite and rutile structures.

In lithium chloride, bromide and iodide, magnesium sulfide and selenide and strontium chloride the inter-atomic distances depend on the anion radius alone, for the anions are in mutual contact; the observed anion-anion distances agree satisfactorily with the calculated radii. In lithium fluoride, sodium chloride, bromide and iodide and magnesium oxide the observed anion-cation distances are larger than those calculated because of double repulsion; the anions are approaching mutual contact, and the repulsive forces between them as well as those between anion and cation are operative.

In crystals containing eighteen-shell cations and not easily deformable anions (F^-), the agreement between the calculated and observed radii is good; for deformable anions ($O^=$, Cl^-, Br^-, I^-), the observed inter-atomic distances are shorter than those calculated.

The theoretical result is derived that ionic compounds MX_2 will crystallize with the fluorite structure if the radius ratio R_M/R_X is greater than 0.65, and with the rutile (or anatase) structure if it is less. This result is experimentally substantiated.

It is also shown that theoretically a binary compound should have the sphalerite or wurzite structure instead of the sodium chloride structure if the radius ratio is less than 0.33. The oxide, sulfide, selenide and telluride of beryllium conform to this requirement, and are to be considered as ionic crystals. It is found, however, that such "tetrahedral" crystals are particularly apt to show deformation, and it is suggested that this is a tendency of the anion to share an electron pair with each cation.

A brief discussion of crystals containing complex ions is given.

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THE PRINCIPLES DETERMINING THE STRUCTURE OF COMPLEX IONIC CRYSTALS

BY LINUS PAULING

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1. The Relative Stability of Alternative Structures of Ionic Crystals.—The elucidation of the factors determining the relative stability of alternative crystalline structures of a substance would be of the greatest significance in the development of the theory of the solid state. Why, for example, do some of the alkali halides crystallize with the sodium chloride structure and some with the cesium chloride structure? Why does titanium dioxide under different conditions assume the different structures of rutile, brookite and anatase? Why does aluminum fluosilicate, $Al_2SiO_4F_2$, crystallize with the structure of topaz and not with some other structure? These questions are answered formally by the statement that in each case the structure with the minimum free energy is stable. This answer, however, is not satisfying; what is desired in our atomistic and quantum theoretical era is the explanation of this minimum free energy in terms of atoms or ions and their properties.

Efforts to provide such a treatment for simple alternative structures, such as the sodium chloride and cesium chloride structures and the fluoride and rutile structures, have been made with the aid of the Born potential expression and modifications of it. Assuming that all ions repel each other according to a high inverse power of the distance between them (the repulsive potential being proportional to r^{-n}), the equilibrium energy of a crystal is given by

$$\Phi = -\frac{z^2e^2A}{R}\left(1-\frac{1}{n}\right) \tag{1}$$

in which R is the equilibrium distance between two adjacent ions in the crystal, and A is the Madelung constant characteristic of the structure. A knowledge of how R changes from structure to structure for a given substance would then allow the prediction of which structure is stable, if Equation 1 were accurate. Methods of calculating R have been suggested.[1] It is found, however, that Equation 1 is in error by at least 2% in some cases,[1b] and this error of around 5000 cal./mole suffices to invalidate the theory in applications of this kind. An explanation of the sodium chloride–cesium chloride transition which accounts for the observed properties of the alkali halides has been reported,[2] but the considerations involved (including deformation phenomena) have not yet been given quantitative formulation.

The application of these methods to more complex crystals would involve the highly laborious calculation of the Madelung constant for a number of complicated ionic arrangements. Furthermore, the methods provide no way of determining the possible structures for which calculations should be made. An infinite number of possible atomic arrangements for a complicated substance such as a silicate are provided by the theory of space groups. There is desired a set of simple rules, which need not be rigorous in their derivation nor universal in their application, with the aid of which the few relatively stable structures can be identified among the multitude possible for a given substance. These rules could be used in the prediction of atomic arrangements for comparison with x-ray data. They would also provide a criterion for the probable correctness of structures suggested by but not rigorously deduced from experimental measurements. Finally, they would permit the intuitive understanding of the stability of crystals in terms of visualizable interionic interactions.

2. The Application of the Coördination Theory in the Determination of the Structures of Complex Crystals.—As a result of the recent increase in knowledge of the effective radii of various ions in crystals,[3] Professor W. L. Bragg has suggested and applied a simple and useful theory leading to the selection of possible structures for certain complex crystals. His fundamental hypothesis is this: if a crystal is composed of large ions and small ions, its structure will be determined essentially by the large ions, and may approximate a close-packed arrangement of the large ions alone,

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[1] (a) F. Hund, *Z. Physik*, **34**, 833 (1925); (b) Linus Pauling, THIS JOURNAL, **50**, 1036 (1928); *Z. Krist.*, **67**, 377 (1928).

[2] Linus Pauling, *ibid.*, **69**, 35 (1928).

[3] Wasastjerna, *Soc. Sci. Fenn. Comm. Phys. Math.*, **38**, 1 (1923).

with the small ions tucked away in the interstices in such a way that each one is equidistant from four or six large ions. In some cases not all of the close-packed positions are occupied by ions, and an open structure results. To apply this theory one determines the unit of structure in the usual way, and finds by trial some close-packed arrangement of the large ions of known crystal radius (usually oxygen ions with a radius of 1.35–1.40 Å.) compatible with this unit. The other ions are then introduced into the possible positions in such a way as to give agreement with the observed intensities of reflection of x-rays, the large ions being also shifted somewhat from the close-packed positions if necessary. With the aid of this method Bragg and his co-workers have made a very significant attack on the important problem of the structure of silicates, involving the determination of structures for beryl, $Be_3Al_2Si_6O_{18}$,[4] chrysoberyl, $BeAl_2O_4$,[5] olivine, $(Mg, Fe)_2SiO_4$,[6] chondrodite, $H_2Mg_5Si_2O_{10}$, humite, $H_2Mg_7Si_3O_{14}$, clinohumite, $H_2Mg_9Si_4O_{18}$,[7] phenacite, Be_2SiO_4,[8] etc.

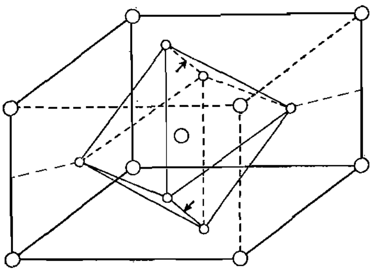

Fig. 1.—The unit of structure for rutile. Large circles represent titanium ions; small circles oxygen ions. An octahedron with a titanium ion at its center and oxygen ions at its corners is shown. The two edges marked with arrows are shared with adjoining octahedra.

During the investigation of the structure of brookite,[9] the orthorhombic form of titanium dioxide, a somewhat different method for predicting possible structures for ionic crystals was developed, based upon the assumption of the coordination of the anions in the crystal about the cations in such a way that each cation designates the center of a polyhedron, the corners of which are occupied by anions. This method leads for a given substance to a small number of possible simple structures, for each of which the size of the unit of structure, the space-group symmetry and the positions of all ions are fixed. In some cases, but not all, these structures correspond to close-packing of the large ions; when they do, the theory further indicates the amount and nature of the distortion from the close-packed arrangement.

The structures of rutile and anatase, the two tetragonal forms of titanium dioxide, have been determined by rigorous methods (Figs. 1 and 2). They seem at first sight to have little in common beyond the fact

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[4] W. L. Bragg and J. West, *Proc. Roy. Soc. London*, **111A**, 691 (1926).

[5] W. L. Bragg and G. B. Brown, *ibid.*, **110A**, 34 (1926).

[6] W. L. Bragg and G. B. Brown, *Z. Krist.*, **63**, 538 (1926).

[7] (a) W. L. Bragg and J. West, *Proc. Roy. Soc. London*, **114A**, 450 (1927); (b) W. H. Taylor and J. West, *ibid.*, **117A**, 517 (1928).

[8] W. L. Bragg, *ibid.*, **113A**, 642 (1927).

[9] Linus Pauling and J. H. Sturdivant, *Z. Krist.*, **68**, 239 (1928).

that each is a coördination structure, with six oxygen atoms about each titanium atom at octahedron corners. From a certain point of view, however, they are closely similar. They are both made up of octahedra sharing edges and corners with each other; in rutile two edges of each octahedron are shared and in anatase four. In both crystals the titanium–oxygen distance is a constant, with the value 1.95–1.96 Å. The basic octahedra are only approximately regular; in each crystal they are deformed in such a way as to cause each shared edge to be shortened from 2.76 Å. (the value for regular octahedra) to 2.50 Å., the other edges being correspondingly lengthened.

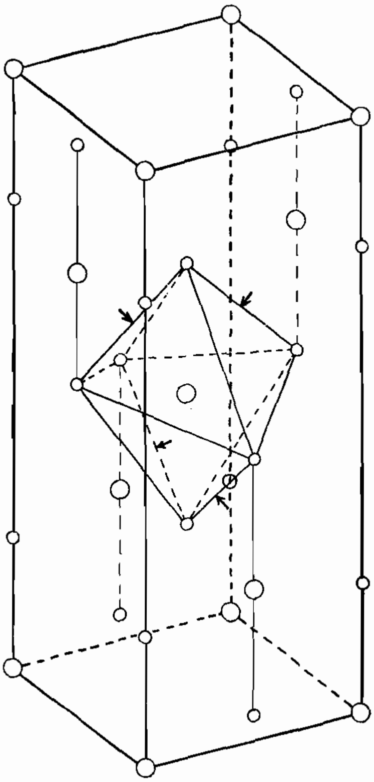

Fig. 2.—The unit of structure of anatase. The titanium octahedron shares the four edges marked with arrows with adjoining octahedra.

As a result of these considerations the following assumptions were made: (1) Brookite is composed of octahedra, each with a titanium ion at its center and oxygen ions at its corners. (2) The octahedra share edges and corners with each other to such an extent as to give the crystals the correct stoichiometric composition. (3) The titanium–oxygen distances throughout are 1.95–1.96 Å. Shared edges of octahedra are shortened to 2.50 Å.

Two structures satisfying these requirements were built out of octahedra. The first was not the structure of brookite. The second, however, had the same space-group symmetry as brookite (V_h^{15}), and the predicted dimensions of the unit of structure agreed within 0.5% with those observed. Structure factors calculated for over fifty forms with the use of the predicted values of the nine parameters determining the atomic arrangement accounted satisfactorily for the observed intensities of reflections on rotation photographs. This extensive agreement is so striking as to permit the structure proposed for brookite (shown in Fig. 3) to be accepted with confidence.

The method was then applied in predicting the structure of the orthorhombic crystal topaz, $Al_2SiO_4F_2$.[10] It was assumed that each aluminum ion is surrounded by four oxygen ions and two fluorine ions at the corners

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[10] Linus Pauling, *Proc. Nat. Acad. Sci.*, **14,** 603 (1928).

of a regular octahedron, and each silicon ion by four oxygen ions at the corners of a regular tetrahedron. The length of edge of octahedron and tetrahedron was taken as 2.72 Å., corresponding to crystal radii of 1.36 Å. for both oxygen and fluorine ions. One structure was built up of these polyhedra. On studying its distribution of microscopic symmetry elements, it was found to have the space-group symmetry of V_h^{16}, which is that of topaz. Its unit of structure approximates that found experimentally, and the predicted values of the fifteen parameters determining the atomic arrangement account for the observed intensities of reflection from the pinacoids. This concordance is sufficient to make it highly probable that the correct structure of topaz has been found (Fig. 4).[11]

3. The Principles Determining the Structure of Complex Ionic Crystals.—The success of the coördination method in predicting structures for brookite and topaz has led to the proposal of a set of principles governing the structure of a rather extensive class of complex ionic crystals.

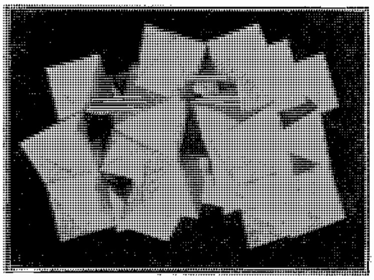

Fig. 3.—The structure of brookite.

The crystals considered are to contain only small cations, with relatively large electric charges, that is, usually trivalent and tetravalent cations, with crystal radii not over about 0.8 Å. All anions are large (over 1.35 Å.) and univalent or divalent. Furthermore, they should not be too highly deformable. The most important anions satisfying this restriction are the oxygen ion and the fluorine ion, with crystal radii 1.35–1.40 Å.[12]

This physical differentiation of the anions and cations under discussion in regard to size and charge finds expression throughout this paper. Markedly different roles are attributed anions and cations in the construction of a crystal; as a result a pronounced distinction between them has been made in the formulation of the structural principles.

Throughout our discussion the crystals will be referred to as composed of ions. This does not signify that the chemical bonds in the crystal are necessarily ionic in the sense of the quantum mechanics; they should not, however, be of the extreme non-polar or shared electron pair type.[13] Thus compounds of copper[14] and many other eighteen-shell atoms cannot be

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[11] Professor W. L. Bragg has written the author that the same ideal structure has been found by J. West (paper to be published in the *Proceedings of the Royal Society*).

[12] The crystal radii used in this paper are those of Pauling, THIS JOURNAL, **49**, 765 (1927).

[13] (a) F. London, *Z. Physik*, **46**, 455 (1928); (b) L. Pauling, *Proc. Nat. Acad. Sci.*, **14**, 359 (1928).

[14] Such as $K_2CuCl_4 \cdot 2H_2O$, whose structure has been determined by S. B. Hendricks and R. G. Dickinson, THIS JOURNAL, **49**, 2149 (1927).

treated in this way. Shared electron pair bonds are also present in complexes containing large atoms with a coördination number of four, such as the molybdate ion, $[MoO_4]^{--}$, the arsenate ion, $[AsO_4]^{--}$, etc.

The principles described in the following six sections have been deduced in part from the empirical study of known crystal structures and in part from considerations of stability involving the crystal energy.

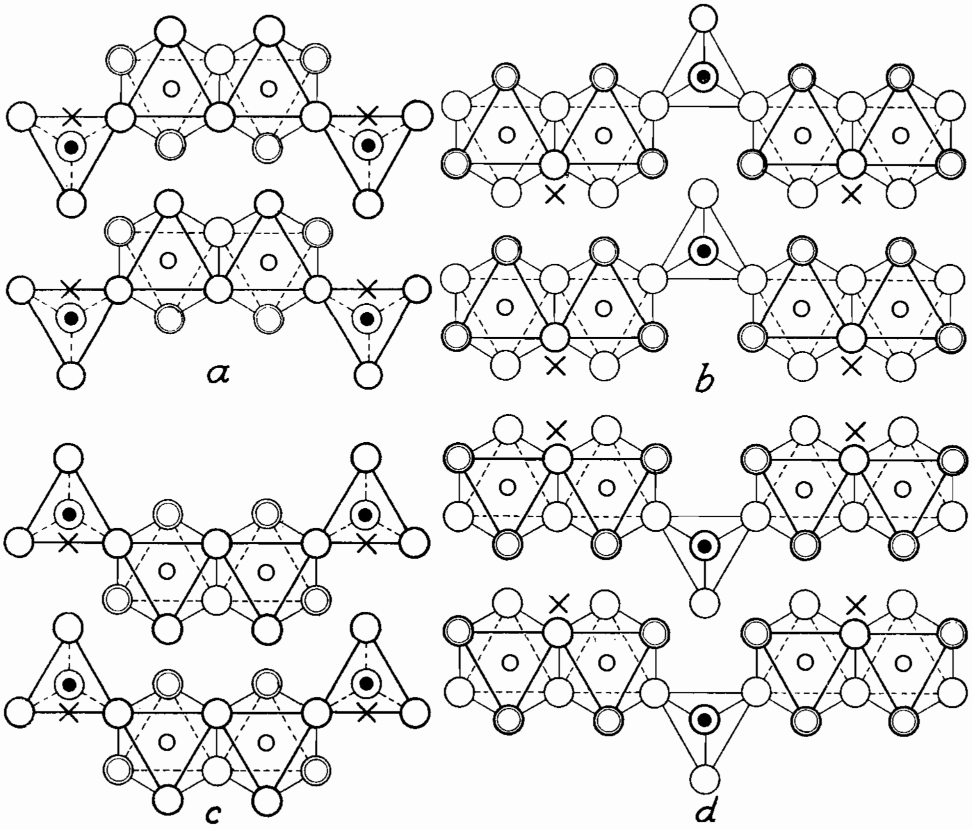

Fig. 4.—The structure of topaz. The layers are to be superposed in the order *abcd*, with *d* uppermost. The crosses are the traces of the corners of the unit of structure in the plane of the paper. Large circles represent oxygen, large double circles fluorine, small open circles aluminum, and small solid circles silicon ions.

4. The Nature of the Coördinated Polyhedra.—*I. A coördinated polyhedron of anions is formed about each cation, the cation–anion distance being determined by the radius sum and the coördination number of the cation by the radius ratio.*

In the case of crystals containing highly charged cations the most important terms in the expression for the crystal energy are those representing the interaction of each cation and the adjacent anions. The next terms in importance are those representing the mutual interaction of the anions. The negative Coulomb energy causes each cation to attract to itself a number of anions, which approach to the distance at which the Coulomb attraction is balanced by the characteristic cation–anion repulsive forces. This distance is given with some accuracy by the sum of the crystal radii of cation and anion.[12]

If too many anions are grouped about one cation, the anion–anion repulsion becomes strong enough to prevent the anions from approaching this closely to the cation. The resultant increase in Coulomb energy causes such a structure to be unstable when the anion–cation distance is increased to a value only slightly greater than the radius sum. Approximate lower limits of the radius ratio (the ratio of cation radius to anion radius) leading to a stable structure with given coördination number can accordingly be calculated purely geometrically.[15,12] The minimum radius ratios for tetrahedra, octahedra and cubes are given in Table I.

TABLE I

RADIUS RATIOS AND COÖRDINATION NUMBERS

Polyhedron	Coördination number	Minimum radius ratio
Tetrahedron	4	$\sqrt{3}/\sqrt{2} - 1 = 0.225$
Octahedron	6	$\sqrt{2} - 1 = 0.414$
Cube	8	$\sqrt{3} - 1 = 0.732$

Since the repulsive forces are determined by the true sizes of ions, and not their crystal radii, the radius ratios to be used in this connection are the ratios of the univalent cation radii to univalent anion radii.[12] Values of this ratio for small ions are given in Table II, together with predicted and observed coördination numbers, the agreement between which is excellent.

TABLE II

COÖRDINATION NUMBERS FOR IONS IN OXIDES

Ion	Radius ratio	Predicted coördination number	Observed coördination number	Strength of electrostatic bonds
B^{+++}	0.20	3 or 4	3 or 4	1 or $^3/_4$
Be^{++}	.25	4	4	$^1/_2$
Li^{+}	.34	4	4	$^1/_4$
Si^{++++}	.37	4	4	1
Al^{+++}	.41	4 or 6	6	$^3/_4$ or $^1/_2$
Mg^{++}	.47	6	6	$^1/_3$
Ti^{++++}	.55	6	6	$^2/_3$
Sc^{+++}	.60	6	6	$^1/_2$
Mo^{++++++}	.53	6	6	1
Nb^{+++++}	.57	6	6	$^5/_6$
Zr^{++++}	.62	6	6 or 8	$^2/_3$ or $^1/_2$

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[15] Such calculations were first made and substantiated by comparison with observed structures in some cases by V. M. Goldschmidt, "Geochemische Verteilungsgesetze der Elemente," Oslo, **1927**.

The radius ratio for B^{+3} is only a little less than the lower limit for tetrahedra. The usual coördination number for boron with oxygen is 3 (in the borate ion, $[BO_3]^{-3}$). It is four, however, in the 12-tungstoborate ion,[16] in which a stabilizing influence is exerted by the tungsten octahedra.

So far as I know, Al^{+3} has the coördination number 6 in all of its compounds with oxygen the structures of which have been determined. The coördination number 4 would also be expected for it, however; it is probable that it forms tetrahedra in some of its compounds, as, for example, γ-alumina, the cubic form of Al_2O_3, and the feldspars, in which there occurs replacement of Na^+ and Si^{+4} by Ca^{++} and Al^{+3}. This possibility is further discussed in Section 11.

Zr^{+4} has the coördination number 8 in zircon. The polyhedron of oxygen ions about it is, however, not a cube. It is on account of the ease with which these polyhedra are distorted that large cations, with coördination numbers greater than six, are not included in the field of application of the suggested principles. Octahedra and tetrahedra retain their approximate shapes even under the action of strong distorting forces, and, moreover, rules have been formulated governing the distortion that they do undergo (Section 9).

5. The Number of Polyhedra with a Common Corner. The Electrostatic Valence Principle.—The number of polyhedra with a common corner can be determined by the use of an extended conception of electrostatic valence. Let ze be the electric charge of a cation and ν its coördination number. Then the *strength of the electrostatic valence bond* going to each corner of the polyhedron of anions about it is defined as

$$s = \frac{z}{\nu} \tag{2}$$

Let $-\zeta e$ be the charge of the anion located at a corner shared among several polyhedra. We now postulate the following *electrostatic valence principle: II. In a stable coördination structure the electric charge of each anion tends to compensate the strength of the electrostatic valence bonds reaching to it from the cations at the centers of the polyhedra of which it forms a corner; that is, for each anion*

$$\zeta = \Sigma_i \frac{z_i}{\nu_i} = \Sigma_i s_i \tag{3}$$

In justification of this principle it may be pointed out that it places the anions with large negative charges in positions of large positive potentials; for the bond strength of a cation gives approximately its contribution to the total positive potential at the polyhedron corner (the factor $1/\nu$ accounting for the larger cation–anion distance and the greater number of adjacent anions in the case of cations with larger coördination number),

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[16] Pauling, unpublished material.

and the application of the principle requires that the sum of these potentials be large in case the valence of the anion is large.

It is not to be anticipated that Equation 3 will be rigorously satisfied by all crystals. It should, however, be always satisfied approximately. As a matter of fact, almost all crystals which have been investigated conform to the principle. Equation 3 is necessarily true for all crystals the anions of which are crystallographically equivalent, such as corundum, Al_2O_3,[17] rutile, anatase, spinel, $MgAl_2O_4$, garnet, $Ca_3Al_2Si_3O_{12}$,[18] cryolithionite, $Na_3Li_3Al_2F_{12}$,[19] etc. It is also satisfied by topaz; each oxygen ion, common to one silicon and two aluminum ions, has $\Sigma s_i = 2$ (see Table II for a list of values of s), while each fluorine ion, attached to two aluminum ions only, has $\Sigma s_i = 1$. Similarly in beryl some oxygen ions are shared between two silicon ions, and some between one silicon, one beryllium and one aluminum ion; in each case $\Sigma s_i = 2$. In chondrodite, $H_2Mg_5Si_2O_{10}$, humite, $H_2Mg_7Si_3O_{14}$, and clinohumite, $H_2Mg_9Si_4O_{18}$, there are oxygen ions common to one silicon tetrahedron and three magnesium octahedra ($\Sigma s_i = 2$), and OH^- groups common to three magnesium octahedra ($\Sigma s_i = 1$). This list of examples could be largely extended.

6. The Sharing of Edges and Faces.—The electrostatic valence principle indicates the number of polyhedra with a common corner but makes no prediction as to the number of corners common to two polyhedra; that is, whether they share one corner only, two corners defining an edge, or three or more corners defining a face. In rutile, brookite and anatase, for example, each oxygen ion is common to three titanium octahedra (and hence has $\Sigma s_i = 2$, satisfying Equation 3); but the number of edges shared by one octahedron with adjoining octahedra is two in rutile, three in brookite and four in anatase. In corundum on the other hand, each aluminum octahedron shares one face and three edges with other octahedra. The reason for this difference is contained in the following rule. *III. The presence of shared edges, and particularly of shared faces, in a coördinated structure decreases its stability; this effect is large for cations with large valence and small coördination number, and is especially large in case the radius ratio approaches the lower limit of stability of the polyhedron.*

This decrease in stability arises from the cation–cation Coulomb terms. The sharing of an edge between two regular tetrahedra brings the cations at their centers to a distance from each other only 0.58 times that obtaining in case the tetrahedra share a corner only; and the sharing of a face decreases this distance to 0.33 times its original value (Fig. 5). The corresponding positive Coulomb terms cause a large increase in the crystal energy and decrease in the stability of the structure, especially for highly

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[17] Linus Pauling and S. B. Hendricks, This Journal, **47**, 781 (1925).

[18] G. Menzer, *Z. Krist.*, **63**, 157 (1926).

[19] G. Menzer, *ibid.*, **66**, 457 (1927).

charged cations. The effect is not so large for regular octahedra, amounting to a decrease in the cation–cation distance to the fractional value 0.71 for a shared edge and 0.58 for a shared face.

These calculated decreases are valid only in case the change in structure is not compensated by deformation of the polyhedra. Some compensating deformation will always occur; the rules governing deformation (Section 9) show that it will be small in case the radius ratio approaches the lower limit of stability for the polyhedron, and will increase with the radius ratio.

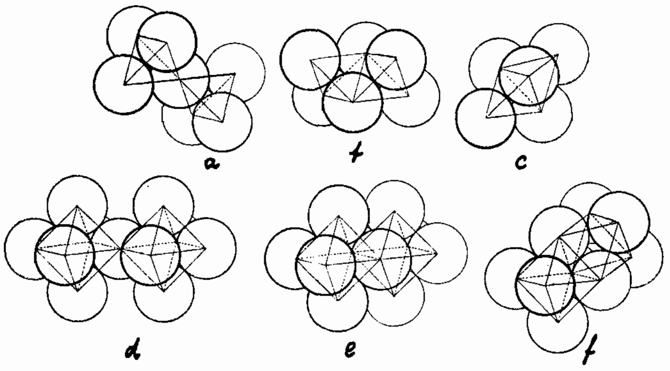

Fig. 5.—*a*, *b* and *c* show two tetrahedra of oxygen ions with a corner, an edge and a face in common; *d*, *e* and *f* show two octahedra of oxygen ions with a corner, an edge and a face in common.

In agreement with expectation, silicon tetrahedra tend to share only corners with other polyhedra when this is possible (as in topaz, $Al_2SiO_4F_2$, etc.), titanium octahedra share only corners and edges, while aluminum octahedra, when constrained by the stoichiometrical formula of the substance, will share faces in some cases, as in corundum, Al_2O_3. The effect of large radius ratio in diminishing the instability due to an increase in the number of shared edges is shown by the approximate equality in free energy of rutile, brookite and anatase, with two, three and four shared edges, respectively. As a matter of fact, the order of stability is just that of the number of shared edges, rutile being the most stable,[20] in agreement with expectation. Many other dioxides also crystallize with the rutile structure but no other is known with the brookite or anatase structure.

The effect of small valence and large coördination number is further shown by the observation that silicon tetrahedra, which share corners only with aluminum octahedra, share edges with magnesium octahedra (in olivine, chondrodite, humite, clinohumite) and with zirconium polyhedra with coördination number eight (in zircon).

7. The Nature of Contiguous Polyhedra.—*IV. In a crystal con-*

[20] C. Doelter, "Handbuch der Mineralchemie," Theodor Steinkopff, Dresden, 1918, Vol. III, Part 1, p. 15.

taining different cations those with large valence and small coördination number tend not to share polyhedron elements with each other. This rule follows directly from the fact that cations with high electric charges tend to be as far apart from each other as possible, in order to reduce their contribution to the Coulomb energy of the crystal.

The rule requires that in silicates the silicon tetrahedra share no elements with each other if the oxygen–silicon ratio is equal to or greater than four (topaz, zircon, olivine, orthosilicates in general). If stoichiometrically necessary, corners will be shared between silicon tetrahedra, but not edges or faces. In the various forms of silicon dioxide all four corners of each tetrahedron are shared with adjoining tetrahedra. In diorthosilicates the Si_2O_7 group is formed of two tetrahedra sharing a corner. The metasilicates should not contain groups of two tetrahedra with a common edge, but rather chains or rings, each tetrahedron sharing two corners (as in beryl, with a ring of six tetrahedra, stable because of the approximation of the tetrahedral angle to 120°). Other silicates are no doubt similar. It is of interest that the electrostatic valence principle requires that corners shared between two silicon tetrahedra be not shared also with other polyhedra; this is true for beryl.

8. The Rule of Parsimony.—*V. The number of essentially different kinds of constituents in a crystal tends to be small.* First, the electrostatic bonds satisfied by all chemically similar anions should be the same if possible (topaz, all oxygen ions common to two aluminum octahedra and one silicon tetrahedron, all fluorine ions common to two aluminum octahedra). This does not require the anions to be crystallographically equivalent (in topaz the oxygen ions are crystallographically of three kinds, in brookite of two kinds); crystallographic non-equivalence does not imply essential difference from the standpoint of the coördination theory. Often the preceding rules do not permit all anions to be alike, as, for example, in the case of silicates with an oxygen–silicon ratio greater than four, in which the four orthosilicate oxygens are necessarily different from the others. In these cases the number of different kinds of anions will, however, be small.

Second, the polyhedra circumscribed about all chemically identical cations should, if possible, be chemically similar, and similar in their contiguous environment, that is, in the nature of the sharing of corners, edges and faces with other polyhedra. For example, each aluminum octahedron in topaz has as corners four oxygen and two fluorine ions, and each shares two edges with other octahedra and four corners with silicon tetrahedra. The titanium octahedron in rutile shares two edges, in brookite three and in anatase four, but no structure is known in which these different octahedra occur together. The polyhedra which are similar in these respects may or may not be crystallographically equivalent, for they may differ in their remote environment. Thus the contiguously similar tetrahedra of silicon atoms about carbon atoms in carborundum are crystallographically of several kinds (five in carborundum I).

9. Distortion of the Polyhedra.—The above rules suffice to indicate the nature of the structure of a given crystal, so that a structure can be composed of regular polyhedra in accordance with them, and its space-group symmetry and approximate dimensions compared with those found by x-ray analysis. In this way a structure can be identified as giving approximately the correct atomic arrangement (as was done for brookite and for topaz); but the actual atomic arrangement may differ considerably from this "ideal" arrangement corresponding to regular polyhedra, as a resultant of distortion of the polyhedra. The investigation of the agreement between observed intensities of x-ray reflections and structure factors calculated for all atomic arrangements involving small displacements from the ideal arrangement would be extremely laborious. It is accordingly desirable to be able to predict with some accuracy the nature and the amount of the distortion to be expected for a given structure.

In not too complicated cases this can be done theoretically by finding the minimum in the crystal energy with respect to variations in the parameters determining the structure, with the use of a theoretical expression for the interionic repulsion potential. Such calculations have been carried out for rutile and anatase,[21] leading to the result that in each case the shared edges of the titanium octahedra are shortened to the length 2.50 Å., other edges being compensatorily lengthened. This distortion is actually found experimentally for these crystals. It was accordingly assumed to hold for brookite also, and the atomic arrangement derived in this way was shown to be in complete agreement with the observed intensities of x-ray reflection.

In general it is not possible to make such calculations on account of the excessive labor involved. It can be seen, however, that the cation–cation repulsion will shorten shared edges and the edges of shared faces, and reasonably confident application may be made of the following rule. Polyhedra of oxygen ions about trivalent and tetravalent cations are distorted in such a way as to shorten shared edges and the edges bounding shared faces to a length of about 2.50 Å. Edges bounding shared faces have been observed to be shortened to 2.50 Å. in corundum, Al_2O_3, and to 2.55 Å. in hematite, Fe_2O_3, in agreement with the foregoing rule.

It is furthermore to be anticipated that the cation–cation repulsion will operate in some cases to displace the cations from the centers of their coördinated polyhedra. This action will be large only in case the radius ratio approaches the lower limit for stability, so that the size of the polyhedron is partially determined by the characteristic anion–anion repulsive

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[21] Linus Pauling, *Z. Krist.*, **67**, 377 (1928).

forces (the distribution of closely neighboring cations must, of course, be one-sided in addition). Hematite and corundum provide an example of this effect. In these crystals each octahedron shares a face with another octahedron. Now in an iron octahedron, with radius ratio about 0.48, the repulsive forces principally effective in determining the interionic distances are those between iron and oxygen ions. The Coulomb repulsion of the two iron ions accordingly can produce only a small displacement of these ions from the octahedron centers; the iron ions in hematite are observed to be 2.06 Å. from the oxygen ions defining the shared face and 1.99 Å. from the other oxygen ions. In an aluminum octahedron, on the other hand, with radius ratio 0.41, the characteristic repulsive forces between oxygen ions as well as those between oxygen and aluminum ions are operative; as a result of this "double repulsion"[12] the distance from the center of the octahedron to a corner is somewhat greater than the sum of the crystal radii of aluminum and oxygen. The aluminum ions are correspondingly mobile and the aluminum–aluminum Coulomb repulsion is to be expected to cause a large displacement in their positions. This is observed; the two aluminum–oxygen distances in corundum are 1.99 Å. and 1.85 Å.

The nature and approximate amount of the distortion to be expected in other cases can be similarly estimated; an example will be given in a later paper.[16]

10. The Close-Packing of Large Ions.—In piling together polyhedra in the attempt to predict a possible structure for a crystal with the aid of the principles described above, the recognition from the observed dimensions of the unit of structure that the atomic arrangement is probably based on a close-packed arrangement of the anions is often of very considerable assistance, for it indicates the probable orientation of the polyhedra, which can then be grouped together to form the completed structure. This was done in the determination of the structure of topaz and contributed considerably to the ease of solution of the problem. The approximation of the dimensions of the unit of structure of topaz to those of a close-packed structure does not, however, suffice to determine the positions of the anions, for there are two types of close-packing, simple hexagonal and double hexagonal,[22] which have these dimensions. This ambiguity

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[22] An infinity of equally close-packed arrangements of spheres can be made from the close-packed layers A, with a sphere at $X = 0$, $Y = 0$ (X, Y and Z being hexagonal coördinates), B, with a sphere at $X = {}^1/_3$, $Y = {}^2/_3$, and C, with a sphere at $X = {}^2/_3$, $Y = {}^1/_3$. For simple hexagonal close-packing these layers are superposed in the order ABABAB..., for cubic close-packing in the order ABCABC... for double hexagonal close-packing in the order ABACABAC..., and so on, with ever-increasing complexity. In only the first two are the spheres crystallographically equivalent, and only these two have been generally recognized in the past; this restriction is, however, undesirable from the standpoint of the coördination theory.

was no serious obstacle in the prediction of the structure by the coördination method; the octahedra and tetrahedra were suitably piled together and the resultant arrangement of oxygen and fluorine ions was found to be double hexagonal close-packing.

Brookite is also based upon a double hexagonal close-packed arrangement of the oxygen ions. The dimensions of the unit of structure differ so much on account of distortion from those for the ideal arrangement, however, that the existence of close-packing was recognized only after the structure had been determined.

It may be pointed out that in some structures easily derivable with the coördination theory, such as the rutile structure, the anion arrangement approximates no type of close-packing whatever.

11. **Applications of the Theory.**—As an illustration of the application of the foregoing principles some predictions may be made regarding the structure of cyanite, andalusite and sillimanite, the three forms of Al_2SiO_5. From the rule of parsimony we expect all aluminum octahedra to be similar and all silicon tetrahedra to be similar. Let the number of octahedra one corner of which is formed by the i^{th} oxygen ion be α_i; then the stoichiometrical oxygen–aluminum ratio, 5:2, requires that

$$\sum_i \frac{1}{\alpha_i} = \frac{5}{2} \qquad (4)$$

in which the sum is taken over the six oxygen ions forming one octahedron. Four out of five oxygen ions, in accordance with Rule IV, will be distinguished through being attached to silicon ions; this fact is expressed by the equation

$$\sum_i{}' \frac{1}{\alpha_i} = 2 \qquad (5)$$

in which the prime signifies that the sum is to be taken over these oxygen ions only. Let us now assume that the oxygen ions are of only two kinds with respect to their values of α, those attached to silicon ions, n_1 in number, forming one class, and those not attached to silicon ions, n_2 in number, forming the other class. Equations 4 and 5 then become

$$\left.\begin{aligned} \frac{n_1}{\alpha_1} + \frac{n_2}{\alpha_2} &= 5/2 \\ \frac{n_1}{\alpha_1} &= 2 \end{aligned}\right\} \text{ with } n_1 + n_2 = 6 \qquad (6)$$

The only solution of these equations involving integers is $n_1 = 4$, $\alpha_1 = 2$, $n_2 = 2$, $\alpha_2 = 4$. Thus about each aluminum ion there will be four oxygen ions common to two aluminum octahedra and one silicon tetrahedron, and two oxygen ions common to four octahedra.[23] For both kinds of oxy-

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[23] It is possible that the aluminum octahedra may be of more than one kind. In this case average values of the sums would have to be used in Equations 4 and 5, and the equations would no longer possess a single solution.

gen ions $\Sigma s_i = 2$, so that the principle of electrostatic valence, which was not used in the derivation of Equation 6, is satisfied.

This result, while limiting considerably the number of possible structures for these crystals, by no means determines their structures. Further information is provided by Rule III, from which it is to be expected that the silicon tetrahedra share only corners with aluminum octahedra, and the octahedra share only corners and edges (and possibly one face) with each other.

These predictions are not incompatible with Professor Bragg's assignment of a cubic close-packed arrangement of oxygen ions to cyanite.[7a] They are, however, in pronounced disagreement with the complete atomic arrangement proposed by Taylor and Jackson,[24] whose suggested structure conflicts with most of our principles. Their structure is far from parsimonious, with four essentially different kinds of octahedra and two of tetrahedra. Each silicon tetrahedron shares a face with an octahedron, contrary to Rule III. The electrostatic valence principle is not even approximately satisfied; one oxygen ion, common to four aluminum octahedra and one silicon tetrahedron, has $\Sigma s_i = 3$, while another, common to two octahedra only, has $\Sigma s_i = 1$. For these reasons the atomic arrangement seems highly improbable.

The coördination theory and the principles governing coördinated structures provide the foundation for an interpretation of the structure of the complex silicates and other complex ionic crystals which may ultimately lead to the understanding of the nature and the explanation of the properties of these interesting substances. This will be achieved completely only after the investigation of the structures of many crystals with x-rays. To illustrate the clarification introduced by the new conception the following by no means exhaustive examples are discussed.

Let us consider first the silicates of divalent cations with coördination Number 6, and hence with electrostatic bond strength $s = {}^1/_3$. An oxygen ion forming one corner of a silicon tetrahedron would have $\Sigma s_i = 2$ if it also formed a corner of three R^{++} octahedra; if it were not attached to a silicon ion, it would have to form a corner of six R^{++} octahedra to satisfy the electrostatic valence principle. But six octahedra can share a corner only by combining in the way given by the sodium chloride structure, and this arrangement, involving the sharing of many edges, is expected not to be stable as a part of the structure of a complex silicate.[25] Accordingly, we conclude that no oxygen ions not attached to silicon occur in these silicates; that is, the oxygen–silicon ratio cannot be greater than

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[24] W. H. Taylor and W. W. Jackson, *Proc. Roy. Soc. London,* **119A,** 132 (1928).

[25] The instability of the sodium chloride structure for oxides is shown by the heat of the reactions $CaO + H_2O = Ca(OH)_2 + 15{,}500$ cal. and $MgO + H_2O = Mg(OH)_2 + 9000$ cal.

4:1. The silicates which will occur are orthosilicates, $R^{++}{}_2SiO_4$, metasilicates, $R^{++}SiO_3$, etc. This is verified by observation; no basic silicates of such cations are known, although many normal silicates such as forsterite Mg_2SiO_4, etc., exist.

A univalent anion (F^-, OH^-) may be shared among three R^{++} octahedra alone, so that compounds may occur in which these anions are present in addition to the SiO_4 groups. Such compounds are known: $Mg_3SiO_4(F, OH)_2$, prolectite, $Mg_5(SiO_4)_2(F, OH)_2$, chondrodite, etc.

Compounds of simple structure according to the coördination theory are those in which the number of essentially different kinds of anions is small. In a simple orthosilicate containing aluminum and a divalent cation each oxygen ion would form the corner of a silicon tetrahedron ($s = 1$), an aluminum octahedron ($s = {}^1/_2$), and one or two R^{++} polyhedra (one tetrahedron or two polyhedra with $\nu = 8$). The composition of the substance would then be given by the formula $R^{++}{}_3Al_2Si_3O_{12}$. Similarly, in simple metasilicates there would occur such oxygen ions in addition to those common to two silicon tetrahedra; the corresponding formula is $R^{++}{}_3Al_2Si_6O_{18}$. This result is in striking agreement with observation. The most important double orthosilicates of divalent and trivalent metals are the garnets: $Ca_3Al_2Si_3O_{12}$, grossular, $Ca_3Cr_2Si_3O_{12}$, uvarovite, $Ca_3Fe_2Si_3O_{12}$, topazolite, etc., and the only double metasilicate is beryl, $Be_3Al_2Si_6O_{18}$.

The radius ratio of potassium ion and oxygen ion is 0.76, so that the coördination number to be expected for potassium ion in silicates is 8, the corresponding electrostatic bond strength being ${}^1/_8$. In potassium aluminum silicates containing aluminum octahedra the electrostatic valence principle would require at least four potassium polyhedra to have a common corner together with a silicon tetrahedron and an aluminum octahedron; this is not spatially possible. It is accordingly highly probable that in these compounds, the structure of none of which has yet been satisfactorily investigated with x-rays, the aluminum ions have a coördination number of 4. There could then occur oxygen ions with $\Sigma s_i = 2$ common to a silicon tetrahedron, an aluminum tetrahedron and two potassium polyhedra. The potassium–aluminum ratio would then be 1:1. In a large number of silicates, in particular the important feldspars, this ratio is observed: $KAlSiO_4$, phakelite, $KAlSi_2O_6$, leucite, $KAlSi_3O_8$, potassium feldspar (microcline, orthoclase), $(K, Na)_8Al_8Si_9O_{34}$, nepheline, etc. In other silicates containing more than this amount of aluminum, such as muscovite, $H_2KAl_3Si_3O_{12}$, etc., it is probable that the excess aluminum ions usually have the coördination Number 6.

Other alkali ions (except lithium) also probably have the coördination Number 8 as a rule, and should similarly have a tendency to a 1:1 ratio with aluminum; this is shown in $NaAlSi_3O_8$, albite, $H_2Na_2Al_2Si_3O_{12}$, natrolite, $H_2Cs_4Al_4Si_9O_{27}$, pollucite, etc.

In spodumene, $LiAlSi_2O_6$ and petalite, $LiAlSi_4O_{10}$, it is possible that oxygen ions (with $\Sigma s_i = 2$) are common to a silicon tetrahedron, an aluminum tetrahedron and a lithium tetrahedron (the radius ratio for lithium ion is 0.33).

No aluminum silicates of alkali metals are known in which the $Al^{+3}:R^{+1}$ ratio is less than 1:1.

Summary

A set of principles governing the structure of complex ionic crystals, based upon the assumption of a coördinated arrangement of anions about each cation at the corners of an approximately regular polyhedron, is formulated with the aid of considerations based upon the crystal energy. Included in the set is a new electrostatic principle which is of wide application and considerable power.

It is shown that the known structures of many complex crystals, in particular the complex silicates, satisfy the requirements of these principles.

As an illustration of the application of the principles in the prediction of structures with the coördination theory, some properties of the structures of the three forms of Al_2SiO_5, cyanite, andalusite and sillimanite, are predicted.

It is further shown that the theory requires that no stable basic silicates of divalent metals exist, and that in aluminum silicates of alkali metals there should be at least one aluminum ion for every alkali ion.

The structures of aluminum silicates of divalent metals which are simplest from the coördination standpoint are shown to correspond to the formulas $R_3^{++}Al_2Si_3O_{12}$ and $R_3^{++}Al_2Si_6O_{18}$, which include the most important minerals of this class, the garnets and beryl.

PASADENA, CALIFORNIA

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THE NATURE OF THE CHEMICAL BOND. III. THE TRANSITION FROM ONE EXTREME BOND TYPE TO ANOTHER[1]

By Linus Pauling

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A question which has been keenly argued for a number of years is the following: if it were possible continuously to vary one or more of the parameters determining the nature of a system such as a molecule or a crystal, say the effective nuclear charges, then would the transition from one extreme bond type to another take place continuously, or would it show discontinuities? For example, are there possible all intermediate bond types between the pure ionic bond and the pure electron-pair bond? With the development of our knowledge of the nature of the chemical bond it has become evident that this question and others like it cannot be answered categorically. It is necessary to define the terms used and to indicate the point of view adopted; and then it may turn out, as with this question, that no statement of universal application can be made.

In the following sections, after a discussion of the properties of ionic compounds and compounds containing electron-pair bonds, the transition from one extreme to the other is considered. It is concluded that in some cases the transition could take place continuously, whereas in others an effective discontinuity would appear.

Bond Type and Atomic Arrangement

The properties of a compound depend on two main factors, the nature of the bonds between the atoms, and the nature of the atomic arrangement. It is convenient to consider that actual bonds approach more or less closely one or another of certain postulated extreme bond types (ionic, electron-pair, ion-dipole, one-electron, three-electron, metallic, etc.), or

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[1] A part of the material of this paper was presented to the American Chemical Society at Buffalo, New York, September 2, 1931, under the title "The Structure of Crystals and the Nature of the Chemical Bond."

are intermediate between one extreme type and another, or involve two or more co-existent types. The satisfactory description of the atomic arrangement in a crystal or molecule necessitates the complete determination of the position of the atoms relative to one another. Sometimes individual details of the atomic arrangement are of interest; for example, in case the atoms are held together in part by strong bonds and in part by very weak bonds, it is instructive to mention the type of atomic aggregate formed by the strong bonds (finite molecules or complex ions, or molecules or complex ions of very great extent in one, two or three dimensions). In other cases the number of nearest neighbors of each atom (its coördination number) and their relative positions are items of interest.

There is, of course, a close relation between atomic arrangement and bond type. Thus the four single bonds of a carbon atom are directed toward the corners of a tetrahedron. But tetrahedral and octahedral configurations are also assumed in ionic compounds, so that it is by no means always possible to deduce the bond type from a knowledge of the atomic arrangement.

An abrupt change in properties in a series of compounds, as in the melting points or boiling points of halides, is often taken as indicating an abrupt change in bond type. Thus of the fluorides

	NaF	MgF_2	AlF_3	SiF_4	PF_5	SF_6
M. p.	980°	1400°	1040°	−77°	−83°	−55°

those of high melting points have been described as salts, and the others as covalent compounds. Actually the Al–F bond is no doubt closely similar to the Si–F bond. The abrupt change in properties between AlF_3 and SiF_4 is due to a change in atomic arrangement. In NaF, MgF_2 and AlF_3 the coördination number of the metal (six) is greater than the stoichiometric ratio of non-metal to metal atoms, so that each non-metal atom or ion is held jointly by two or more metal atoms or ions, resulting in high melting and boiling points. In SiF_4, PF_5 and SF_6 the coördination number is just equal to this ratio. The discrete molecules of composition given by the formulas are held only loosely together, and the substances melt and boil easily. As pointed out long ago by Kossel, this ease of fusion and volatilization would be expected for symmetrical ionic molecules, and is not sound evidence for the presence of electron-pair bonds. Volatility does not depend mainly on bond type, but on the atomic arrangement and the distribution of bonds.

The Ionic Bond

The theoretical treatment of the properties of ionic crystals and molecules has been carried farther than that of other types of atomic aggregates. The Born theory of crystal energy permits the calculation to within a few per cent. of the energy of dissociation of an ionic crystal into gaseous ions when the structure of the crystal and the equilibrium interionic distances are known. Moreover, it is now possible to predict interionic distances to within 2 or 3%, with the use either of Goldschmidt's set[2] of ionic radii, derived from the experimentally observed interionic distances in crystals of simple structure, many of which were prepared for the first time and studied with x-rays in his Mineralogical Institute in Oslo, or of a closely similar set obtained[3] by a method of treatment based on the theory of the electron distribution in atoms and ions. The screening constants[4] used in the derivation of this set were derived in part theoretically (for light ions) and in part from the experimental values of the mole refraction of atoms and ions. It has been recently found[5] that screening constants can be obtained purely from observed ionization potentials and x-ray term values. The new set of screening constants is in nearly complete agreement with the old one, which gives a feeling of confidence in this method of treating the properties of many-electron atoms and monatomic ions.

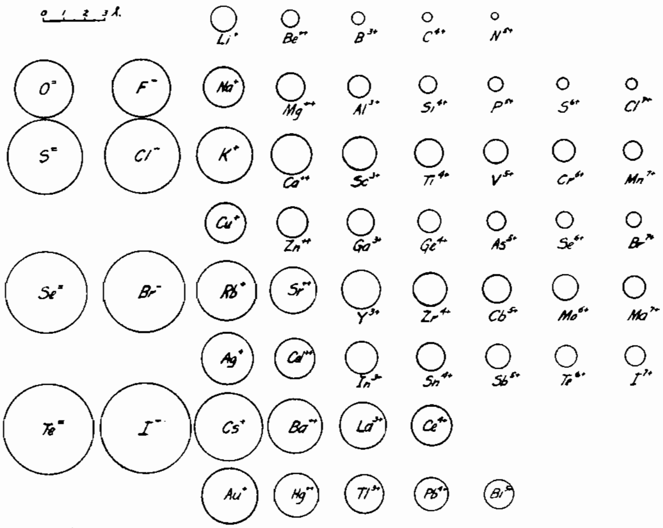

Fig. 1.—The sizes of spherically-symmetrical ions. The radii of the spheres are taken equal to the crystal radii of the ions.

The fundamental character of the understanding of ionic crystals which has been obtained is seen from the nature of the dependence of ionic radii on atomic number, shown in Fig. 3 of Ref. 3. The univalent radii lie on

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[2] V. M. Goldschmidt, "Verteilungsgesetze der Elemente," Oslo, 1926, Vol. VII.

[3] Linus Pauling, THIS JOURNAL, **49**, 765 (1927).

[4] Linus Pauling, *Proc. Roy. Soc.* (London), **A114**, 181 (1927)

[5] Linus Pauling and J. Sherman, *Z. Krist.*, **81**, 1 (1932).

a smooth curve for each isoelectronic sequence; these are corrected in a systematic way for the effect of increasing Coulomb attraction in pulling highly charged ions more closely together to obtain the crystal radii. As is seen in Fig. 1, anions are very large, larger than all cations except those of the alkali metals. Moreover, the anions occur in pairs of nearly the same radius, $O^=$ and F^-, etc. This is the reason that hydroxyl ion and fluorine ion so often replace each other isomorphously in minerals, such as topaz, $Al_2SiO_4(OH,F)_2$. (The proton has little effect on the crystal radius.)

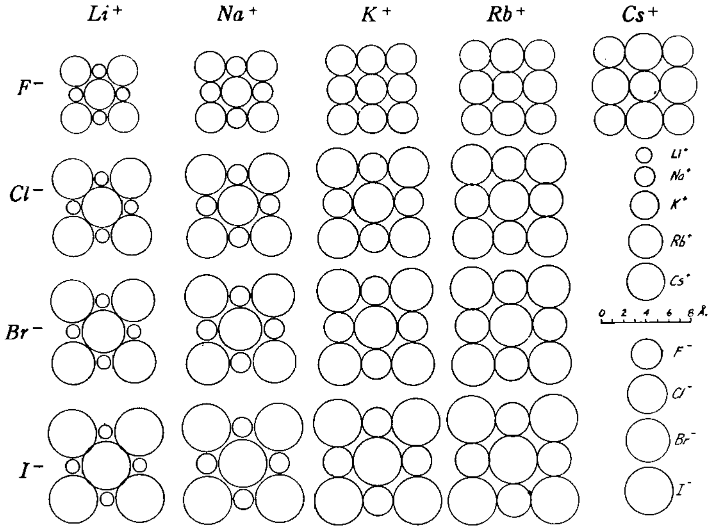

Fig. 2.—The arrangement of ions in cube-face layers of alkali halide crystals with the sodium chloride structure.

The equilibrium interionic distances and accordingly the properties of crystals are influenced not only by the sum of the radii of anion and cation, but also by their ratio, as discussed by Van Arkel and especially by Goldschmidt. This is shown in Fig. 2, representing the alkali halide crystals with the sodium chloride structure. In most of the crystals the anions and cations are in contact. In LiCl, LiBr and LiI, however, the anions are so large relative to the cations that they come into mutual contact, and the size of the unit of structure is determined by the anion radius alone, the cations being left to rattle around in the interstices. This determination of the dimensions of the units and the arrangement of the anions by the anions alone has been especially discussed by W. L. Bragg and co-workers,[6] who have utilized it extensively in studying the structures of silicate minerals. In LiF, NaCl, NaBr and NaI the phe-

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[6] W. L. Bragg and J. West, *Proc. Roy. Soc.* (London), **A114**, 450 (1927).

nomenon of *double repulsion* (anion–cation as well as anion–anion repulsion operative) causes the unit to be larger than would be expected from either the anion–cation or anion–anion radius sum. Anion contact and double repulsion have a striking effect on the course of the properties of the alkali halides, particularly the melting points and boiling points.[7]

The conception of simple ionic crystals as coördinated structures, developed by Ewald, Goldschmidt and others, has been shown to be applicable to complex crystals by W. L. Bragg's determination of the structure of a number of the silicate minerals,[8] and through the study of brookite[9] and topaz[10] led ultimately to the formulation of a set of principles governing the structure of complex ionic crystals.[11] These rules may be illustrated by the application of one of them to the question of the isomorphous replacement of OH^- by F^-. The electrostatic valence rule states that in a stable crystal each anion tends to have its charge balanced by the electrostatic bonds of adjacent cations, the strength of a bond from a cation being taken as the ratio of its charge to its coördination number; in other words, the valence of the cation is considered as evenly distributed among the anions coördinated about it. Thus Si^{4+} with coördination number 4 has bonds of strength 1, Al^{3+} with coördination number 6, bonds of strength $^1/_2$. In topaz, $Al_2SiO_4(OH,F)_2$; chondrodite, $Mg_5Si_2O_8(OH,F)_2$; etc., the OH^- ions are in positions of total strength of bonds from cations other than hydrogen equal to 1, and so they may be replaced by F^- ions. But in staurolite, $H_2FeAl_4Si_2O_{12}$, there are not two oxygens in positions of total bond strength 1, but rather four with total bond strength 3/2, suggesting strongly the presence of two $[OHO]^=$ groups. In consequence fluorine should not be expected to occur in this mineral, in agreement with observation.

The Electron-Pair Bond

It was shown by G. N. Lewis and Irving Langmuir that unique electronic structures involving electron-pair bonds can be assigned with considerable certainty to a great many molecules and crystals. For many others, however, decision between two or more alternative structures has been difficult; moreover, the theory has not led to predictions regarding atomic arrangements other than the postulated tetrahedral arrangement of four electron pairs. Considerable further progress has now been made possible through the deduction from the quantum mechanics of a set of rules regarding electron-pair bonds, and in particular the discovery of a simple semi-quantitative treatment of bond eigenfunctions which

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[7] Linus Pauling, This Journal, **50**, 1036 (1928).

[8] W. L. Bragg, *Z. Krist.*, **74**, 237 (1930).

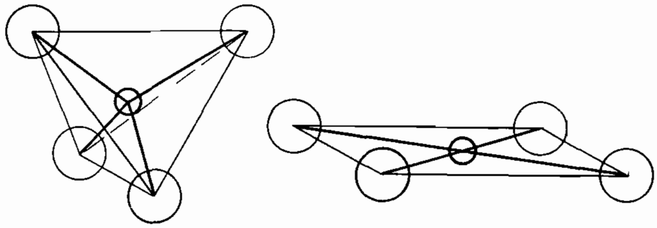
[9] Linus Pauling and J. H. Sturdivant, *ibid.*, **68**, 239 (1928).

[10] Linus Pauling, *Proc. Nat. Acad. Sci.*, **14**, 603 (1928).

[11] Linus Pauling, This Journal, **51**, 1010 (1929).

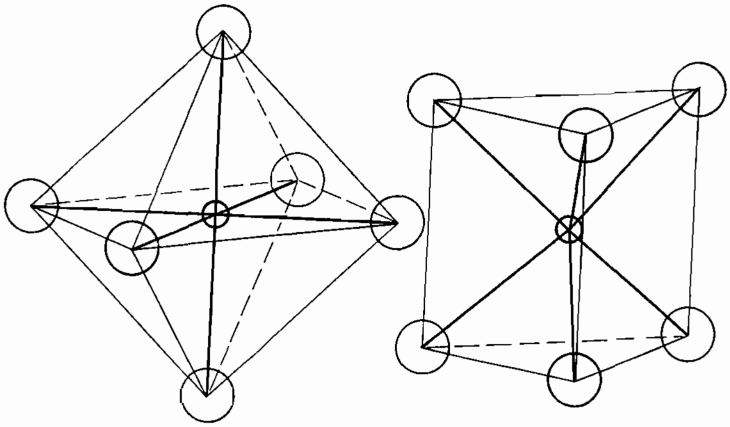
gives much information regarding the strength and mutual orientation of the bonds which can be formed by various atoms.[12]

It has been found that the strength and direction of an electron-pair bond formed by an atom are determined essentially by one electronic eigenfunction. The bond tends to be formed in the direction in which the eigenfunction has its maximum value, and the greater the concentration of the eigenfunction in the bond direction the stronger the bond will be. The spherically-symmetrical *s* eigenfunction can form a bond in any direction of strength 1 according to the semi-quantitative treatment, and a *p* eigenfunction a bond of strength 1.732 in either of two opposite directions. But in most atoms which form four or more bonds



Tetrahedral, sp^3 (2.000). C in diamond and compounds. Zn in $[Zn(CN)_4]^{=}$, etc.

Square, dsp^2 (2.694). Ni in $[Ni(CN)_4]^{=}$, Pd in $[PdCl_4]^{=}$, Pt in $[PtCl_4]^{=}$, Au in $[AuCl_4]^{-}$, etc.



Octahedral, d^2sp^3 (2.923). Co in $[Co(CN)_6]^{\equiv}$, Pd in $[PdCl_6]^{=}$, Pt in $[PtCl_6]^{=}$, etc.

Trigonal–prismatic, (2.983). Mo in MoS_2, and perhaps in $[Mo(CN)_6]^{=}$.

Fig. 3.—The relative orientations of various electron-pair bonds.

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[12] (a) Linus Pauling, *Proc. Nat. Acad. Sci.*, **14**, 359 (1928); (b) THIS JOURNAL, **53**, 1367 (1931); (c) *Phys. Rev.*, **37**, 1185 (1931); (d) J. C. Slater, *ibid.*, **37**, 481 (1931); **38**, 1109 (1931).

the *s* and *p* eigenfunctions do not retain their identity, being instead combined to form new eigenfunctions, better suited to bond formation. The best bond eigenfunction which can be formed from the one *s* and three *p* eigenfunctions in a given shell has the strength 2.000. Moreover, three other equivalent bond eigenfunctions can also be formed, and the four bonds are directed toward the corners of a regular tetrahedron (Fig. 3). This result immediately gives the quantum-mechanical justification of the chemist's tetrahedral carbon atom, with all its properties, such as free rotation about a single bond (except when restricted by steric effects) and lack of it about a double bond, and shows that many other atoms direct their bonds toward tetrahedron corners.

The nature of possible bond eigenfunctions involving *d* eigenfunctions depends on the number of *d* eigenfunctions available. Bivalent nickel contains eight unshared 3*d* electrons, which require at least four of the five 3*d* eigenfunctions, leaving only one for bond formation. When this is combined with the 4*s* and the three 4*p* eigenfunctions of nearly the same energy, it is found that not five but only four equivalent bond eigenfunctions, of strength 2.694, can be formed, and that these are directed toward the corners of a square. Thus the $[Ni(CN)_4]^{=}$ ion should have a square rather than a tetrahedral configuration. This was suggested for complexes containing bivalent palladium and platinum by Werner, and was verified by Dickinson[13] by the x-ray study of K_2PdCl_4 and K_2PtCl_4. We expect a similar configuration for complexes of trivalent copper, silver and gold.

When two *d* eigenfunctions are available, as in trivalent cobalt, quadrivalent palladium and platinum, etc., six equivalent bond eigenfunctions of strength 2.923 and directed toward the corners of a regular octahedron can be formed. These form the bonds in a great many octahedral complexes.

It is interesting to note, as pointed out to me by Mr. J. L. Hoard, that these considerations lead to an explanation of the stability of trivalent cobalt in electron-pair bond complexes as compared to ionic compounds. The formation of complexes does not change the equilibrium between bivalent and trivalent iron very much, as is seen from the electrode potentials, while a great change is produced in the equilibrium between bivalent and trivalent cobalt.

$$\left.\begin{array}{rcll} Fe^{++} & = & Fe^{+++} + E^- & -0.74\text{ v.} \\ [Fe(CN)_6]^{\overline{\equiv}} & = & [Fe(CN)_6]^{\equiv} + E^- & -0.49\text{ v.} \end{array}\right\rangle -0.25\text{ v.}$$

$$\left.\begin{array}{rcll} Co^{++} & = & Co^{+++} + E^- & -1.8\text{ v.} \\ [Co(CN)_6]^{\overline{\equiv}} & = & [Co(CN)_6]^{\equiv} + E^- & +0.3\text{ v.} \end{array}\right\rangle -2.1\text{ v.}$$

The effect is so pronounced that covalent compounds of bivalent cobalt are difficult to prepare, decomposing water with the liberation of hydro-

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[13] R. G. Dickinson, THIS JOURNAL, **44**, 2404 (1922).

gen. The explanation is contained in Fig. 4. In the ions Co^{++}, Co^{+++}, Fe^{++}, and Fe^{+++} there is room for all unshared electrons in the 3*d* subshell or inner subshells. When octahedral bonds are formed only three 3*d* eigenfunctions are left for occupancy by unshared electrons. These are enough for bivalent and trivalent iron and for trivalent cobalt, but they hold only six of the seven electrons of bivalent cobalt. The seventh electron must accordingly occupy an outer unstable orbit, causing the complex to become unstable.

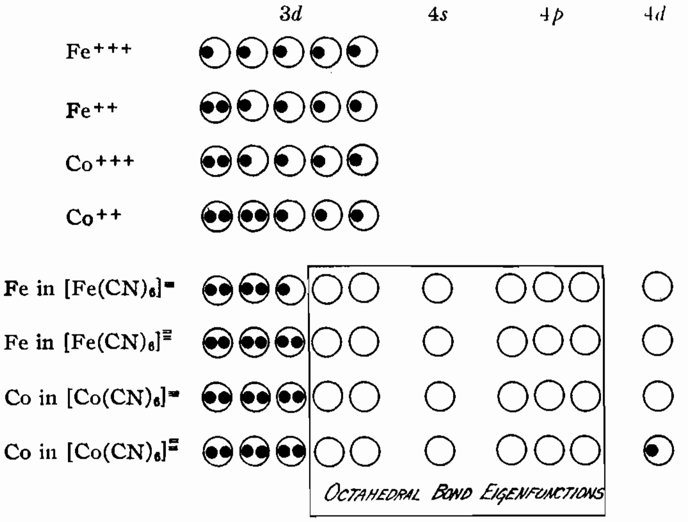

Fig. 4.—A diagram representing the electronic configurations of certain complex ions. Each circle represents a single-electron positional eigenfunction, each dot an electron.

The structure[14] of the mineral molybdenite, MoS_2, in which each molybdenum atom is surrounded by six sulfur atoms at the corners of a triangular prism, has long been puzzling, for if the crystal were composed of ions an octahedral arrangement would be more stable, and the large number of octahedral complexes containing electron-pair bonds would suggest an octahedral electron-pair bond structure also. But the molybdenum atom contains only two unshared *d* electrons, and it has been recently found by Mr. Ralph Hultgren that in this case six equivalent bonds of strength 2.983 (considerably greater than that of octahedral bond eigenfunctions) directed toward the corners of a trigonal prism may be formed. The theoretical ratio of altitude to base of the prism is 1000, while the experimental value is 1.007 ± 0.038. It would be interesting to determine whether a similar configuration holds for $[Mo(CN)_6]^{=}$; a di-substituted complex such as $[Mo(CN)_4Cl_2]^{=}$ should then exist in three isomeric forms.

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[14] R. G. Dickinson and Linus Pauling, THIS JOURNAL, **45**, 1466 (1923).

The Transition from One Bond Type to Another

The question as to whether or not the transition from one extreme bond type to another would take place continuously as one or more parameters determining the nature of the atoms involved were varied can now, I believe, be satisfactorily answered. The quantum mechanics shows that if, for a polyatomic system having a given atomic arrangement, there are two possible electronic states with nearly the same energy and with the same multiplicity, then it is necessary to consider mixed states, with an eigenfunction for the system formed by linear combination of the eigenfunctions for the first two states. The actual state of the system would lie somewhere between the two postulated extremes. If the states have different multiplicities, however, they cannot be combined with one another (so long as spin-orbit interactions of the electrons are negligible). So although every energy level of a system changes continuously as parameters defining the system are changed, the normal state may show a discontinuity at the crossing of two non-combining levels.

This discussion is most easily made precise by the use of the energy integral. If ψ represents an arbitrary normalized wave function for a system, then the integral

$$E = \int \psi^* H \psi d\tau$$

in which H is the Hamiltonian operator, gives a value of E which must be equal to W_0, the energy of the lowest state of the system, or be greater than W_0. For E to be equal to W_0 it is necessary that ψ be the eigenfunction for the normal state of the system, and the closer ψ approaches this eigenfunction the smaller the difference $E - W_0$ will become. Now let us set up a function ψ_1 of the coördinates of the system which represents a conceivable state of the system, for example, a state corresponding to a given Lewis electronic formula for a molecule. We can then evaluate the electronic energy E_1 as a function of the internuclear distances by substituting ψ_1 for ψ in the above equation. Similarly a function ψ_2 corresponding to an alternative electronic formula can be used to calculate E_2. If E_1 lies far below E_2, then the function ψ_1 is a much better approximation to the normal state of the system than ψ_2, and, in the absence of further alternatives, the electronic formula corresponding to ψ_1 is to be accepted. In general, if ψ_1 and ψ_2 have the same symmetry character and especially the same multiplicity (that is, the same number of unpaired electrons), values of E for a more general function $a\psi_1 + b\psi_2$ should be calculated. When E_1 and E_2 are not much different in value and when the interaction terms between ψ_1 and ψ_2 are large, it is found that the function giving the best approximation to the eigenfunction for the normal state of the system is neither ψ_1 nor ψ_2, but the combination of them, with the coefficients a and b of the same order of magnitude. In this case neither electronic formula alone can be assigned the molecule, but instead both, with one perhaps more important than the other. The molecule could be described as fluctuating rapidly between the two electronic formulas, and achieving stability greater than that of either formula through the "resonance energy" of this fluctuation.

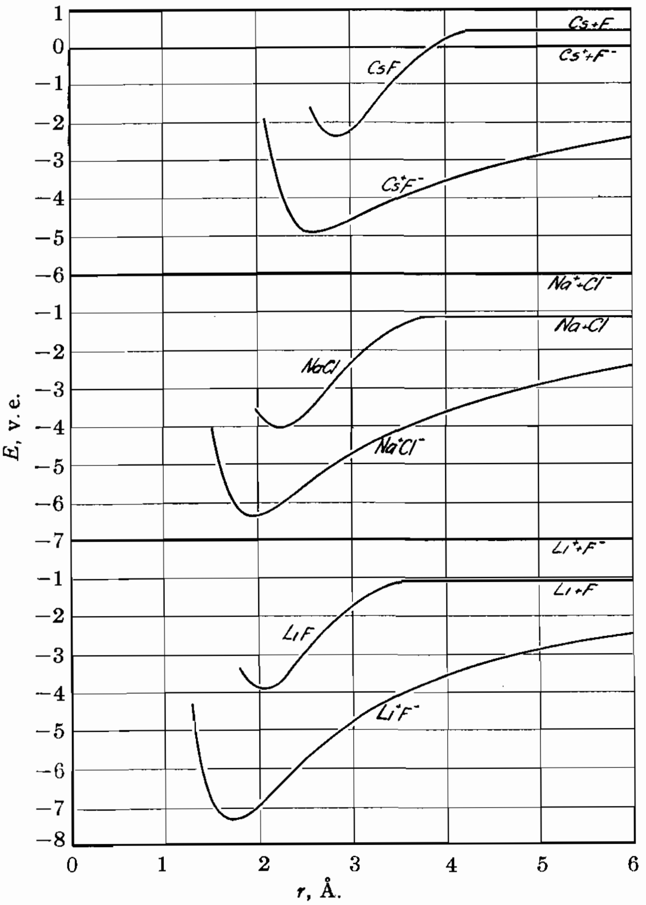

Fig. 5.—Potential energy curves for alkali halide molecules. The upper curve of each pair corresponds to electron-pair bond formation ($\mathrm{Cs}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{F}}}:$, etc.), the lower to an ionic structure ($\mathrm{Cs}^+\mathrm{F}^-$, etc.).

It is impossible to carry out this program of directly evaluating the energy integral except in the simplest cases; but rough energy curves for various electronic structures can often be constructed by semi-empirical methods, and the discussion outlined above carried out with them. Thus information regarding the repulsive forces between ions obtained from the observed properties of ionic crystals can be used for ionic states of molecules. In Fig. 5 the lower curve of each pair represents the electronic energy as a function of the internuclear separation for extreme ionic molecules CsF, NaCl and LiF. The attractive potential is taken as the Coulomb potential $-e^2/r$, polarization being neglected. (Polarization might lower the minimum of each curve by 1 or 2 v. e.) The repulsive potential used is b/r^9, with b given the values which lead to the observed equilibrium separations in the crystals. The upper curves, which represent shared-electron-pair structures $\mathrm{Cs}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{F}}}:$, etc., are Morse curves with a dissociation energy of about 3 v. e., a value found to be correct to within ±1 v. e. for most electron-pair bonds. The relative positions of the curves are determined by ionization potentials and electron affinities.[15] It is seen that the ionic structures are much more stable than the electron-pair bond structures, so that the normal states of these alkali halide molecules (and presumably of the others) can be described as essentially ionic. There is, no doubt, some contribution of the electron-pair bond structure to the function $a\,\psi_{\text{ionic}} + b\,\psi_{\text{electron-pair}}$ which best approximates the normal state; but the coefficient b is small compared with a, which is nearly unity.

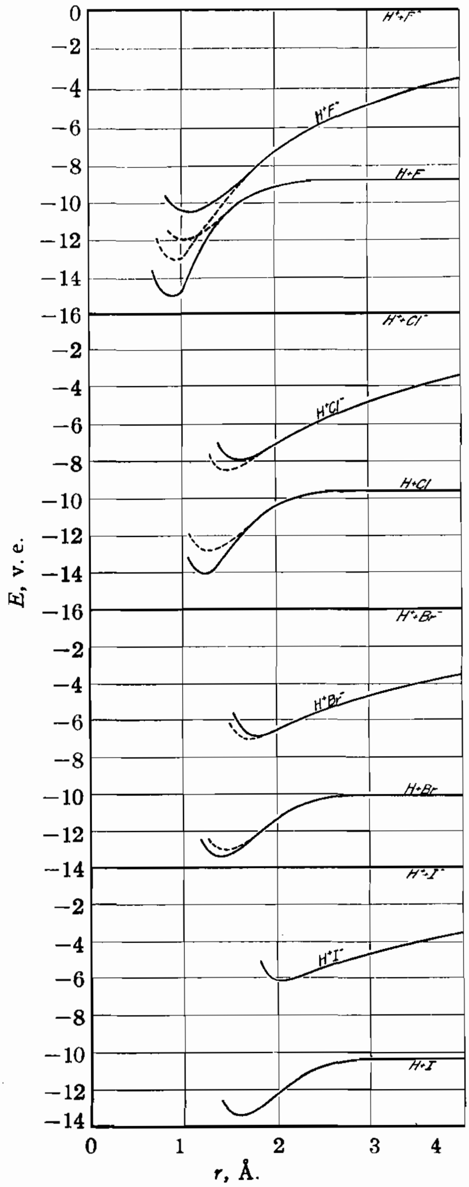

Fig. 6.—Potential energy curves for hydrogen halide molecules.

In Fig. 6 similar curves are shown for the hydrogen halide molecules. The electron-pair bond structures $\mathrm{H}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{F}}}:$, etc., are

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[15] The values used are from a paper by Mr. J. Sherman, which will appear early in 1932 in *Chemical Reviews*.

represented by Morse curves of about 3 v. e. dissociation energy, with their minima at distances given by electron-pair bond radii.[16] The ionic curves were calculated with the use of hydrogen-like eigenfunctions, as described in a previous paper.[4] The screening constants used are from the revised set.[5] Polarization has been neglected.

It is seen that for hydrogen fluoride the two curves intersect, the minimum for the ionic curve lying below the other. In the region around r = 1 Å. the interaction between the two assumed structures would be large, and the resonance energy would be expected to amount to 1 or 2 v. e. A potential curve representing the normal state has been drawn in, corresponding to a combination of the ionic and electron-pair bond structures. The curve is drawn so that the minimum lies at the observed equilibrium separation of the nuclei, and at the energy level given by thermochemical data. An excited state also formed by combining the two original structures is shown.[17] In the eigenfunction $a\ \psi_{\text{ionic}} + b\ \psi_{\text{electron-pair}}$ approximating that of the normal state, the coefficients a and b are of the same order of magnitude, with a somewhat larger than b. The normal HF molecule is represented by neither the formula H^+F^- nor $\mathrm{H}:\underset{..}{\overset{..}{\mathrm{F}}}:$, but by both, with H^+F^- somewhat more important than $\mathrm{H}:\underset{..}{\overset{..}{\mathrm{F}}}:$. The bond is largely ionic.

The curves for HCl, HBr and HI do not cross, in the main because the ionic radii of Cl^-, Br^- and I^- are much larger than that of F^-. Accordingly the normal states of these molecules are essentially of the electron-pair bond type, and the formulas $\mathrm{H}:\underset{..}{\overset{..}{\mathrm{Cl}}}:$, $\mathrm{H}:\underset{..}{\overset{..}{\mathrm{Br}}}:$, and $\mathrm{H}:\underset{..}{\overset{..}{\mathrm{I}}}:$ may be used as giving a reasonably accurate picture of the state of the molecules. This conclusion had been reached before on the basis of other arguments, especially the tendency of fluorine alone of the halogens to form hydrogen bonds.

There is no doubt some interaction of the two structures for these molecules also, changing the curves by a small amount, as indicated for HCl and HBr.

It is not possible at the present time to carry out similar calculations for more complicated molecules, inasmuch as a small change in internuclear distance produces a very large change in the Coulomb energy of highly charged ions, and the equilibrium distances cannot yet be accurately predicted. Certain less specific conclusions can, however, be drawn. For example, the energy curves for a number of structures of SiF_4 (the pure ionic $Si^{4+}F^-{}_4$, and those with one, two, three or four fluorine atoms attached by electron-pair bonds) are found to have their minima

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[16] Taken from a set contained in a paper by Linus Pauling and M. L. Huggins, to appear in *Z. Krist.*

[17] The values of a and b for this state must be such as to make the function orthogonal to that of the normal state.

close together. Neither the ionic extreme $Si^{4+}F^{-}_4$ nor the electron-pair bond extreme $\begin{array}{c} :\ddot{F}: \\ :\ddot{F}:\ddot{Si}:\ddot{F}: \\ :\ddot{F}: \end{array}$ represents the actual normal state of the molecule, which instead lies somewhere between them. There is little evidence as to which extreme is approached more closely. A tetrahedral configuration would be expected in either case.

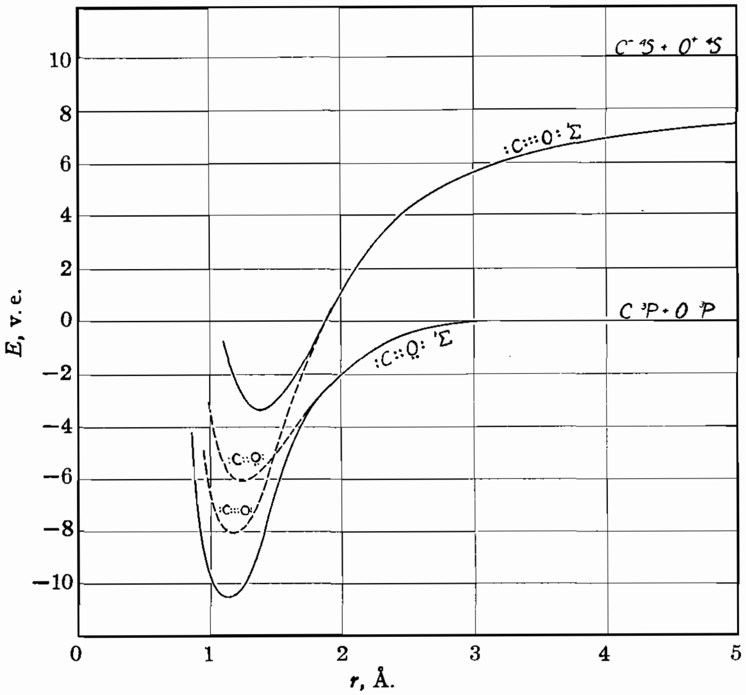

Fig. 7.—Potential energy curves for the carbon monoxide molecule.

Silica, the silicates and, in general, crystals containing oxygen or fluorine and metal atoms which can form noble-gas type cations are found to satisfy the electrostatic valence rule and the other rules for ionic crystals, which indicates that the ionic character of these substances is of greatest importance. The sulfides of metals other than the alkalies and alkaline earths, on the other hand, do not satisfy these rules; magnetic evidence further shows these substances not to be ionic.

The discussion of electronic energy curves also throws light on such questions as the structure of the carbon monoxide molecule. The empirical study of potential curves obtained from band spectral data has shown[18] that for atoms in the first row of the periodic system a double bond leads

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[18] An account of this work will be published at some future time.

to a dissociation energy of about 6 v. e. and a triple bond to 9 v. e. In Fig. 7 the Morse curve due to normal atoms C^3P and O^3P, extended by dashes to the left, corresponds to the double-bonded structure :C::Ö:. The upper curve with its dashed extension corresponds to the structure :C:::O:, formed from the ions C$^-$ ^4S and O$^+$ ^4S. In drawing this curve a Coulomb curve for large r was combined with a 9 v. e. Morse curve for small r in such a way as to make the total dissociation energy 9 v. e. plus $\frac{e^2}{r_0}\left(1 - \frac{1}{n}\right)$, with n placed equal to 5 and r_0 to 1.25 Å. The electron affinity of carbon was estimated at 3.5 v. e.

It is evident that the normal state of CO is not the double-bonded state, especially since the normal molecule is found experimentally to lie 10.3 v. e. (rather than 6 v. e.) below the normal atoms. The triple-bonded ionic structure leads to a curve which crosses the other, dropping to about -8 v. e. Strong interaction between these two $^1\Sigma$ structures is to be expected for small values of r, giving rise to combined states represented by the two potential curves drawn in the figure. The normal state of CO is accordingly a combination of :C::Ö: and :C:::O:, with the latter of greater importance. On separating the nuclei the electronic structure changes, until from about 2 Å. on the double-bonded structure alone is present.[19]

The Magnetic Criterion[12b]

Many compounds of transition elements behave differently from the substances discussed above, for the reason that the lowest ionic state and the lowest electron-pair bond state may contain different numbers of unpaired electrons, so that they cannot be combined with one another. An octahedral complex $[\mathrm{FeX_6}]^{\equiv}$ forms a good example. If the complex contained extreme ionic bonds, the singlet ions X$^-$ and the Fe^{+++} ion (with a stable state of maximum multiplicity, in accordance with the rules of line spectra) would produce a $^6\Sigma$ complex, containing five unpaired electrons, as shown in Fig. 4. An unstable ionic $^2\Sigma$ state would also be formed by pairing four of the electrons; it would lie several volt-electrons above the normal state. With extreme electron-pair bonds the normal state, involving $3d^2$ $4s$ $4p^3$ bond eigenfunctions, would be a $^2\Sigma$ state. A $^6\Sigma$ state, with the much less stable $4s$ $4p^3$ $4d^2$ bonds, would lie much higher. The energy levels of an actual complex would lie somewhere on the curves shown in Fig. 8. The normal state would be either $^2\Sigma$, mainly the octahedral electron-pair bond state with a small contribu-

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[19] The arguments for the triple-bonded ionic structure presented by N. V. Sidgwick [*Chem. Rev.*, 9, 77 (1931)] in the main support this structure also. Thus we may expect for :C::Ö: an electric moment with oxygen negative. for :C:::O: one with oxygen positive (the electronic structure being symmetrical, and oxygen having the larger nuclear charge), so that the combined structure could well lead to the observed very small electric moment.

tion from the excited ionic extreme, or $^6\Sigma$, mainly ionic with a small contribution from the excited electron-pair bond extreme. It is accordingly convenient to designate the $^2\Sigma$ state as essentially of the electron-pair bond type, and the $^6\Sigma$ state as essentially ionic, and to take the intersection of the two curves as a discontinuity in the normal state.

The multiplicity can be determined from the experimental values of the magnetic susceptibility, the magnetic moment in Bohr magnetons being equal to $2\sqrt{S(S+1)}$, in which S is the spin quantum number. (The multiplicity is $2S + 1$.) The moments for $^2\Sigma$ and $^6\Sigma$ are 1.73 and 5.91, respectively. The experimental values for $K_3Fe(CN)_6$ and $(NH_4)_3FeF_6$ are 2.0 and 5.88, respectively, so that the bonds in the $[Fe(CN)_6]^{\equiv}$ ion are electron-pair bonds, and those in $[FeF_6]^{\equiv}$ are ionic.

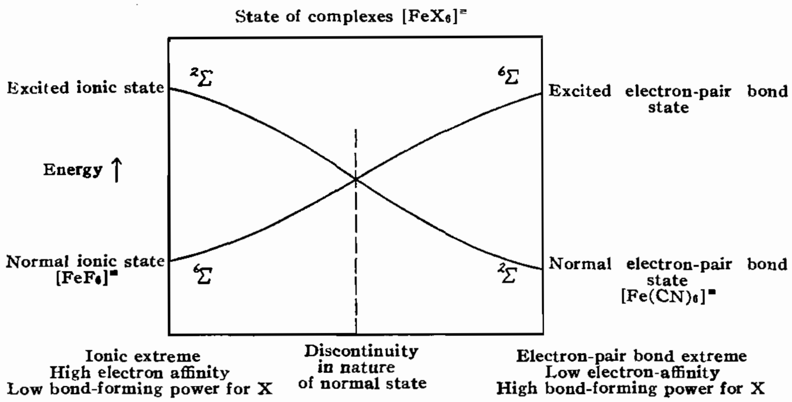

Fig. 8.—Diagram of two energy levels for complexes $[FeX_6]^{\equiv}$, showing an effective discontinuity in the normal state.

The magnetic criterion is particularly valuable because it provides a basis for differentiating sharply between essentially ionic and essentially electron-pair bonds. Experimental data have as yet been obtained for only a few of the interesting compounds, but these indicate that oxides and fluorides of most metals are ionic. Electron-pair bonds are formed by most of the transition elements with sulfur, selenium, tellurium, phosphorus, arsenic and antimony, as in the sulfide minerals (pyrite, molybdenite, skutterudite, etc.). The halogens other than fluorine form electron-pair bonds with metals of the palladium and platinum groups and sometimes, but not always, with iron-group metals.

Summary

After a discussion of the properties of substances containing ionic bonds and electron-pair bonds, it is shown that the transition from one extreme bond type to another could take place continuously in some cases (when

the normal states for the two extremes have the same number of unpaired electrons), and not in others. A method of treatment of bond type based on electronic energy curves is developed. Its application shows the normal alkali halide molecules to be essentially ionic. HF is largely ionic, while HCl, HBr and HI contain electron-pair bonds. The normal state of CO corresponds to both structures $:\mathrm{C}::\ddot{\mathrm{O}}:$ and $:\mathrm{C}:::\mathrm{O}:$, with the latter predominant. Some general statements based on observed magnetic moments are made relative to the types of bonds formed by metals of the transition groups.

PASADENA, CALIFORNIA

[Reprint from the Journal of the American Chemical Society, 54, 3570 (1932).]

[Contribution from the Gates Chemical Laboratory, California Institute of Technology, No. 326]

THE NATURE OF THE CHEMICAL BOND. IV. THE ENERGY OF SINGLE BONDS AND THE RELATIVE ELECTRONEGATIVITY OF ATOMS

By Linus Pauling

Received May 18, 1932 Published September 5, 1932

Recent developments in the application of the quantum mechanics to problems of molecular structure[1] have indicated that the properties of a bond between two atoms often are determined mainly by one single-electron orbital wave function for each atom, and are not strongly affected by the other atoms in the molecule; for when the wave function for a molecule containing single covalent bonds is set up with the use of single-electron orbital wave functions, it is found that each bond function tends to overlap to the maximum extent the other function involved in one bond, and to avoid overlapping all others, so that the resonance integrals other than those characteristic of the bonds are small. The empirical evidence of interatomic distances supports this view; it has been possible to formulate a set of covalent radii for use in purely covalent molecules (in which each atom forms covalent bonds to a number determined by its position in the periodic system) which accounts satisfactorily for observed distances in molecules to which a single Lewis electronic structure can be assigned.[2] It has also been found that changing the covalence of an atom, and hence the nature of the bond function, produces a change in the radius.[3]

Independence of the bonds in a molecule would require that the total energy of formation of the molecule from separate atoms be expressible as the sum of constant energy terms characteristic of the various bonds. This is found to be nearly true for molecules to which a single Lewis electronic structure can be assigned, the deviations from constancy of bond energy rarely exceeding 2 or 3%. Data on the heats of formation and heats of combustion of gaseous molecules may accordingly be used to evaluate the energies of various bonds. This procedure is adopted in the following pages. It is then shown that the energies of bonds, when discussed with the aid of the postulate of the additivity of the energies of normal covalent bonds, throw much light on their nature, in particular on the amount of ionic character possessed by them, and permit the localization of

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[1] Linus Pauling, This Journal, **53**, 1367, 3225 (1931); **54**, 988 (1932); J. C. Slater, *Phys. Rev.*, **37**, 481 (1931); **38**, 1109 (1931); F. Hund, *Z. Physik*, **73**, 1, 565 (1932).

[2] Linus Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932). Examples of molecules which resonate among several Lewis structures are given in this paper. Further discussion of the nitrous oxide molecule is given in a later note, Linus Pauling, *ibid.*, July, 1932.

[3] Linus Pauling and M. L. Huggins, *Z. Krist.*, to be published.

atoms on an "electronegativity map," with the aid of which their properties may be conveniently discussed. It is also found that bond energies provide evidence in regard to a number of questions relating to the structure of simple molecules, such as O_4, O_3, P_4, etc.

Extreme Ionic Bonds and Normal Covalent Bonds.—Before discussing the nature of actual bonds it is desirable to specify the sense in which the terms ionic and covalent will be used.

Early discussions of molecules such as the hydrogen halides treated them as consisting of ions which deformed each other to some extent. Now the wave functions corresponding to the normal and all excited states of F^-, for example, form a complete orthogonal set, so that any electronic structure of the HF molecule, even a normal covalent structure, could be accurately represented by a wave function built up from the wave functions for F^-, the contributions of excited states being considered to result from the deforming action of the proton. If, then, we are to distinguish at all between ionic bonds and bonds of other types, some arbitrary decision as to the extent to which excited ionic states are to be considered in constructing wave functions must be made. A number of phenomena formerly explained qualitatively as due to mutual polarization and deformation of ions have been quantitatively accounted for in other ways, and it has become evident that deformation of ions does not have the importance in determining the properties of molecules that it was formerly ascribed. Consequently I prefer, in an approximate treatment, to consider only states in which electrons occupy the most stable orbits in atoms or ions, and so to select for the wave function representing an extreme ionic molecule a function formed from those for normal undeformed ions.

A bond between two identical atoms, as H:H, Cl:Cl, C:C, etc., may be considered to be a normal covalent bond, involving a pair of electrons and two single-electron orbital wave functions, one for each atom. The wave function representing it may not be closely approximated by a function of the Heitler–London type, $\psi(1)\varphi(2) - \varphi(1)\psi(2)$, but may involve ionic terms $\varphi(1)\varphi(2)$ and $\psi(1)\psi(2)$, corresponding to A^+A^- and A^-A^+, these two occurring, of course, with the same coefficient. The contribution of these terms to the normal state of the hydrogen molecule has been discussed by Slater.[4] In the wave function representing the bond between unlike atoms A and B the terms corresponding to A^+B^- and A^-B^+ will occur with the same coefficient, equal to that for A:A or B:B, if the two atoms have the same degree of electronegativity. Such a function may be called a normal covalent bond wave function, and the bond a normal covalent bond. If one atom is more electronegative than the other, the wave function can be formed by adding to the normal covalent bond wave function an additional ionic term.

[4] J. C. Slater, *Phys. Rev.*, **35**, 509 (1930).

The Additivity of the Energies of Normal Covalent Bonds. The Hydrogen Halides and the Halogen Halides.—It is found that there exists a convincing body of empirical evidence in support of the postulate[5] that *the energies of normal covalent bonds are additive;* that is

$$A:B = {}^1/_2\,\{A:A + B:B\}$$

where the symbol A:B means the energy of the normal covalent bond between A and B, etc. The energy of a normal covalent bond between A and B would be given by the integral $\int \psi^* H \psi d\tau$, with ψ the normalized normal covalent wave function. Inasmuch as the energy integral for any wave function for a system must be equal to or greater than the energy of the lowest state of the system, the energy of the actual bond between A and B must be at least as great as that for a normal covalent bond. Hence if the postulate of additivity is correct, the difference Δ between the actual bond energy and that predicted from additivity must be zero or positive, and the greater the ionic character of the bond, the greater will be the value of Δ.

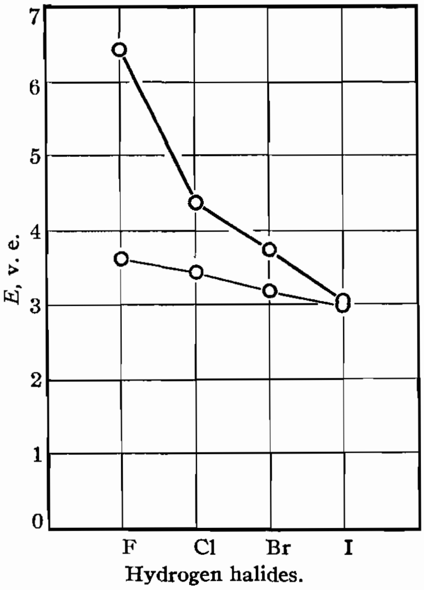

Fig. 1.—Bond energies for hydrogen halides: observed values are connected by heavy lines, values calculated for normal covalent bonds by light lines.

In Table I and Figs. 1 and 2 are given bond energies for hydrogen and the halogens, and their binary compounds, together with the deviations from additivity. The values of Δ are usually known more accurately than the bond energies themselves because they can be directly measured as heats of reaction. It is seen that *the values of Δ are positive for all of these compounds,* which provides strong support for the postulate. Moreover, the values are in agreement with previously formed conceptions as to the nature of the bonds in these molecules. A recent discussion[6] of energy curves has shown HF to be largely ionic, while HCl, HBr and HI are largely covalent, with HI nearly a normal covalent molecule. These descriptions are in complete accord with the course of the Δ-values.

BrCl approaches the normal covalent type still more closely than HI, with a deviation from additivity of less than 1%. The values of Δ for

[5] Linus Pauling and Don M. Yost, *Proc. Nat. Acad. Sci.*, **18**, 414 (1932).

[6] Pauling, This Journal, **54**, 988 (1932).

Table I[5]

	H:H	F:F	Cl:Cl	Br:Br	I:I
Bond energy	4.44	2.80	2.468	1.962	1.535 v. e.
		HF	HCl	HBr	HI
Actual bond energy		6.39	4.38	3.74	3.07
Predicted from additivity		3.62	3.45	3.20	2.99
Δ		2.77	0.93	0.54	0.08
		ClF	BrCl	IBr	ICl
Actual bond energy		3.82	2.231	1.801	2.143
Predicted from additivity		2.63	2.215	1.748	2.001
Δ		1.19	0.016	0.053	0.142

IBr and ICl are also small, but that for ClF is even larger than for HCl, showing that the bond in chlorine fluoride is more ionic in character than that in hydrogen chloride.

It is perhaps desirable to point out that the bond type has no direct connection with ease of electrolytic dissociation in aqueous solution. Thus the nearly normal covalent molecule HI ionizes completely in water, whereas the largely ionic HF is only partially ionized.

Bond Energies for Light Atoms and Halogens.—In the calculation of bond energies from heats of formation and heats of combustion the following energies of reaction were assumed[7] in addition to those given in Table I.

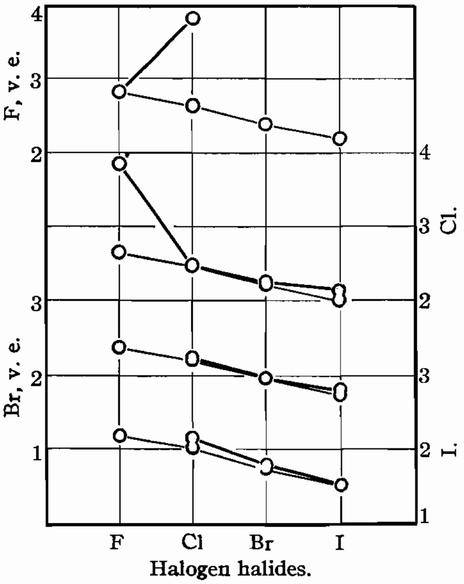

Fig. 2.—Bond energies for halogen halides.

$$\begin{aligned}
2O &= O_2 + 5.09 \text{ v. e.}\\
2N &= N_2 + 9.10 \text{ v. e.}\\
H_2 + {}^1/_2\, O_2 &= H_2O(g) + 2.508 \text{ v. e.}\\
H_2 + {}^1/_2\, O_2 &= H_2O(l) + 2.966 \text{ v. e.}\\
C\,{}^3P &= C_{\text{graphite}} + 6.61 \text{ v. e.}\\
C^{*}\,{}^5S &= C_{\text{graphite}} + 7.61 \text{ v. e.}\\
C_{\text{graphite}} + O_2 &= CO_2 + 4.094 \text{ v. e.}\\
2Br &= Br_2(l) + 2.293 \text{ v. e.}\\
2I &= I_2(c) + 2.188 \text{ v. e.}
\end{aligned}$$

Some doubt has been thrown on the value 9.1 v. e. for the dissociation energy of N_2 by the recent experiments of Tate and Lozier,[8] whose interpre-

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[7] Values of thermal quantities used throughout this paper are from "International Critical Tables," Landolt-Börnstein, or Kharasch's compilation of heats of combustion, *Bur. Standards J. Research*, **2**, 359 (1929), except where otherwise indicated.

[8] J. T. Tate and W. W. Lozier, *Phys. Rev.*, **39**, 254 (1932).

tation of their results has in turn, however, been criticized by Arnot.[9] The value 6.61 v. e. for the heat of sublimation of graphite to normal carbon atoms is very uncertain, and the assumed value of 1.00 v. e. for the excitation energy to the $2s2p^3\ ^5S$ state is also uncertain. It is not essential for the discussion of deviations from additivity that these energy quantities be known; but it is convenient to deal with definite values for bond energies, even though they are relative to an arbitrarily chosen starting point, so that the values given have been used in this paper. When accurate values of these quantities become known, the bond energies can be easily corrected accordingly.

Compounds of Oxygen and Nitrogen.—From the heat of formation of water from atoms

$$2H + O = H_2O(g) + 9.493 \text{ v. e.}$$

the H:O bond is found to have the energy 4.747 v. e. The equation[10]

$$H_2O_2(l) = H_2O(l) + {}^1/_2\, O_2 + 1.02 \text{ v. e.}$$

combined with the heat of vaporization of H_2O_2, 0.50 v. e., leads to

$$2H + 2O = H_2O_2(g) + 10.99 \text{ v. e.}$$

Making use of the postulate of the constancy of bond energies, we subtract 4.75 v. e. for each H:O bond to obtain 1.49 v. e. for the O:O bond.

The $^1\Sigma$ state of the oxygen molecule, 1.62 v. e. above the normal state, probably corresponds to a double bond between the two atoms. This gives 3.47 v. e. for O::O.

From the heat of formation of ammonia, 0.475 v. e., we obtain

$$N + 3H = NH_3 + 11.685 \text{ v. e.}$$

and the value 3.895 v. e. for the N:H bond.

The heats of formation of OF_2 (−0.40 v. e.), NF_3 (1.13 v. e.), Cl_2O (−0.79 v. e.) and NCl_3 (−2.38 v. e.), lead to the values 2.48 v. e. for O:F, 3.29 v. e. for N:F, 2.12 v. e. for Cl:O, and 1.95 v. e. for N:Cl.

Compounds of Carbon.—Heats of combustion of diamond and the aliphatic hydrocarbons show, as was pointed out by Fajans,[11] that the postulate of the constancy of bond energies is not accurate, for assuming that the H:C bond energy is the same in the higher members of the series as in methane, a value for the C:C bond energy is obtained which is 0.2 v. e. lower than that from diamond. It is difficult to decide how to treat this discrepancy. I have arbitrarily chosen to ignore diamond. The values H:C = 4.34 v. e. and C:C = 3.60 v. e. then give good agreement with experiment for the aliphatic hydrocarbons, as is seen by comparing the heats of formation ($E_{\text{obs.}}$) of gaseous molecules from atoms as calculated from heats of combustion with the sum of the bond energies ($E_{\text{calcd.}}$).

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[9] F. L. Arnot, *Nature*, **129**, 617 (1932).

[10] G. L. Matheson and O. Maass, This Journal, **51**, 674 (1929).

[11] Fajans, *Ber.*, **53**, 643 (1920); **55**, 2826 (1922); *Z. physik. Chem.*, **99**, 395 (1921).

	$E_{obs.}$, v. e.	$E_{calcd.}$, v. e.		$E_{obs.}$, v. e.	$E_{calcd.}$, v. e.
CH_4	17.37	17.36	C_4H_{10}	54.20	54.20
C_2H_6	29.65	29.64	C_6H_{14}	78.77	78.76
C_3H_8	41.91	41.94	C_7H_{16}	91.00	91.05

Similar calculations for saturated cyclic hydrocarbons show that a three-membered ring is unstable to the extent of over 1 v. e., larger rings showing little strain. The table compares observed heats of combustion with those calculated from bond energies.[12]

		$Q_{obs.}$, v. e.	$Q_{calcd.}$, v. e.	Instability, v. e.
Trimethylene	C_3H_6	21.55	20.49	1.06
Methylcyclobutane	C_5H_{10}	34.31	34.15	0.16
Cyclopentane	C_5H_{10}	34.28	34.15	.13
Methylcyclopentane	C_6H_{12}	41.02	40.98	.04
Cyclohexane	C_6H_{12}	41.02	40.98	.04

Heats of combustion of gaseous hydrocarbons containing double bonds lead to the average value 6.46 v. e. for C::C.

		Q, v. e.	E, v. e.	C::C, v. e.
Ethylene	C_2H_4	14.38	23.84	6.48
Propylene	C_3H_6	21.26	36.07	6.43
Isobutylene	C_4H_8	28.07	48.37	6.45
Trimethylethylene	C_5H_{10}	34.86	60.69	6.49
Diallyl	C_6H_{10}	40.26	66.99	6.40
Hexylene	C_6H_{12}	41.66	73.00	6.52

Heats of combustion for hydrocarbons containing triple bonds are uncertain. Thomsen's values lead to C:::C = 8.68 v. e.

	Q, v. e.	E, v. e.	C:::C, v. e.
Acetylene	13.54	17.28	8.60
Allylene	20.18	29.75	8.79
Dipropargyl	38.30	54.14	8.65

It is interesting to note that the unsaturation of a double bond amounts to 0.74 v. e., this being the energy liberated by a reaction leading to the formation of two carbon–carbon single bonds in place of a double bond. For a triple bond the unsaturation is 2.1 v. e.

Five primary alcohols give an average of 3.56 v. e. for C:O, with a maximum deviation of 0.10 v. e., and six ethers give 3.55 v. e., with a maximum deviation of 0.07 v. e. Secondary and tertiary alcohols seem to be 0.3–0.5 v. e. more stable than corresponds to this C:O value. In view of the agreement between ethers and primary alcohols, we select C:O = 3.55 v. e.

Primary, secondary and tertiary amines give the following values for C:N, Thomsen's values of heats of combustion being used.

[12] The heat of combustion of ethylene oxide, C_2H_4O, combined with C:O = 3.55 v. e., shows the three-membered ring involving oxygen to be unstable to the extent of 0.67 v. e.

	C:N, v. e.		C:N, v. e.
CH_3NH_2	2.82	$(CH_3)_2NH$	2.92
$C_2H_5NH_2$	2.87	$(C_2H_5)_2NH$	2.95
$C_3H_7NH_2$	2.80	$(CH_3)_3N$	2.94

Neglecting the possibility that the bond energy in primary amines be slightly less than in secondary and tertiary amines, we take the average value 2.88 v. e. for C:N.

Cyanogen, acetonitrile and hydrogen cyanide (using Thomsen's value for heats of combustion of the first two) lead to 8.86, 8.98, and 8.74 v. e., respectively, for C:::N. The average of these, 8.86 v. e., is very nearly the mean of C:::C = 8.68 v. e. and N:::N = 9.10 v. e. (in N_2).

Heats of combustion of fluorine-substituted hydrocarbons give C:F = 5.40 v. e. as the average of eight values, maximum deviation 0.35 v. e. Twelve chlorine compounds give an average of 3.41 v. e. for C:Cl. The same value is obtained from the heat of formation of CCl_4. Three bromine compounds (heats of combustion from Thomsen) give C:Br = 2.83 v. e., and two iodine compounds, CH_3I and C_2H_5I (Thomsen), give C:I = 2.2 v. e. The last two values are uncertain. Other data, obtained by Berthelot and by Roth and Macheleldt and quoted by Swietoslawski,[13] give the value 2.45 v. e. for C:I.

Bond Energies and the Relative Electronegativity of Atoms.—In Table II there are collected the energies of single bonds obtained in the preceding sections. One additional value, obtained by a method to be described later, is also included: 1.44 v. e. for N:N. Under each bond energy is given the value for a normal covalent bond, calculated from additivity, and below that the difference Δ. It is seen that Δ is positive in twenty of the twenty-one cases. The exception, C:I, may be due to experimental error, and be not real.

Regularities observed in the Δ-values suggest that it is possible to make a rough assignment of the atoms to positions along a scale representing degree of electronegativity, with the assumption that Δ is a function of the linear separation of the loci of the two atoms on the scale, in the way that genes are mapped in a chromosome from crossover data. It is to be observed that the values of $\Delta^{1/2}$ are approximately additive (these values are given directly below those of Δ). For example, the sum of $\Delta^{1/2}$ for H:A and A:F is 2.05, 2.06, 1.91, and 2.06 for A = C, N, O, and Cl, respectively. We accordingly write

$$\Delta_{A:B} = (x_A - x_B)^2 \qquad (1)$$

with Δ measured in volt-electrons, and construct the scale shown in Figs. 3 and 4 on this basis. The reliability of the method is indicated by Fig. 3, in which four distinct procedures are illustrated. The coördinates of the elements on this scale are given in Table III.

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[13] W. Swietoslawski, "Thermochemie," Akademische Verlagsgesellschaft m. b. H., Leipzig, 1928.

TABLE II

	H	C	N	O	F	Cl	Br	I
H	4.44	4.34	3.89	4.75	6.39	4.38	3.74	3.07
		4.02	2.94	2.99	3.62	3.45	3.20	2.99
		0.32	0.95	1.76	2.77	0.93	0.54	0.08
		.57	.98	1.33	1.67	.97	.74	.28
C		3.60	2.88	3.55	5.40	3.41	2.83	2.45
			2.52	2.55	3.20	3.03	2.78	2.57
			0.36	1.00	2.20	0.38	0.05	−0.12
			.60	1.00	1.48	.62	.22	
N			1.44		3.29	1.95		
					2.12	1.95		
					1.17	0.00		
					1.08	.00		
O				1.49	2.48	2.12		
					2.15	1.98		
					0.33	0.14		
					.58	.37		
F					2.80	3.82		
						2.63		
						1.19		
						1.09		
Cl						2.468	2.231	2.143
							2.215	2.001
							0.016	0.142
							.13	.38
Br							1.962	1.801
								1.748
								0.053
								.23
I								1.535

Observed bond energy
Normal covalent bond energy

Δ
$\Delta^{1/2}$

TABLE III

COÖRDINATES OF ELEMENTS ON THE ELECTRONEGATIVITY SCALE

H	0.00	Br	0.75
P	.10	Cl	.94
I	.40	N	.95
S	.43	O	1.40
C	.55	F	2.00

These coördinates, introduced in Equation 1, lead to values of Δ which agree with those of Table II with an average error of 0.09 v. e., excluding H:F. The calculated Δ for H:F is 4.00 v. e., 1.23 v. e. higher than observed; this indicates that Equation 1 is inaccurate when $x_A - x_B$ becomes as large as 2.

The electronegativity map may be used with considerable confidence in predicting bond energies, especially for atoms which lie near each other on the map. It will be observed that the difference in bond energy of H:A and A:F increases rapidly in the order A = C, Cl, O. Now the value of this difference for N is only slightly greater than for Cl, showing that the locus of N on the map should lie just to the right of that for Cl, and that in consequence Δ = 0.00 for N:Cl. The bond energies for N:Cl and Cl:Cl then lead to 1.44 v. e. for N:N, the value given in Table II. This value could be checked if the heat of formation of gaseous hydrazine were known. The predicted value is

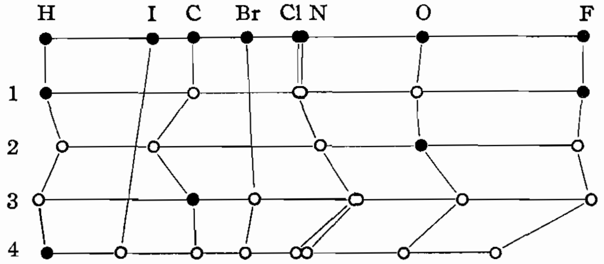

Fig. 3.—The construction of the electronegativity map. Map loci of atoms were obtained by the use of values of $\Delta^{1/2}$ relative to the atoms represented by solid circles: (1) loci taken to give the correct ratio of $\Delta^{1/2}$ for H:A and A:F. Absolute values of $\Delta^{1/2}$ are shown in the other lines, for (2) A:O, (3) C:A and (4) H:A.

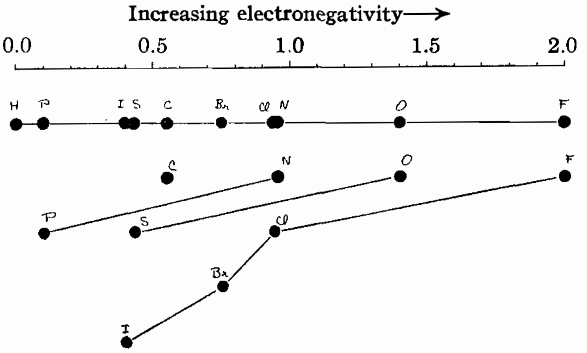

Fig. 4.—Map representing the relative degree of electronegativity of atoms.

$$N_2 + 2H_2 = N_2H_4(g) - 0.96 \text{ v. e.}$$

It may be mentioned that the heats of combustion of hydrazobenzene and azobenzene give 1.59 v. e. for N:N and 4.24 v. e. for N::N, with rather large probable errors.

From the equations

$$\begin{aligned} S(g) &= S_{\text{rhombic}} + 2.89 \text{ v. e.}\\ S_{\text{rh.}} + Cl_2 &= SCl_2\,(g) + 0.34 \text{ v. e.}\\ S_{\text{rh.}} + H_2 &= H_2S + 0.23 \text{ v. e.,}\end{aligned}$$

we obtain S:Cl = 2.85 v. e. and H:S = 3.78 v. e. From

$$2S_{\text{rh.}} + Cl_2 = S_2Cl_2(g) + 0.24 \text{ v. e.}$$

we obtain, with the use of the above S:Cl value, S:S = 2.79 v. e. in S_2Cl_2. The equation

$$^1/_8\, S_8(g) = S_{\text{rh.}} + 0.11 \text{ v. e.}$$

gives S:S = 2.78 v. e., if the S_8 molecule consists of an eight-membered ring involving eight single bonds; the agreement with the S_2Cl_2 value provides strong support for this structure. From these energy values the map position of sulfur was obtained.

The S_6 molecule, supposed to contain six single bonds, is less stable than expected by 0.30 v. e., presumably because of steric effects.

From the trend of map loci with position in the periodic table phosphorus may be placed very near hydrogen on the map, perhaps at about 0.10. This requires Δ to be very small (0.01 v. e.) for H:P. From

$$^1/_4\, P_4(g) + {}^3/_2\, H_2(g) = PH_3(g) + 0.246 \text{ v. e.}$$

we obtain P:H = 2.302 v. e. + C, in which C is one-third of the energy of dissociation of $^1/_4$ $P_4(g)$ into P(g). This then gives, with $\Delta = 0.01$ v. e., the value 0.14 v. e. + $2C$ for P:P. P_4 presumably has a tetrahedral structure, with single bonds at 60° angles;[14] the bonds are 0.14 v. e. weaker than normal P:P bonds, as compared with 0.05 v. e. for S:S bonds in S_6.

The equation

$$^1/_4\, P_4(g) + {}^3/_2\, Cl_2 = PCl_3(g) + 3.30 \text{ v. e.}$$

gives P:Cl = 2.41 v. e. + C.

The extent to which Equation 1 is valid and the accuracy of the map are graphically shown in Fig. 5. The vertical lines, representing Δ-values, should increase in height with the square of their distance from the diagonal.

It is evident that the map and Equation 1 can be used for the prediction of the energies of bonds for which no experimental data are available, the values being trustworthy to about 0.05 v. e. for map distances less than 0.50, and 0.1–0.2 v. e. for distances up to 1 or 1.5. Table IV contains predicted values, with the aid of which heats of formation of purely covalent compounds containing single bonds, such as SF_2 (but not SF_6), can be calculated. In some cases all data needed for testing these values are available except heats of vaporization or sublimation. Thus the heat of formation of S_2Br_2(l), 0.09 v. e., agrees with the bond energies if the heat of vaporization of S_2Br_2 be 0.44 v. e., which is a not unreasonable value (that for Br_2 being 0.33 v. e.). The somewhat doubtful value 0.0 v. e. reported

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[14] R. Hultgren, *Phys. Rev.*, **40**, 891 (1932).

for the heat of formation of S_2I_2(c) leads to a heat of sublimation of 0.9 v. e. (that for I_2 being 0.65 v. e.). Similarly the heats of formation of PBr_3(l), 1.97 v. e., and PI_3(c), 0.48 v. e., lead to the reasonable values 0.51 v. e. and 0.98 v. e. for the heat of vaporization of PBr_3 and the heat of sublimation of PI_3, respectively.

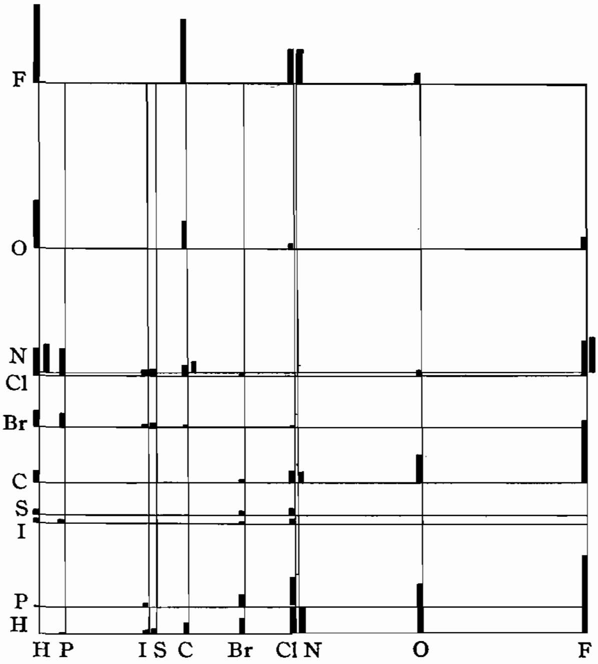


Fig. 5.—In this figure ordinates and abscissas represent loci on the electronegativity map, and the heavy vertical lines are drawn to the height Δ, the observed deviation from additivity of bonds, attributed to their ionic character. Equation 1 in the text requires that these heights increase with the square of the distance from the diagonal.

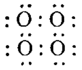
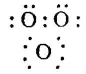
Table IV

Predicted Bond Energies

N:O	1.67 v. e.	S:N	2.38 v. e.
Br:N	1.74	S:O	3.08
I:N	1.79	S:F	5.25
Br:O	2.15	P:I	0.93 + C
I:O	2.52	P:S	1.56 + C
Br:F	3.94	P:C	3.17 + C
I:F	4.72	P:Br	1.47 + C
I:S	2.16	P:N	1.51 + C
S:C	3.20	P:O	2.50 + C
S:Br	2.47	P:F	5.08 + C

Assuming that the energy of formation of crystalline silicon (with the diamond structure) is the energy of the Si:Si bonds, the heats of formation 15.70 and 6.20 v. e. of gaseous SiF_4 and $SiCl_4$ lead to values of 1.98 and 1.24 for $\Delta^{1/2}$ for Si:F and Si:Cl, respectively. These substantiate the map position of about −0.15 obtained by extrapolating the series Cl, S, P. This and many other map positions which could be similarly obtained are not included in Fig. 4 and Table III, however, because of the somewhat greater uncertainty attached to them. With this map position, the heat of formation of SiH_4 should be about 0.08 v. e., or less if the metallic character of crystalline silicon makes some contribution to its energy. The value 0.5 v. e. given in "International Critical Tables" is without doubt too large; Landolt–Börnstein reports −0.29 v. e.

Arsenic, antimony, selenium, and tellurium no doubt lie close to hydrogen on the map, so that single-bond energies can be obtained for them from the heats of formation of hydrides, as in the case of phosphorus, by assuming Δ to be very small. Crystals of selenium and tellurium contain long spiral strings, in which each atom is presumably held to two others by covalent bonds, and those of arsenic and antimony contain layers, in which each atom is presumably similarly attached to three others. With $\Delta_{M:H}$ very small, the heat of reaction of such a string or layer with hydrogen should be nearly zero, so that the observed negative heats of reaction for the crystals give just the energy necessary to separate the strings or layers in the crystals. This energy is, per atom, 1.08 v. e. for selenium, 1.52 v. e. for tellurium, 1.92 v. e. for arsenic, and 1.5 v. e. for antimony, the last value being probably too low because of error in the reported heat of formation of the hydride.

The observed value of the heat of formation of O_4 from atoms, 10.19 v. e., is so much greater than the energy of four O:O bonds, 5.96 v. e., that the structure  $\begin{matrix}:\ddot{O}:\ddot{O}:\\ :\underset{..}{\ddot{O}}:\underset{..}{\ddot{O}}:\end{matrix}$ for this molecule must be rejected. The corresponding values for ozone are 6.15 v. e. and 4.47 v. e., causing the structure  $\begin{matrix}:\ddot{O}:\ddot{O}:\\ \cdot\,\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}\,\cdot\end{matrix}$ to be rejected also. Ozone probably has a structure like that of SO_2, as suggested by Lewis. The very small heat of formation of O_4 from $2O_2$ and the ease with which dissociation occurs (even crystalline oxygen showing some paramagnetism) indicate that O_4 consists of two $^3\Sigma O_2$ molecules held together loosely by van der Waals forces, the exchange terms being larger for two triplet molecules combining to a singlet than they are for singlet molecules.

The metallic elements may also be roughly located on the map, though the significance and usefulness of their map positions is not so great as for the non-metals.

The property of electronegativity discussed in this paper and defined by Equation 1 is not analogous to the electron affinity of atoms, but is closely related to the intuitive conception of electronegativity possessed by the chemist. The relation to the periodic system is the expected one. Fluorine and oxygen are by far the most electronegative atoms, with fluorine much more electronegative than oxygen. The series C, N, O, F is almost uniform. Fluorine is much more electronegative than the other halogens, and deserves to be classed by itself as a superhalogen. OF_2 should be called oxygen fluoride, and Cl_2O chlorine oxide, the more electronegative element being written last. In nitrogen trichloride, NCl_3, nitrogen and chlorine are neither positive nor negative, the bonds being normal covalent bonds, and the molecule the best example of a normal covalent molecule that we have, other than the symmetrical molecules. Nitrogen trichloride would decompose into gaseous elementary molecules with no heat effect if elementary nitrogen contained single N:N bonds. Since the triple bond in N_2 is 4.78 v. e. more stable than three N:N bonds, half this energy quantity, 2.39 v. e., is emitted during the decomposition of NCl_3. The contribution of ionic terms, giving $\Delta = 1.17$ v. e., overcomes this for NF_3, and leads to a positive heat of formation.

Summary

After the discussion and definition of extreme ionic bonds and normal covalent bonds, values of the energy of twenty-one single bonds are obtained from experimental values of heats of formation and combustion of gaseous molecules, with the use of the assumption that the energy of formation from separated atoms of a molecule to which a single Lewis electronic structure can be assigned is the sum of constant terms representing the various bonds. The postulate of the additivity of the energies of normal covalent bonds is then formulated, and it is found that deviations from additivity, Δ, are positive for all bonds (with one doubtful exception), and increase as the ionic character of the bond increases. An assignment of atoms to positions on a map representing relative degree of electronegativity is then made with the use of the Δ-values, according to the equation $\Delta_{A:B} = (x_A - x_B)^2$, where x_A and x_B represent the coördinates of atoms A and B on the map. Values of the energy of twenty bonds for which experimental data are not available are predicted by means of this equation, and a number of questions regarding the structure of molecules are discussed.

PASADENA, CALIFORNIA

CHAPTER 1

The Nature of the Chemical Bond Fifty Years Later: The Relative Electronegativity of Atoms Seen in Perspective

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CONTENTS

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MOLECULAR STRUCTURE AND ENERGETICS, Vol. 1

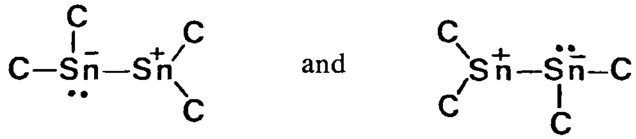
1. INTRODUCTION

Some 50 years have now passed since the publication of a series of papers bearing the title "The Nature of the Chemical Bond."[1-7] These papers have provided chemists, physicists, biologists, and mineralogists with the conceptual framework, based on simple valence bond theory and the theory of hybrid bond orbitals, required to investigate a myriad of problems involving the nature of the bonding exhibited in molecules and solids. The ideas contained in these papers were subsequently elaborated on in *The Nature of the Chemical Bond,*[8] which is probably the most often-cited book in the scientific literature.[9]

In the meantime there have occurred many novel experimental findings, and advances in theoretical methodology and computer technology have been so extensive that computer calculations of certain molecular and solid state properties rival or sometimes even exceed experimental results in accuracy.[10] Indeed, sophisticated computer programs have now become one of the pieces of laboratory equipment of many experimental scientists. Nevertheless, there remains a critical need for the simple conceptual models, which are firmly rooted in quantum mechanics, contained in *The Nature of the Chemical Bond* and the work of such investigators as Roald Hoffmann,[11] to assist in providing a systematization and rationalization of the ever-increasing profusion of established experimental facts and to understand the results of sophisticated computer calculations.[12] It must not be forgotten that computational quantum chemistry employs algorithms that always are subject to breakdown in a way that is not obvious to a nontheoretician (eg, the incorrect diagonalization of certain spurious matrices), and there remains a multitude of possible problems, including linear dependence of the basis set employed, symmetry breaking, nonconvergence, the use of minimal sets, and the effect of configuration interaction on specific properties. Thus the computer cannot be viewed as a black box any more than any other piece of laboratory equipment can be so regarded. The chapters in this series manifest the successful interaction of simple bonding concepts, sophisticated theoretical investigations, and recent experimental results.

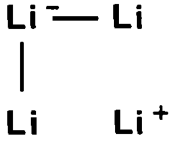
There exists yet another aspect of the importance of the concepts of simple valence bond theory and the theory of hybrid bond orbitals, namely, their usefulness in leading to the discovery of novel ideas. We shall cite as examples a number of recent discoveries in our own laboratory. First, the concepts of simple valence bond theory and the theory of hybrid bond orbitals have been employed to elucidate the unusual bonding angles and structures often displayed by compounds containing transition metals or elements of the lanthanide or actinide series.[13-29] Just as the tetrahedral bond angle 109.47° is characteristic of sp^3 hybrid bond orbitals, it was found that the bond angles 73.15° and 133.62° are characteristic of sp^3d^5 hybrid bond orbitals and the bond angles 54.88°, 100.43°, and 145.37° are characteristic of sp^{3}d^{5}f^7 hybrid bond orbitals. The implications of this discovery have been explored in detail in the aforementioned papers.

Second, the theory of hybrid bond orbitals was utilized recently to discover a new type of chemical bond involving the resonating unshared electron pair.[30,31] For example, bis(bistrimethylsilylmethyl) tin(II), $\{(CH_3)_3Si\}_2HCSnCH\{Si(CH_3)_3\}_2$, forms dimers in the solid state having a tin–tin bond characterized by resonance of an unshared electron pair or



When there is electronic resonance, the bond lengths, bond angles, and nuclear positions are intermediate between those corresponding to the individual resonance structures, as found in the crystal structure of the tin dimer.[32] This type of bond, that is, a single bond plus a resonating unshared electron pair, was subsequently found to occur on the {100} surfaces of silicon.[33]

Finally, the use of simple valence bond theory has led recently to a significant discovery concerning the nature of metals. Many years ago one of us noticed, based on an analysis of the experimental values of the saturation ferromagnetic moment per atom of the metals of the iron group and their alloys, that for a substance to have metallic properties, 0.72 orbital per atom, the "metallic orbital," must be available to permit the unsynchronized resonance that confers metallic properties on a substance.[34–38] Using lithium as an example, unsynchronized resonance refers to such structures as follows.



Successive pivoting resonances of a covalent bond allows for electrical conduction to occur, as shown in Figure 1-1. A test of this theory was provided by gray and white tin. Gray tin is not metallic because all its valence orbitals are used for bonding and there is no metallic orbital available. White tin, on the other hand, has the metallic orbital available and therefore has metallic properties.

The development during the past year of a statistical theory of unsynchronized resonance of covalent bonds in a metal, with atoms restricted by the electroneutrality principle to forming bonds only in number $v - 1$, v, and $v + 1$, with v the metallic valence, has led directly to the value 0.70 ± 0.02 for the number of metallic orbitals per atom.[39] This theory also has led to the conclusions that stability of a metal or alloy increases with increase in the ligancy and that for a given value of the ligancy, stability is a maxi-

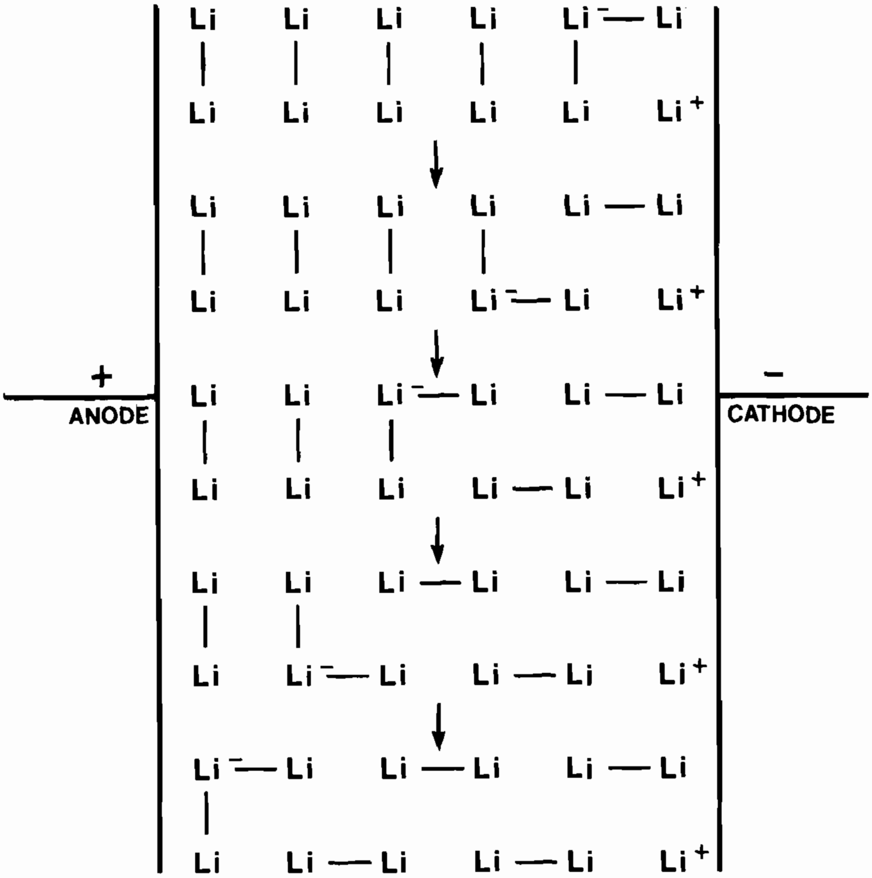


Figure 1-1. Motion of an electron from the cathode to the anode by successive pivoting resonances of a covalent bond.

mum for valence equal to half the ligancy. These results, along with consideration of the repulsion of unshared electron pairs on adjacent atoms, go far toward explaining the selection of different structures by different elemental metals and intermetallic compounds. This theory has just been applied to comprehend the anomalous behavior of vanadium sesquioxide (V_2O_3) in the solid state.[40]

One of the most pervasive ideas to emerge from the series of papers entitled "The Nature of the Chemical Bond" is the concept of the relative electronegativity of atoms. The sections that follow examine some of the consequences of this concept.

2. THE RELATIVE ELECTRONEGATIVITY OF ATOMS

The original table of values of the electronegativity of elements[4,41] was developed on the basis of quantum mechanical argument about the differences in bond energy of a bond between unlike atoms, A—B, and the average energy of the corresponding bonds between like atoms, A—A and B—B. Electronegativity was defined as the qualitative property that describes "the power of an atom in a molecule to attract electrons to itself."[42] Shortly after the original proposal of the concept of the relative electronegativity of atoms, Mulliken pointed out that the average of the first ionization energy and the electron affinity of an atom should be a measure of its electronegativity.[43,44] It has been recognized, however, that the Mulliken value of the electronegativity of hydrogen is too high, as is shown by several properties of the elements. For example, it is larger than the value for iodine, whereas the standard electrode potentials place it below iodine.[45] The original approach to electronegativity has been extended by Haïssinsky[46] and by Huggins,[47] and, more recently, an extensive set of values has been calculated from thermochemical data by Allred.[48] Jaffé and co-workers considered the dependence of electronegativity on the amount of hybridization and determined values of the orbital electronegativity using the Mulliken approach.[49–52] A rather complete discussion of the various ways of calculating electronegativity values is found in the recently published books by Moeller[53] and by Huheey.[54] Despite the many variations on a theme, it is fairly clear that the original electronegativity scale,[55] or one that differs only slightly from it, should be used in the discussion of the properties of substances and the nature of chemical reactions (see below).

The quantum mechanical argument used in deriving the original electronegativity scale involved the amount of ionic character of a normal covalent bond A—B, and it was evident that the amount of ionic character and accordingly the value of the electric dipole moment of the bond would be closely correlated with the difference $\Delta x = x_A - x_B$ of the two atoms A and B. In the first edition of *The Nature of the Chemical Bond* (1939) the following equation was advanced:

$$\text{amount of ionic character} = 1 - \exp\left[\frac{-(x_A - x_B)^2}{4}\right] \qquad (1\text{-}1)$$

This equation fits the experimental values (the observed dipole moment divided by the electronic charge and the bond length) quite well. Somewhat more accurate equations have been formulated by Nethercot.[56]

Nevertheless, Murrell, Kettle, and Tedder conclude in their book on valence theory[57] that there is no correlation between the electric dipole moment of a bond and the electronegativity difference. They have plotted the values of the electric dipole moments of eight bonds against the difference in the values of the Mulliken electronegativity (see Figure 1-2). (The bond moments for OH, NH, PH, NF, and PF are calculated from the observed values for H_2O, NH_3, PH_3 NF_3, and PF_3 with the assumption of vector addition.) It is seen from Figure 1-2 that the conclusion of a lack of correlation is justified.

There are two main reasons for the failure to obtain a correlation. The first is the use of erroneous values for x, especially for the hydrogen atom.

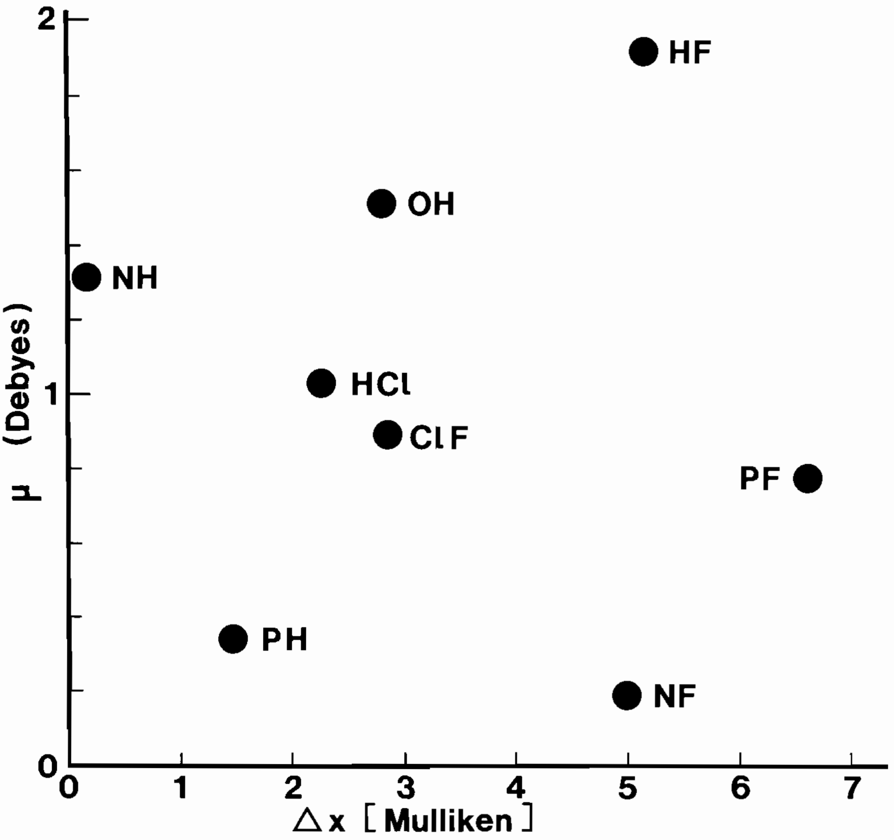


Figure 1-2. Bond moments μ of some bonds plotted against the difference in Mulliken electronegativity of the bonded atoms. (Redrawn from Reference 57, p.359.)

TABLE 1-1. Electronegativity Values

	H	Li	Be	B	C	N	O	F
Row 1[a]	7.17	2.96	2.86	3.83	5.61	7.34	9.99	12.32
Row 2[b]	2.67	1.10	1.09	1.43	2.09	1.73	3.72	4.59
Row 3[c]	2.1	1.0	1.5	2.0	2.5	3.0	3.5	4.0
	Na	Mg	Al	Si	P	S	Cl	
Row 1[a]	2.94	2.47	2.97	4.35	5.72	7.60	9.45	
Row 2[b]	1.09	0.92	1.11	1.62	2.13	2.83	3.52	
Row 3[c]	0.9	1.2	1.5	1.8	2.1	2.5	3.0	

[a] Mulliken electronegativity values, from Reference 57.

[b] Mulliken values divided by 2.69 (ie, the ratio of the sum of the first-row values to the sum of the third-row values).

[c] Values from Reference 8c.

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Table 1-2. Bond Moments (Debye Units)

HF	1.91	NH	1.32
HCl	1.03	PH	0.34
ClF	0.88	NF	0.18
OH	1.51	PF	0.77

Table 1-1 gives the values of the Mulliken electronegativity, the results of dividing these values by 2.69, and the values from *The Nature of the Chemical Bond.* (The factor 2.69 is the ratio of the sum of the first-row values to the sum of the third-row values.) The second reason for the failure to obtain a correlation is neglect of some of the structural features. Let us consider the factor 2.69 now.

Values of the bond moments (in debye units) for the eight bonds shown in Figure 1-2 are given in Table 1-2. In Figure 1-3 the large circles represent

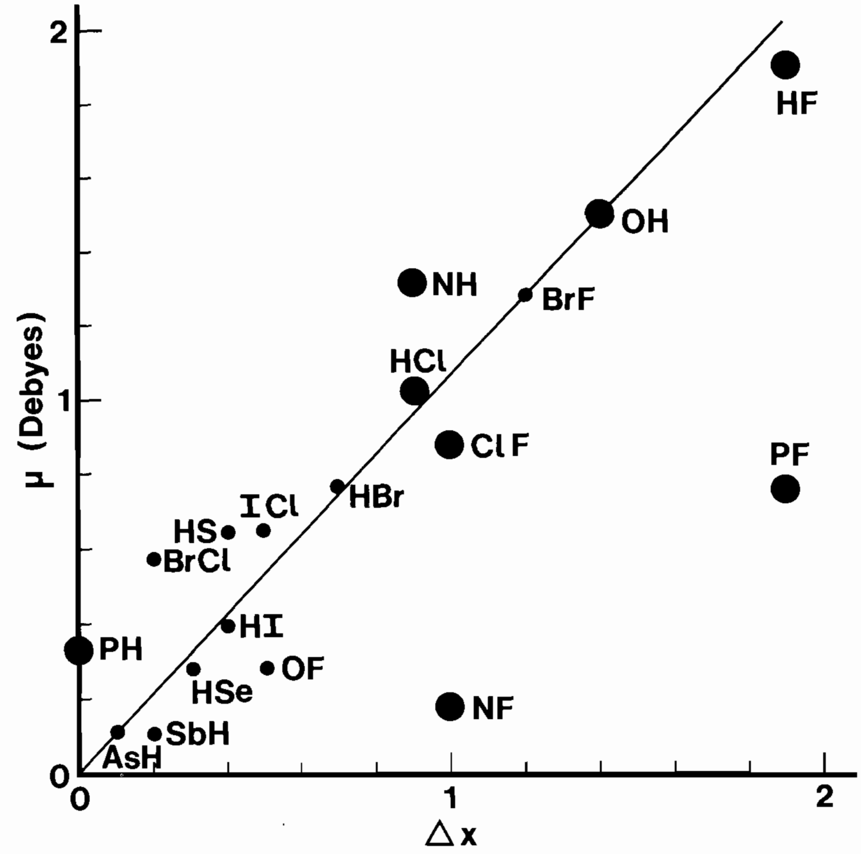


Figure 1-3. Bond moments μ plotted against the difference in the original electronegativity values; large circles represent bond moments for the bonds displayed in Figure 1-1.

these values plotted against the original values of Δx. It is seen that a straight line approximates six of the eight values reasonably well, and also the other values corresponding to bonds of similar nature, those in HBr, HI, BrF, BrCl, ICl, H_2S, H_2Se, OF_2, AsH_3, and SbH_3.

There are two points in Figure 1-3 that deviate strikingly from the general correlation between the bond dipole moment and Δx, those for NF_3 and PF_3. This deviation calls our attention again to the principle that in the discussion of the properties of molecules it is essential to take all the structural features into consideration. In formulating Figures 1-2 and 1-3 the bonds in each molecule were assumed to be single bonds. In fact, the bonds in OF_2, NF_3, and PF_3 have some double-bond character, of the sort reported long ago for other molecules containing fluorine atoms.

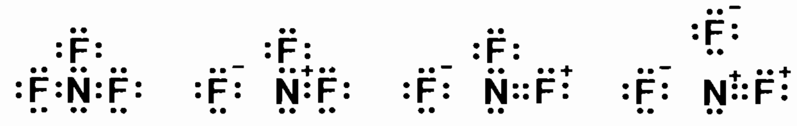
3. CORRELATION OF DOUBLE-BOND CHARACTER IN ONE BOND WITH IONIC CHARACTER IN ANOTHER

Brockway discovered in 1937 that the carbon–fluorine bond lengths in CF_4, CH_2F_2, CHF_2Cl, and CF_2Cl_2 are significantly shorter than those in CH_3F, CH_2FCl, and $CHFCl_2$, and he attributed this difference to the contribution of structures such as $F^-\overset{|}{\underset{|}{C}}{=}F^+$, that is, to the formation of a double bond to one fluorine atom in correlation with an ionic bond to another. This effect (which is discussed on pages 314 and 315 of the third edition of *The Nature of the Chemical Bond*), would be expected to occur in other molecules to an extent determined essentially by the amount of ionic character of the single bonds and the tendency of the ligated atoms to form double bonds, which is much greater for first-row atoms (F, O, N, C) than for other atoms.

It is customary to use the line between two atomic symbols, A—B, to represent a normal covalent bond, with the usual amount of ionic character. In the discussion that follows, A:B is used to represent a pure covalent single bond, and A^+B^- to represent the ionic structure that is hybridized with A:B to give A—B. A pure covalent double bond is represented by A=B. Thus in the molecule NF_3 we might describe each NF bond as involving $N^+\ :\overset{..}{\underset{..}{F}}:^-$, $N\ :\underset{..}{F}:$, and $N\!:\ :\overset{..}{F}:^+$, that is, as having some covalent double-bond character.

4. THE NITROGEN TRIFLUORIDE MOLECULE

In NF_3, with each atom having four orbitals in its outer shell, there is no way for one fluorine atom to be attached to the nitrogen atom by a double bond and the other two by single bonds and to provide orbitals for the unshared electron pairs. Only four possible kinds of structure are allowed by the electroneutrality principle:



1 (1 structure) 2 (3 structures) 3 (6 structures) 4 (3 structures)

The three structures of type **4** are unstable for two reasons: the presence of electric charges of the same sign on adjacent atoms, and the use by the nitrogen atom of only three orbitals. The contribution of these structures to the normal state of the molecule is accordingly small, and we may take it to be zero. Also, structures of type **3**, with a double bond and the transfer of the positive charge to a fluorine atom, are stabilized by the formation of an additional covalent bond with use of the fourth orbital and may accordingly make a greater contribution to the normal state; moreover, there is an extra factor 2 for the six structures of type **3** over the three of type **1**.

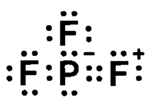
The possible, but presumably small contributions of the unshared electron pairs to the dipole moment may be ignored as a first approximation. The pure covalent bonds make no contribution to the dipole moment. Moreover, resonance among the six structures of type **3** leads to resultant zero charge on each fluorine atom, so that these structures do not contribute. Each of the three structures of type **2** contributes the amount ϵr to the bond moment of the bond to one fluorine atom, ϵ being the electronic charge 4.80 (in units 10^{-10} esu) and r the bond length in Ångström units (Å). For N^+-F^-, with $r = 1.371$ Å, the value of ϵr is 6.58 debyes (D). The experimental value of the bond moment (Table 1-2) is 0.18 D. Accordingly, each structure of type **2** contributes to the normal state of the molecule to the extent $0.18/6.58 = 2.74\%$.

Equation 1-1 with $\Delta x = 1$ for N—F leads to 22.1% ionic character and bond moment 1.46 D, a little above the straight line in Figure 1-3. Let us assume that the contribution of the pure covalent structure **1** has the value of 47.2%, calculated from the value 77.9% for each bond (22.1% ionic character). Since the three structures of type **2** contribute $3 \times 2.74\% = 8.2\%$, the structures of type **3** contribute the remainder, 44.6%. This value leads to 14.9% for the amount of double-bond character of each of the bonds in the NF_3 molecule, close to the value 15% for CHF_3, $CClF_3$, and ClF_3 calculated from the shortening of the bond length,[59] which is by 0.05 Å.

5. THE PHOSPHORUS TRIFLUORIDE MOLECULE

For PF_3 the observed value of the bond moment with the same calculation yields 10.5% for each of the type **2** structures, a total of 31.5% for these structures. Equation 1 gives 59.4% ionic character for $\Delta x = 1.9$ ($x = 2.1$ for P, 4.0 for F). This value corresponds to 6.7% contribution of the pure covalent structure **1**, hence to 61.8% contribution of the structures of type **3**. The corresponding amount of double-bond character of the phosphorus–fluorine bonds in PF_3 is thus given as 20.6%.

This amount is, however, only roughly compatible with the observed bond length, 1.535 Å. The value of the bond length for the single P—F bond, obtained with use of the Schomaker–Stevenson correction,[60] is 1.69 Å. The difference 0.155 Å between this value and the observed value corresponds to bond number about 1.50,[60] rather than to 1.206. The large value of the bond number is explained by the assumption of a transargononic structure, with five outer orbitals, by the phosphorus atom, with use of one of its 3d orbitals. For each of the structures **1** to **3**, a corresponding transargononic structure can be contemplated in which a single covalent bond becomes a double covalent bond; for example, structure **1** becomes:



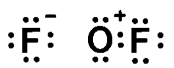
Here the phosphorus atom has four shared electron pairs and one unshared pair, using five orbitals. (In PCl_5, eg, the transargononic phosphorus atom has five shared pairs in its outer shell.) However, because of the electroneutrality principle such a structure is allowed only for structure **1**. Transargononic structures do not occur for first-row atoms, so this phenomenon is not found in NF_3. These ideas concerning the bonding in NF_3 and PF_3 are implicit in the discussion by Marynick, Rosen and Liebman[61] of the inversion barriers of these molecules.

6. THE OXYGEN DIFLUORIDE MOLECULE

Another molecule in which the bonds are expected to have some double-bond character, in correlation with ionic character, is OF_2. The amount of double-bond character would be smaller than for NF_3, however, because the value of Δx is smaller (0.5 versus 1.0) and because there are only two fluorine atoms, rather than three.

The molecule has bond angle 104.2° and bond length 1.390 Å.[62] We consider the following structures:

5
(1 structure)



6
(2 structures)

7
(2 structures)

The observed value of the electric dipole moment of the molecule is 0.297 D, which corresponds to 0.24 D for the moment of the bond. The value of ϵr, 6.67 D, leads to 3.60% as the contribution of each of the two structures of type **6** to the ground state of the molecule. The ionic character corresponding to $\Delta x = 0.5$ is 6.06% from Equation 1-1, which gives bond moment 0.41 D, which would lie close to the straight line in Figure 1-3.

The contribution of structure **5** to the normal state is calculated to be 82.9% from the amount of covalent character 93.9% (ionic character 6.1%) given by Equation 1-1. This value and the value 7.2% for the structures of type **6** lead to 9.9% for the structures of type **7**, hence to 5.0% of double-bond character, corresponding to a decrease in bond length by only 0.01 Å.

7. ELECTRONEGATIVITY EQUALIZATION

An idea based on electronegativity that has come into vogue in recent years is the concept of electronegativity equalization. The principle of electronegativity equalization, originally proposed by Sanderson[63,64] and extended by a number of other workers,[50,65–69] states that "When two or more elements initially different in electronegativity combine chemically, they become adjusted to the same, intermediate electronegativity within the compound." In spite of its acceptance, this idea seems to be self-contradictory inasmuch as electronegativity is defined as "the power of an atom *in a molecule* to attract electrons to itself."[42] Recently, Bratsch has published an article developing equalization with the original units, and he discussed the resolution of this difficulty.[70]

Table 1-3 compares the partial charges calculated using Equation 1-1, including the effect of double-bond character, and according to the prescription of Bratsch for the molecules discussed earlier as well as for NH_3 and H_2O, for which double bonding is not possible. It is seen that the partial charges agree better when double-bond character is taken into account in

TABLE 1-3. Comparison of Partial Charges

Molecule	Atom	Equation 1-1	Inclusion of double-bond character	Electronegativity equalization
NF_3	N	+0.663	+0.081	+0.215
	F	−0.221	−0.027	−0.072
NH_3	N	−0.550	—	−0.223
	H	+0.183	—	+0.074
PF_3	P	+1.783	+0.382	+0.509
	F	−0.594	−0.127	−0.170
OF_2	O	+0.122	+0.072	+0.099
	F	−0.061	−0.036	−0.050
H_2O	O	−0.775	—	−0.273
	H	+0.387	—	+0.137

cases of NF_3 and PF_3; for OF_2 the differences are too small to be significant. Nevertheless, it is not clear why there is such large disagreement in the partial charges calculated for NH_3 and for H_2O using these two methods. Indeed, electron spectroscopy for chemical analysis (ESCA) measurements indicate a "Pauling" partial charge of about −0.82 on nitrogen in NH_3 and a partial charge of about −0.66 on oxygen in H_2O.[71] For OF_2, the O1s binding energy measured by Koepke and Jolly[72] implies a "Pauling" partial charge of about +0.27 when the correlation given on page 124 of Reference 71 is employed. Although the manner in which one should account for the distribution of charge in molecules is a subject of much debate, it would be interesting to see what kind of correlation is obtained between ESCA core shifts and the partial charges calculated according to the Bratsch prescription. The efficacious correlation between ESCA core shifts and "Pauling" charges is well established.[71,73]

8. CONCLUSIONS

The foregoing presentation illustrates the point that in the discussion of the electric dipole moment of a molecule, or in fact of the interatomic distances, bond angles, or any other property, it may be necessary to take into account the possibility that the electronic structure does not correspond completely to the simplest valence bond formula that can be written for the molecule. In NF_3 the simplest formula, with three single covalent bonds with some ionic character, is found by considering the observed value of the electric dipole moment to be in resonance with formulas in which one fluorine atom is attached with an ionic bond, one with a single pure covalent bond, and one with a double covalent bond. The resultant bonds have about 15% of double-bond character. A similar discussion of PF_3 leads to about 21% of double-bond character. Moreover, values of the electric dipole moment of normal covalent single bonds are not well correlated with the Mulliken set of values of the electronegativity of atoms, but are well correlated with the original set.

ACKNOWLEDGMENT

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Chapter 3

METALLIC BONDING

Contents

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The Nature of the Interatomic Forces in Metals

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It has been generally assumed that in the transition elements (Fe, Co, Ni, Cu, etc.) the $3d$ shell is filled with ten electrons or is nearly filled, and that the d electrons make no significant contribution to the cohesive forces in metals. Evidence is presented here to show that about half of the d orbitals (2.56 of the total of 5) are involved in bond formation, through hybridization with the $4s$ and $4p$ orbitals, and that the number of covalent bonds resonating among the available interatomic positions increases from one to nearly six in the sequence K, Ca, Sc, Ti, V, Cr, remains nearly constant from Cr to Ni, and begins to decrease with Cu. The remaining 2.44 d orbitals, with very small interatomic overlapping, are occupied by nonbonding electrons which are mainly responsible for the ferromagnetic and paramagnetic properties of the metals. This point of view provides a qualitative explanation of many properties of the transition metals (including those of the palladium and platinum groups), such as interatomic distance, characteristic temperature, hardness, compressibility, and coefficient of thermal expansion, and it accounts satisfactorily for the observed values of the atomic saturation magnetic moments of the ferromagnetic elements iron, cobalt, and nickel and their alloys. It is also shown to provide a reason for the occurrence of the positive exchange integrals which give rise to ferromagnetism.

DURING the year 1926–1927 I had the great privilege of working as a Guggenheim Fellow in Munich under the direction of Professor Arnold Sommerfeld. At that time he was interested in the systematization of the new quantum mechanics and its application to problems of spectroscopy and atomic structure. It was not until the following year, after the pioneer work of Pauli[1] on the small temperature-independent paramagnetism of the alkali metals, that Professor Sommerfeld and his students began their development of the quantum-mechanical theory of metals.[2]

Their special field of investigation dealt with the electrical and thermal properties of metals. More recently considerable attention has been paid to the question of the nature of the interatomic forces in metals, which are significant for properties such as density, compressibility, crystal energy, and hardness; and it has been found possible to treat this problem in a reasonably satisfactory way for the case of the alkali metals, with a single valence electron per atom.[3] The extension of the theory to other elements has also been attempted.

In recent years I have formed, on the basis mainly of empirical arguments, a conception of the nature of the interatomic forces in metals which has some novel features. According to this view, the metallic bond is very closely related to the ordinary covalent or electron-pair bond; some of the electrons of an atom in a metal are involved with those of neighboring atoms in the interaction described as covalent-bond formation, with the bonds resonating among the available positions in the usual case that the number of positions exceeds the number of bonds. Moreover, all or most of the outer electrons of the atom, *including for the transition elements the d electrons* ($3d$, $4d$, and $5d$ for the iron, palladium, and platinum transition groups, respectively), take part in bond formation. (It has been assumed by most of the investigators in this field that the d electrons make no significant contribution to the cohesive forces.) It is shown below that this point of view leads to a qualitative explanation of many properties of metals, including their magnetic properties.

The combination of two lithium atoms to give the molecule Li_2 is described as involving the formation of a covalent bond.between the atoms. In a crystal of fluorine, F_2, the repulsion of the unshared outer electron pairs keeps the molecules spaced so that the minimum intermolecular

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[1] W. Pauli, Zeits. f. Physik **41**, 81 (1927).

[2] A. Sommerfeld, Naturwiss. **15**, 825 (1927); A. Sommerfeld, W. V. Houston, and C. Eckart, Zeits. f. Physik **47**, 1 (1928); A. Sommerfeld and N. H. Frank, Rev. Mod. Phys. **3**, 1 (1931); A. Sommerfeld and H. Bethe, *Handbuch der Physik*, Vol. 24, second edition.

[3] J. C. Slater, Phys. Rev. **35**, 504 (1930); **45**, 794 (1934); E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933); **46**, 509 (1934); F. Seitz, Phys. Rev. **47**, 400 (1935); K. Fuchs, Proc. Roy. Soc. **A151**, 585 (1935); H. M. Krutter, Phys. Rev. **48**, 664·(1935); M. F. Manning and H. M. Krutter, Phys. Rev. **51**, 761 (1937); W. Shockley, Phys. Rev. **51**, 129 (1937).

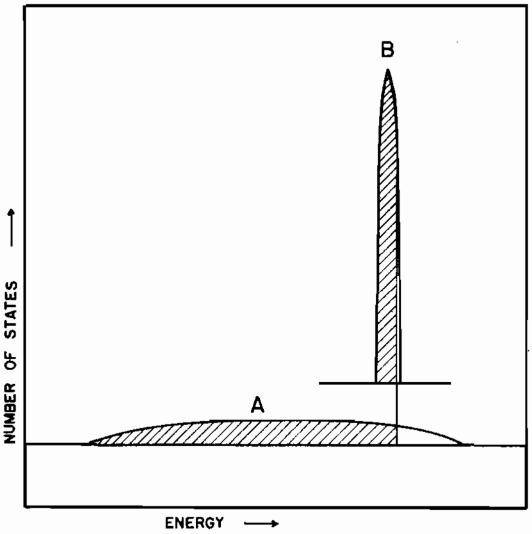

FIG. 1. Electronic states for iron-group atoms, showing number of states as qualitative function of electronic energy. Electrons in band *A* are paired with similar electrons of neighboring atoms to form bonds. Electrons in band *B* are *d* electrons with small interatomic interaction; they remain unpaired until the band is half-filled. The shaded area represents occupancy of the states by electrons in nickel, with 0.6 electron lacking from a completely filled *B* band. (States corresponding to occupancy of bond orbitals by unshared electron pairs are not shown in the diagram.)

internuclear distance is about twice as great as the intramolecular internuclear distance; there is no chance for resonance of a bond from one pair to another pair of atoms. Moreover, in fluorine all of the orbitals are occupied, so that resonance could occur only by the synchronous interaction of two or more molecules. In a crystal of lithium formed from Li_2 molecules, on the other hand, the conditions for resonance are satisfied; the molecules would be expected to approach one another closely, and each lithium atom has four *L* orbitals which might be used for bond formation. It is accordingly reasonable to think of the lithium crystal as involving covalent bonds resonating among the available positions. (Around each atom in the body-centered structure there are fourteen positions for bonds, eight at cube corners and six (with internuclear distance 15 percent larger) at cube face centers. On the average one of these is occupied by a bond.) Since the conditions for one-electron bond formation are satisfied,[4] it may be considered that these bonds also make some contribution to the structure of the crystal.

This qualitative description of the interactions in the metal is compatible with quantum mechanical treatments which have been given the problem,[5] and it leads to an understanding of such properties as the ratio of about 1.5 of crystal energy of alkali metals to bond energy of their diatomic molecules (the increase being the contribution of the resonance energy), and the increase in interatomic distance by about 15 percent from the diatomic molecule to the crystal.

The alkaline earth metals, by assuming the configuration *nsnp*, are able to form twice as many bonds as the alkalis. Similarly the succeeding elements in the periodic table can form bonds in increasing number.

The possibility that only some of the outer electrons enter into bond formation needs to be considered. There is a close relation between interatomic distance and bond type, and the values of the interatomic distances in the sequence[6] K, *A*2, 4.62A; Ca, *A*1, *A*3, 3.93–3.95A; Sc, not yet investigated; Ti, *A*3, 2.92–2.95A; V, *A*2, 2.63A; Cr, *A*2, 2.49A, as well as those in the similar sequences from Rb to Mo and Cs to W, indicate that the number of bonds resonating among the available positions increases from one to nearly six.

This conclusion is given strong support by the magnetic properties of the metals. Let us consider vanadium as an example. The configuration of the normal vanadium atom is $3d^34s^2$. If only the two 4*s* electrons were involved in bond formation (perhaps with promotion of one to 4*p*) the core of the atom, with the configuration $3d^3$, would have a large magnetic dipole moment,[7] and in consequence the metal would show ferromagnetism or large paramagnetism, decreasing in magnitude with increasing temperature. Instead vanadium is only weakly paramagnetic (molal susceptibility at room temperature 60×10^{-6} cgsmu.) and its paramagnetism is nearly temperature-independent; there is, indeed, a small in-

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[4] L. Pauling, J. Am. Chem. Soc. **53**, 3225 (1931).

[5] See in particular J. C. Slater, Phys. Rev. **35**, 509 (1930).

[6] The symbols *A*1, *A*2, and *A*3 represent the three simple metal structures: cubic closest packed, body centered, and hexagonal closest packed, respectively.

[7] Values 3.8 to 4.0 Bohr magnetons are observed for iron-group ions with this configuration.

crease in susceptibility with increasing temperature. This behavior is that expected if all five outer electrons take part in bond formation, with pairing of spins as in the usual electron-pair bond. The observed paramagnetic properties are then explained, as in Pauli's theory of the temperature-independent paramagnetism of the alkali metals, by the assumption that some of the electrons occupy excited levels with unpaired spins (that is, that under equilibrium conditions some of the bonds are broken), the number of these unpaired electrons increasing with increasing temperature. Since diamagnetism or small temperature-independent paramagnetism is observed for all of the metals K, Ca, Ti, V, Cr, Rb, Sr, Zr, Cb, Mo, Cs, Ba, La, Ta, and W, it seems necessary to accept the conclusion that all of the outer electrons take part in bond formation.

The *d* orbitals alone are not especially well suited to use in bond formation, but hybridization of *d*, *s*, and *p* orbitals leads to the best bond orbitals known,[8] such as the d^2sp^3 orbitals in octahedral complexes ($[Fe(CN)_6]^{\equiv}$, $[PtCl_6]^{=}$, etc.). There are available a total of nine relatively stable orbitals: five $3d$, one $4s$, and three $4p$ for the iron-group elements, and corresponding sets for the other series; and there exists accordingly the possibility that as many as nine outer electrons per atom enter into bond formation. The number of bonds would then be six for chromium, seven for manganese, eight for iron, and nine for cobalt; at nickel, with ten electrons, one unshared pair would occupy one of the nine orbitals, leaving only eight bonds, and the continued decrease in the number of bonds would lead to seven for copper, six for zinc, five for gallium, four for germanium, three for arsenic, two for selenium, and one for bromine.

It is indicated by the observed interatomic distances and shown by magnetic data that there occurs some deviation from this simple and attractive scheme in the middle region of the sequence. From chromium to cobalt the interatomic distances do not continue to decrease in value, as expected with increase in the number of bonds; instead they remain nearly constant: Cr, *A*2, 2.49A; Mn, no simple structure; Fe, *A*2, 2.48A, *A*1, 2.52A; Co, *A*1, *A*3, 2.50–2.51A; Ni, *A*1, *A*3, 2.49A; Cu, *A*1, 2.55A; Zn, *A*3, 2.66, 2.91A. This indicates that there are only about six bonds per atom for iron, cobalt, and nickel, and still fewer for copper and the succeeding elements.

The values for the atomic saturation magnetization at the absolute zero, σ_A, for the ferromagnetic metals iron, cobalt, and nickel are 2.22, 1.71, and 0.61 Bohr magnetons per atom, respectively.[9] These numbers are the average numbers of unpaired electron spins in the metals (the approximation of the *g* factor to 2 found in gyromagnetic experiments shows that the orbital moment is nearly completely quenched, as in complex ions containing the transition elements).

In the past the following interpretation has been given these numbers.[10] In nickel, for example, it has been assumed that the $3d$ shell is occupied by 9.39 (on the average) of the total of ten outer electrons, with 0.61 electron in the $4s$ shell. The 0.61 *s* electron alone was assumed to interact strongly between atoms, and to give rise to the principal cohesive forces in the metal. This interaction would quench the magnetic moments of the *s* electrons almost completely. The hole of 0.61 electron in the nearly completed *d* shell was then assumed to give a corresponding magnetic moment to the atom, the interaction of *d* orbitals of adjacent atoms being considered to be small.[11] It was similarly assumed that the cohesion of cobalt is due to 0.71 *s* electron, that

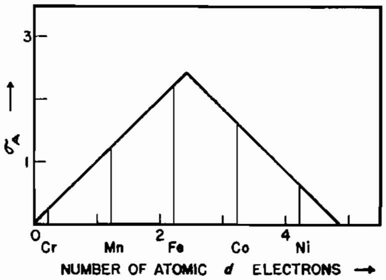

FIG. 2. Predicted dependence of atomic saturation magnetic moment σ_A as function of number of atomic *d* electrons.

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[8] L. Pauling, J. Am. Chem. Soc. **53**, 1367 (1931).

[9] P. Weiss and R. Forrer, Ann. de physique **12**, 279 (1929); E. C. Stoner, *Magnetism and Matter* (Methuen and Co., London, 1934), p. 366.

[10] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Oxford University Press, 1936), pp. 190, 222, 316.

[11] J. C. Slater, Rev. Mod. Phys. **6**, 272 (1934), has also concluded that the *d* electrons do not take much part in cohesion.

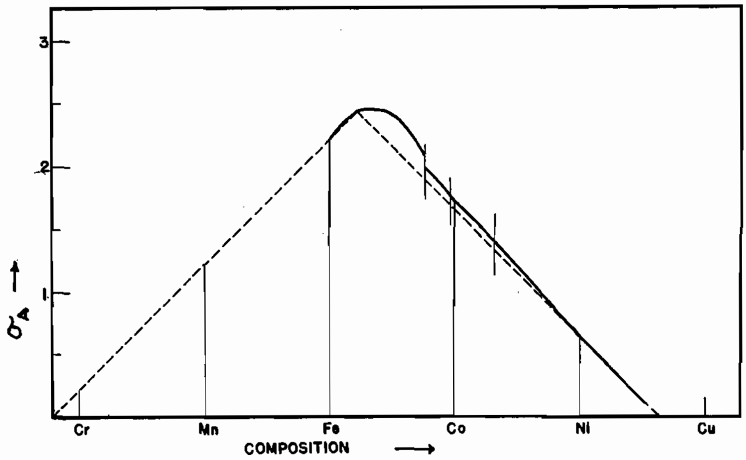

FIG. 3. Comparison of experimental values (solid curves) and predicted values (dashed lines) of σ_A for Fe-Co, Co-Ni, and Ni-Cu alloys. The short vertical lines indicate change in crystal structure.

of iron to 0.22 *s* electron, and that of copper to one *s* electron (the *d* shell for copper having its full complement of ten electrons). The difficulties of accounting for the interatomic distances and mechanical properties of the metals in this way are obvious.

Our picture, on the other hand, is that some of the $3d$ orbitals, as well as the $4s$ and $4p$ orbitals, are used for the formation of five or six bonds per atom. Instead of assuming the configuration $3d^{10}4s$ for copper, with bonding by the $4s$ electron only, we assume a configuration such as $d^2d^2d^2ddspp$ (to list the independent orbitals separately), so that each atom contains three unshared pairs in the *d* shell and five electrons used in forming bonds with surrounding atoms. This structure, involving only unshared and shared electron pairs, accounts satisfactorily for the observed diamagnetism of the metal.

Our knowledge of the properties of orbitals indicates that some of the $3d$ orbitals might be combined with the $4s$ and $4p$ orbitals to form bond orbitals in metals, the other $3d$ orbitals being unsuited to bond formation, but does not suffice to give a theoretical derivation of the number of *d* orbitals in each of these classes. Empirical evidence, outlined below, indicates that about 2.44 *d* orbitals (on the average) show only weak interatomic interactions, and that the remaining 2.56 *d* orbitals combine with the *s* orbital and the *p* orbitals to form hybrid bond orbitals.

In Fig. 1 there is indicated the division of the nine outer orbitals into these two classes. It is assumed that electrons occupying orbitals of the first class (weak interatomic interactions) in an atom tend to remain unpaired (Hund's rule of maximum multiplicity), and that electrons occupying orbitals of the second class pair with similar electrons of adjacent atoms. Let us call these orbitals *atomic orbitals* and *bond orbitals*, respectively. In copper all of the atomic orbitals are occupied by pairs. In nickel, with $\sigma_A = 0.61$, there are 0.61 unpaired electrons in atomic orbitals, and in cobalt 1.71. (The deviation from unity of the difference between the values for cobalt and nickel may be the result of experimental error in the cobalt value, which is uncertain because of the magnetic hardness of this element.) This indicates that the energy diagram of Fig. 1 does not change very much from metal to metal. Substantiation of this is provided by the values of σ_A for copper-nickel alloys,[12] which decrease linearly with mole fraction of copper from $\sigma_A = 0.61$ for pure nickel toward the value zero for mole fraction 0.6 of copper, and by the related values for zinc-nickel and other alloys.[13] The value $\sigma_A = 2.61$ would accordingly be expected for iron, if there were 2.61 or more *d* orbitals in the atomic orbital class. We conclude from the observed value $\sigma_A = 2.22$ for iron that

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[12] M. Alder, *Dissertation* (Zurich, 1916), quoted by Stoner, reference 9, p. 537.

[13] C. Sadron, Ann. de physique **17**, 371 (1932).

the number of orbitals in this class is less than 2.61, and lies between 2.22 and 2.61.

If it be assumed that one electron is removed from these atomic orbitals at each step Ni-Co-Fe, the number of orbitals is determined as 2.44 ±0.03. There is shown as Fig. 2 a diagram representing the expected change of atomic saturation moment σ_A with change in number of electrons. It is seen that σ_A is predicted to rise to a maximum value of 2.44 Bohr magnetons at a point 23 percent of the way from iron to cobalt. It is indeed observed[14] that the atomic saturation moment for iron-cobalt alloys rises to its maximum value, 2.47 Bohr magnetons, at 26 atomic percent cobalt. Curves showing measured values of σ_A for iron-cobalt, cobalt-nickel, and nickel-copper alloys are compared with the theoretical curve for 2.44 atomic *d* orbitals in Fig. 3. The experimental values are seen to indicate a tendency for the class of atomic *d* orbitals to remain half-filled with electrons (maximum multiplicity) over a small range of composition; the values of σ_A remain close to the maximum until an excess of about 0.25 electron is present, and then slowly decrease to the expected line.

There are no data available for testing the predicted numbers 0.22 and 1.22 of unpaired electron spins for chromium and manganese, respectively.

It seems probable that the palladium and platinum transition groups approximate the iron group very closely. For example, the paramagnetic susceptibility of palladium-gold alloys falls to zero at 60 atomic percent gold, the paramagnetic susceptibility of palladium containing hydrogen becomes zero at 60 atomic percent hydrogen, and the saturation moment of nickel is changed very little by the addition of palladium.[15]

It is of interest to calculate the number of bonding electrons, which we assume for the elements Cr to Ni to be all of the outer electrons except those in the atomic *d* orbitals. For chromium this number is $6-0.22=5.78$, and the same value is found for the other atoms also; this supports the evidence from interatomic distances that there is little change in bond type from chromium to nickel.

There are 2.56 *d* orbitals available for bond formation. To form 5.78 bonds these would hybridize with the *s* orbital and 2.22 of the less stable *p* orbitals. In copper, with one electron more than nickel, there is available an additional 0.39 electron after the hole in the atomic *d* orbitals is filled. This might take part in bond formation, with use of additional $4p$ orbital. However, the increase in interatomic distance from nickel to copper suggests that it forms part of an unshared pair with part of the bonding electrons, thus decreasing the effective number of bonds.

To this treatment of the metals the objection might be raised that it requires the considerable promotion of electrons to higher levels (for the separated atoms): thus, whereas Mott and Jones[16] consider that only the configurations $3d^84s^2$, $3d^94s$, and $3d^{10}$, which give states lying within an energy range of about 1.5 ev, can be considered for nickel, our treatment requires consideration of configurations such as d^7sp^2, which probably lie about 10 ev above the normal state. It is not the energy of the configuration of the isolated atom which is significant, however, but that of the metal itself, and the additional bond energy of the metal with this configuration compensates for the instability of the atom. The crystal energy (heat of sublimation) of a metal provides little information regarding the structure of the metal because it is the difference of two quantities, the energy of the metal and the energy of the separated atoms. It is properties such as interatomic distance, compressibility, and coefficient of thermal expansion, characteristic of the metal itself, which give information about the nature of the bonds.

We have mentioned that the increase in effective number of bonds from one to about six in the series of metals K to Cr, its approximate constancy to Ni, and subsequent decrease are compatible with the observed course of inter-

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[14] P. Weiss and R. Forrer, Ann. de physique **12**, 279 (1929). Mention should also be made of the moments found for iron, cobalt, and nickel by measurement of the paramagnetic susceptibility above the Curie point, the values being 3.15–3.20, 3.15, and 1.61–1.78 Bohr magnetons, respectively (W. Sucksmith and R. R. Pearce, Proc. Roy. Soc. **A167**, 189 (1938)). The root-mean-square values predicted from the magneton numbers on the assumption that the iron atoms contain either two or three unpaired electron spins, the cobalt atoms one or two, and the nickel atoms zero or one are 3.09, 2.56, and 1.35 Bohr magnetons, respectively. The reason for the only very approximate agreement is not known.

[15] Mott and Jones, reference 10, pp. 197, 199, 200.

[16] Reference 10, p. 190.

atomic distances for this sequence of elements. A similar behavior is observed for the sequences Rb to Ag and Cs to Au. In each of these three sequences the maximum or minimum values (corresponding to maximum strength of bonds) of the compressibility, coefficient of thermal expansion, characteristic temperature, melting point, and hardness occur for the metals to which we have assigned the maximum number of bonds.[17]

In the development of the quantum mechanical theory of ferromagnetism by Heisenberg, Frenkel, Bloch, Slater, and other investigators the assumption has been made that the exchange integrals between the unpaired *d* electrons of adjacent atoms are positive in sign. It has in the past been very difficult to understand why this should occur, since exchange integrals between atoms are usually negative. The situation is clarified by our picture of the structure of the transition metals. A large negative value of an exchange integral (corresponding to a strong covalent bond) results from the large overlapping of the orbitals of two atoms. Good bond orbitals can be formed by hybridization of the outer *d*, *s*, and *p* orbitals of the metal atoms, and we expect that all the *d* orbitals which are able to form strong bonds will enter into bond formation. The remaining *d* orbitals will hence be those which avoid overlapping with the orbitals of adjacent atoms. The exchange integrals of these atomic *d* orbitals will accordingly be small in absolute value, and may be positive.[18] This conclusion agrees with the observation that the transition metals may be either paramagnetic or ferromagnetic, the absolute magnitude of the exchange integrals in either case being about 1 kcal./mole.

It is obvious that many factors may enter into the determination of the sign of the exchange integral.[19] We would predict that in an atom which formed many strong bonds with its neighbors the *d* orbitals with negative exchange integrals would be drawn into bond formation, and that unpaired electrons in the remaining *d* orbitals could give rise to ferromagnetism. The condition for ferromagnetism that the metal atoms form a large number of strong bonds is satisfied by the ferromagnetic elements. We would also expect that manganese would develop ferromagnetic properties in alloys in which its atoms form more and stronger bonds with surrounding atoms than in the element itself. This may occur in the Heusler alloys (such as Cu_2AlMn and Cu_2SnMn).

In this discussion of the transition elements we have considered only the orbitals $(n-1)d\ ns\ np$. It seems probable that in some metals use is made also of the *nd* orbitals in bond formation. In gray tin, with the diamond structure, the four orbitals $5s5p^3$ are used with four outer electrons in the formation of tetrahedral bonds, the 4*d* shell being filled with ten electrons. The structure of white tin, in which each atom has six nearest neighbors (four at 3.016A and two at 3.175A), becomes reasonable if it is assumed that one of the 4*d* electrons is promoted to the 5*d* shell, and that six bonds are formed with use of the orbitals $4d5s5p^35d$.

This arrangement of bonds for white tin is not to be considered as the only one contributing to the structure of the metal. An atom in a metal shows great versatility in the formation of bonds. There is little difference in stability of structures involving not only different numbers of bonds but also varied types of coordination, and in consequence an atom in a metal can form bonds after deformation of the original structure which are approximately as strong as the original bonds. This gives a metal its ability to heal itself after deformation, which underlies such characteristic metallic properties as malleability and ductility.

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[17] The minimum reported values of the compressibility occur for the three sequences at Ni, Mo, and Pt, respectively; the minima of the coefficient of thermal expansion at Fe, Pd, and W; the maxima of the characteristic temperature at Cr, Ru, and W or Ir; those of the melting point at Ti, Mo, and W; and those of the hardness at Cr, Ru, and Os.

[18] Examination of the form of the exchange integral shows that it is necessarily positive if the two orbitals are orthogonal.

[19] This question has been discussed by J. C. Slater, Phys. Rev. **36**, 57 (1930).

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Atomic Radii and Interatomic Distances in Metals[1]

BY LINUS PAULING

The problem of the nature of the interatomic forces in the elementary metals and in intermetallic compounds and other alloys continues to be puzzling, despite the clarification of some questions which has been provided by quantum mechanical considerations.[2] It has been my opinion,[1,3] contrary to that of other investigators,[4,5] that the metallic bond is very closely related to the covalent (shared-electron-pair) bond, and that each atom in a metal may be considered as forming covalent bonds with neighboring atoms, the covalent bonds resonating among the available interatomic positions. It was shown in the first paper of this series[1] that the number of covalent bonds resonating among the available positions about an atom (the metallic valence of the atom) increases from one to nearly six (5.78) in the sequence K, Ca, Sc, Ti, V, Cr in the first long period of the periodic table, remains nearly constant from Cr to Ni, and begins to decrease with Cu. This concept, which is substantiated by the magnetic properties of the metals and their alloys, provides a qualitative explanation of many properties of the transition metals (including those of the palladium and platinum groups), such as characteristic temperature (heat capacity at low temperatures), hardness, compressibility, coefficient of thermal expansion, and the general trend of interatomic distances. It will be shown in the following pages that it also permits the formulation of a system of atomic radii which can be used for the calculation of interatomic distances in metals and intermetallic compounds and for the interpretation of observed interatomic distances in terms of the electronic structure of the crystals. These atomic radii (which may be called metallic radii) are found, as expected, to show an intimate relation to the covalent radii of the atoms—a relation which, in its general nature, permitted Goldschmidt[6] over twenty years ago to use data taken from both metals and ordinary covalent crystals in formulating a table of atomic radii, and which has been recognized[3] as providing very strong support for the concept that metallic bonds are essentially resonating covalent bonds.

The Relation of Atomic Radius to Bond Type

In the discussion of metallic radii we may make a choice between two immediate alternative procedures. The first, which I shall adopt, is to consider the dependence of the radius on the type of the bond, defined as the number (which may be fractional) of shared electron pairs involved (corresponding to the single, double, and triple bonds in ordinary covalent molecules and crystals), and then to consider separately the effect of resonance in stabilizing the crystal and decreasing the interatomic distance. This procedure is similar to that which we have used in the discussion of interatomic distances in resonating molecules.[7a] The alternative procedure would be to assign to each bond a number, the bond order, to represent the strength of the bond with inclusion of the resonance effect as well as of the bond type.[8]

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[1] "The Nature of the Interatomic Forces in Metals. II." For paper I of this series see L. Pauling, *Phys. Rev.*, **54**, 899 (1938).

[2] A. Sommerfeld and H. Bethe, "Handbuch der Physik," Vol. 24, second edition; N. F. Mott and H. Jones, "The Theory of the Properties of Metals and Alloys," Oxford University Press, Oxford, 1936; F. Seitz, "The Modern Theory of Solids," McGraw-Hill Book Co., New York, N. Y., 1940.

[3] L. Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, 1940, chap. XI.

[4] J. D. Bernal, *Trans. Faraday Soc.*, **25**, 367 (1929)

[5] W. L. Bragg, *J. Roy. Soc Arts.* **85**. 430 (1937).

[6] V. M. Goldschmidt, "Geochemische Verteilungsgesetze der Elemente," Vol. VII, Oslo, 1926.

[7] L. Pauling, *Proc. Natl. Acad. Sci.*, **18**, 293 (1932); L. Pauling, L. O. Brockway and J. Y. Beach, THIS JOURNAL, **57**, 2705 (1935); L. Pauling and L. O. Brockway, *ibid.*, **59**, 1223 (1937); ref. 3, Chap. V.

[8] W. G. Penney, *Proc. Roy. Soc.* (London), **A158**, 306 (1937).

Because the empirical information about the effect on interatomic distances of change in coördination number is not sufficiently extensive for our purpose, we make use of our knowledge of normal covalent radii. The available evidence indicates that the differences between single-bond, double-bond, and triple-bond radii are very nearly the same for all atoms,[9] and hence that an expression can be found for a term to be added to the single-bond covalent radius for any atom to give approximately the radius corresponding to another bond type. The carbon–carbon bond distances are 1.542, 1.330, and 1.204 Å. for a single bond, double bond, and triple bond, respectively, the double-bond and triple-bond radius corrections hence being −0.106 and −0.169 Å. The ratio of these numbers is just equal to log 2/log 3; accordingly the bond-type correction may be taken proportional to the logarithm of the bond number, n

$$-\Delta R(n) = 0.353 \log n \qquad (1)$$

Here ΔR is $R(n) - R(1)$, in Å., and n is the number of shared electron pairs involved in the bond. This logarithmic relation is, of course, to be expected in consequence of the exponential character of interatomic forces.

Atomic radii calculated with this expression need to be corrected for the stabilizing (bond-shortening) effect of resonance energy for use in resonating molecules or crystals. For example, the interatomic distance in benzene is not 1.418 Å., as given by equation 1 for $n = 3/2$, but is 0.028 Å. smaller, because of the effect of the resonance of the double bonds between two alternative positions. Of the several simple expressions which might be selected to represent empirically the effect of resonance on atomic radius, I have chosen the logarithm of the number of alternative bond arrangements among which resonance occurs, divided by the number of resonating bonds. The observed decrease in radius for benzene, corresponding to the resonance of a double bond between two positions, is 0.047 log 2; a similar expression, 0.017 = 0.036 log 3, is valid for graphite. In general we might expect the resonance correction for v single bonds resonating among N positions to be

$$-\Delta R\ (\text{resonance}) = \frac{A}{v} \log\left\{\frac{N!}{v!\,(N-v)!}\right\} \qquad (2)$$

in which A is approximately 0.04 or 0.05; the expression in brackets is the number of ways of distributing the v bonds among the N positions.

For the case $v = 1$ the expression in equation 2 reduces to $A \log N$, or, since $n = v/N$, to $-A \log n$; and it is found, moreover, that $-A \log n$ is a close approximation for $v > 1$ also, because of the rough approximation of $\{N!/v!(N-v)!\}^{1/v}$ to N/v. The resonance correction for the case of v single bonds resonating among N positions, with $N > v$, may accordingly be incorporated in equation 1 simply by decreasing the value of the constant to about 0.31.

I have chosen to use the equation

$$R(1) - R(n) = 0.300 \log n \qquad (3)$$

in the following considerations. This equation, which is based upon the study of interatomic distances for non-resonating and resonating covalent bonds in simple non-metallic substances of known structure, is found to agree reasonably well with those data for metallic crystals which are suited to a check on its validity, and its use permits a penetrating analysis of the structure of metals and intermetallic compounds to be made. There is some evidence that the constant (taken as 0.300) varies with the kind of atom and with the type of bond; but the evidence is not sufficiently extensive to lead to the determination of the nature of this variation.

The Correction from the A2 Structure to Coördination Number 12

In the A2 structure[10] (with atoms at the points of a cubic body-centered lattice) each atom has eight neighbors at the distance $a_0\sqrt{3}/2$ and six neighbors at the larger distance a_0. If the valence of the atom were used only for bonds to the eight nearest neighbors, the radius for the A2 structure would be that for coördination number 8 (CN8), which by equation 3 is 0.053 Å. less than the radius for CN12. But the bond number n of the eight stronger bonds is somewhat smaller than $v/8$, because part of the bond-forming power of each atom is used for the longer bonds, and accordingly the correction from A2 to CN12 is expected to be less than 0.053 Å.

The amount of this correction depends upon the value of the atomic radius. Zirconium, for example, has $a_0 = 3.61$ Å. for the A2 structure, the effective radii for the shorter and longer bonds being 1.563 and 1.805 Å., respectively. Application of equation 3 leads to $v/8.94$ for the bond number of the shorter bonds, and hence to 0.038 Å. for the correction to CN12. The value observed for this quantity (A3 structure, hexagonal close packing, six contacts with radius 1.583, six with 1.611, average 1.597 Å.) is 0.034 Å., which is slightly less than the calculated correction. A similar small discrepancy is shown by three of the four other metals for which direct experimental comparison of the A2 structure and CN12 can be made. (The fourth metal, chromium, which has a very much greater effective radius for CN12 than for the A2 structure, is discussed in detail in a later section.)

It is seen from Fig. 1 that the discrepancy, though small ($\leq$ 0.01 Å.), is real, and that it depends upon the atomic radius. The discrepancy indicates that the six longer bonds in the A2 structure use more of the bond-forming power of

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[9] Ref. 3, Chap. V.

[10] The symbols A2, etc., are those used in the "Strukturbericht."

TABLE I

METALLIC RADII OF THE ELEMENTS

	Li	Be	B								
v	1	2	3								
R(CN12)	1.549	1.123	0.98								
R(1)	1 225	0.889	.80								
	Na	Mg	Al								
v	1	2	3								
R(CN12)	1.896	1.598	1.429								
R(1)	1.572	1.364	1.248								
	K	Ca	Sc	Ti	V	Cr		Mn		Fe	Co
v	1	2	3	4	5	2.90	5.78	4.16	5.78	5.78	5.78
R(CN12)	2.349	1.970	1.620	1.467	1.338	1.357	1.267	1.306	1.261	1.260	1.252
R(1)	2 025	1 736	1.439	1.324	1.224	1.172		1.168		1.165	1.157
	Rb	Sr	Y	Zr	Cb	Mo		Tc		Ru	Rh
v	1	2	3	4	5	5.78		5.78		5.78	5.78
R(CN12)	2.48	2.148	1.797	1.597	1.456	1.386				1.336	1.342
R(1)	2.16	1.914	1.616	1.454	1.342	1.291				1.241	1.247
	Cs	Ba	La*	Hf	Ta	W		Re		Os	Ir
v	1	2	3	4	5	5.78		5.78		5.78	5.78
R(CN12)	2.67	2.215	1.871	1.585	1.457	1.394		1.373		1.350	1.355
R(1)	2.35	1.981	1.690	1.442	1.343	1.299		1.278		1.255	1.260
	Fa	Ra	Ac	Th	Pa	U		Np		Pu	Am
v	1	2	3	4	5	5.78					
R(CN12)				1.795		1.516					
R(1)				1.652		1.421					
				*Ce	Pr	Nd		Il		Sm	Eu
v				3.2	3.1	3.1				2.8	2
R(CN12)				1.818	1.824	1.818				1.85	2.084
R(1)				1.646	1.648	1.642				1.66	1.850

the atoms than is indicated by equation 3.[11] The curve may be made to pass through the experimental points by changing the factor of equation 3 from 0.300 to 0.70; this change, however, is not compatible with the great body of data on interatomic distances which supports the equation with the smaller factor.

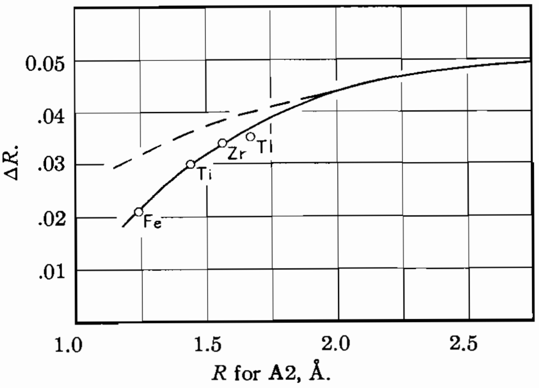

Fig. 1.—The correction $\Delta R = R(\text{CN12}) - R(\text{A2})$ from the A2 structure to coördination number 12. The dashed curve and its extension are calculated by equation 3; the full line passes through the experimental values.

In these circumstances I have chosen to use the empirical curve[12] of Fig. 1 rather than the slightly different theoretical curve for calculating the value of R(CN12) from the observed radius for A2.

Values of Single-bond Radii and Metallic Radii for Coördination Number 12

In Table I there are given values of the metallic radii of the elements for CN12, and of the corresponding single-bond radii $R(1)$, related to R(CN12) by equation 3, with the bond number placed equal to $v/12$. The values of the valence v are those indicated by magnetic properties[1] or by the interatomic distances themselves, as described in the following discussion.

The derivation of the values of the metallic valence of the transition elements from the ob-

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[11] Dr. F. J. Ewing has suggested to me that the octahedral configuration of six atoms in A2, with three intersecting long-bond diagonals, may favor the long bonds through the stabilizing influence of the resonance of an electron pair among the three positions.

[12] The experimental values for metals have been taken from the summary by M. C. Neuburger, *Z. Krist.*, **93**, 1 (1936), reproduced in Ref. 3, p. 409, except where otherwise indicated. SB I, . . . , VII refers to the seven volumes of the "Strukturbericht."

The A2 structure, with a_0 = 3.874 Å., has been reported for thallium by H. Lipson and A. R. Stokes, *Nature*, **148**, 437 (1941). The value 3.502 Å. for a_0 for lithium has been reported by H. Perlitz and E. Aruja, *Phil. Mag.*, **30**, 55 (1940), and 4.282 Å. for sodium by E. Aruja and H. Perlitz, *Z. Krist.*, **100**, 195 (1938). Polonium has been reported by W. H. Beamer and C. R. Maxwell, *J. Chem. Phys.*, **14**, 569 (1946), to have a simple cubic structure with a_0 = 3.34 Å.

TABLE I

METALLIC RADII OF THE ELEMENTS

				C	N	O	F
				4	3	2	1
				0.914	0.88 0.92		
				.771	.70 .74	0.66 0.74	0.64 0.72
				Si	P	S	Cl
				4	3	2	1
				1.316	1.28	1.27	
				1.173	1.10	1.04	0.994
Ni	Cu	Zn	Ga	Ge	As	Se	Br
5.78	5.44	4.44	3.44	4	3	2	1
1.244	1.276	1.379	1.408	1.366	1.39	1.40	
1.149	1.173	1.249	1.245	1.223	1.21	1.17	1.142
Pd	Ag	Cd	In	Sn	Sb	Te	I
5.78	5.44	4.44	3.44	2.44 4	3	2	1
1.373	1.442	1.543	1.660	1.620 1.542	1.59	1.60	
1.278	1.339	1.413	1.497	1.412 1.399	1.41	1.37	1.334
Pt	Au	Hg	Tl	Pb	Bi	Po	At
5.78	5.44	4.44	3.44	2.44	3	2	1
1.385	1.439	1.570	1.712	1.746	1.70	1.76	
1.290	1.336	1.440	1.549	1.538	1.52	1.53	
Cm							
Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
3	3	3	3	3	3	2	3
1.795	1.773	1.770	1.761	1.748	1.743	1.933	1.738
1.614	1.592	1.589	1.580	1.567	1.562	1.699	1.557

served saturation ferromagnetic moments may be summarized.[1] The saturation moment of iron is 2.22 Bohr magnetons, indicating that there are 2.22 unpaired (non-bonding) electrons. The presumption is that the remaining 5.78 electrons outside of the argon-like core are bonding electrons. The constancy of the number of bonding electrons at 5.78 is indicated by the equal change of saturation magnetic moment and average atomic number in alloys of iron with elements preceding or following it in the periodic table. When the average atomic number reaches about 18 + 8.22, however, the saturation magnetic moment ceases to increase, and begins to decrease at the same rate. This indicates that there are 2.44 non-bonding orbitals, which are being occupied by the pairing of electrons. At a point between nickel and copper these orbitals are filled with pairs, and further electrons decrease the metallic valence below 5.78.

These values of the number of bonding electrons are essentially empirical in nature, and their theoretical significance is not clear. The maximum valence of 5.78 is close to the value 6 found by Hultgren[13] for the maximum number of equivalent cylindrical orthogonal bond orbitals which can be formed by hybridization of one *s*, three *p*, and five *d* orbitals. It is likely that a quantum mechanical treatment of metals can be developed which is compatible with the valence numbers assigned here. There now exists a contradiction with the approximate quantum mechanical calculations of electrons in metals which have been made, which, for example, indicate one bonding electron per atom in copper, instead of 5.44. This contradiction may well be resolved in the future by a more thorough theoretical study.

The valences of the rare-earth metals are calculated from their magnetic properties, as reported by Klemm and Bommer.[14] It is from the fine work of these investigators that the lattice constants of the rare-earth metals have in the main been taken. The metals lutecium and ytterbium have only a very small paramagnetism, indicating a completed 4*f* subshell and hence the valences 3 and 2, respectively (with not over 3% of trivalent ytterbium present in the metal). The observed paramagnetism of cerium at room temperature corresponds to about 20% Ce^{4+} and 80% Ce^{3+}, that of praseodymium and that of neodymium to about 10% of the quadripositive ion in each case, and that of samarium to about 20% of the bipositive ion in equilibrium with the tripositive ion.

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(13) R. Hultgren, *Phys. Rev.*, **40**, 891 (1932).

(14) W. Klemm and H. Bommer, *Z. anorg. allgem. Chem.*, **231**, 138 (1937); **241**, 264 (1939); H. Bommer, *ibid.*, **242**, 277 (1939).

Bivalence is similarly shown for europium, and trivalence for the elements gadolinium to thulium.

The A2 structure is reported for europium, and A1 or A3 or both for the others, except samarium. For praseodymium and neodymium lattice constants have been reported for the A3 structure, with, however, the statement that some lines appear on the powder photographs indicating that c_0 should be doubled; possibly the structure is double-hexagonal close packing[3] instead of hexagonal close packing. Samarium is reported[15] to have a complex structure, probably tetragonal face-centered; the value of the radius given in the table is that calculated for a close-packed structure from the density, 6.93 g.cc^{-1}.

Except for chromium, tungsten, uranium, and manganese the metals in the first eleven groups of the table have the normal structures A1, A2, and A3.

Chromium is reported to be trimorphous, with the A2, A3, and A12 structures. The bond distance for the A2 structure, 2.493 Å., leads on correction to 1.267 Å. for R(CN12), which is a reasonable value for the extrapolation of the sequence of the preceding five metals, and hence indicates that the valence is approximately 6; we use the value[1] 5.78 in calculating $R(1)$, which equals 1.172 Å. The value of R(CN12) shown by the modification with the A3 structure (interatomic distances[16] 2.709 (6) and 2.717 (6)) is 1.357 Å., significantly larger than the above value. I think that this large radius is due to a smaller metallic valence of chromium in the A3 modification; that is, to its use of a smaller number of electrons as bonding electrons than in the A2 modification. Use of equation 3 leads to 2.90 for v, which has, with the corresponding value of R(CN12), been entered in the table as an alternative for the chromium atom.

The meaning of the existence of this large chromium atom in the metal is not evident. The calculated valence near 3 suggests comparison with the common tripositive oxidation state of chromium, in the chromic compounds; but it would not be expected that the three unpaired $3d$ electrons of the chromic ion would fail to participate in metallic bond formation—presumably 2.58 of the five $3d$ orbitals are used in bond formation[1] (whereas the $4f$ orbitals of the rare-earth metals, because of their smaller size, are not so used). It might be thought that the recognized stability of a half-filled subshell (which, for example, causes metallic europium to be bivalent) would favor the introduction of 2.44 electrons in the 2.44 non-bonding $3d$ orbitals,[1] with parallel spins, causing the atom to have $v = 3.56$; this would lead to $R(1) = 1.199$ Å., only 0.027 Å. larger than $R(1)$ for the higher-valent type of chromium atom, and this small difference might well result from the change in electronic structure. Another interpretation which is not easily ruled out is that the larger chromium atom contains a pair of $3d$ electrons, with opposed spins, and hence has $v = 4$ and $R(1) = 1.214$ Å.

Chromium is reported[17] also to have a modification with the A12 structure, for which, however, parameter values have not been determined.

Manganese crystallizes in three known modifications, no one of which, however, contains only atoms with the normal expected valence 5.78. For this valence we predict the value 1.168 Å. for $R(1)$, by interpolation between chromium and iron.

The simplest manganese structure is A6, which is cubic close packing with a small tetragonal distortion. The interatomic distances (2.582 (8), 2.669 (4)) lead to R(CN12) = 1.306 Å., and hence, with $R(1) = 1.168$ Å., to $v = 4.16$. This structure hence contains a lower-valent form of manganese, similar to that of chromium: in accordance with the foregoing discussion, the valence might really be 4 (three unpaired non-bonding electrons), 4.56 (2.44 unpaired non-bonding electrons), or 5 (a non-bonding electron pair), the last alternative being improbable.

The A13 modification of manganese[18] (β-manganese) contains 20 atoms in the unit cube, with $a_0 = 6.29$ Å. The atoms are of two kinds, with the following ligands[19]: MnI, 2.36 (3 MnI), 2.53 (3 MnII), 2.67 (6 MnII); MnII, 2.53 (2 MnI), 2.60 (2 MnII), 2.66 (4 MnII), 2.67 (4 MnI), 3.24 (2 MnII). The bond numbers of the bonds, calculated by equation 3 with $R(1) = 1.168$, and the corresponding valences are 0.92, 0.48, 0.28, and $v = 5.88$ for MnI and 0.48, 0.37, 0.28, 0.28, 0.03, and $v = 4.00$ for MnII. We hence conclude that *β-manganese contains two kinds of manganese atoms in the chemical sense as well as in the crystallographic sense:* in the unit cube there are eight atoms (MnI) with the normal large metallic valence and corresponding small size (R(CN12) = 1.261 Å.), and twelve atoms with the smaller valence and larger size (R(CN12) = 1.306 Å). found in the A6 modification.

This fact explains the occurrence of this unusual atomic arrangement, which has been reported for no other metallic element. Although coördination number 12 is the largest possible for spheres of equal size, the configurations of twelve spheres about another sphere shown in cubic close packing (A1) and hexagonal close packing (A3) and the combinations of these structures[3] do not represent the closest packing achievable

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[15] H. Bommer and E. Hohmann, *Z. anorg. allgem. Chem.*, **241**, 268 (1939).

[16] The number in parentheses after each interatomic distance is the number of neighbors at this distance from the atom under consideration.

[17] SB II, 190.

[18] G. D. Preston, *Phil. Mag.*, **5**, 1198 (1928); SB I, 757; SB II, 3.

[19] The ligands of an atom may be defined as the neighboring atoms which are bonded to it. In a metal the nearer neighbors of an atom are considered to be its ligands: for convenience a neighboring atom is not called a ligand if its distance is much greater than that corresponding to bond number 0.05; that is, if the distance is more than about 0.80 Å. greater than the sum of the single-bond radii.

with CN12: this is instead obtained by grouping twelve equal spheres at the corners of a regular trigonal icosahedron about a smaller central sphere, with radius in ratio $\sqrt{2\sqrt{5}/\sqrt{5} - 1} - 1 = 0.901$ to that of the surrounding spheres. The A13 structure is such that each of the smaller atoms (MnI) is surrounded by twelve atoms which approximate closely the regular trigonal icosahedron, whereas each of the larger atoms is surrounded by fourteen atoms (or by twelve, if the two distant atoms are ignored) in a configuration appropriate to a radius ratio slightly greater than unity.

The third modification (α-manganese) of the metal has the A12 structure, with 58 atoms, of four kinds, in a unit cube 8.90 Å. on edge.[20] According to the parameter values reported by Bradley and Thewlis, MnI has sixteen ligands, at 2.71 (12) and 2.82 (4), MnII has sixteen, at 2.49 (3), 2.69 (6), 2.82 (1), 2.89 (3), and 2.96 (3), MnIII has thirteen, at 2.45 (1), 2.49 (1), 2.51 (2), 2.66 (2), 2.67 (6), and 2.96 (1), and MnIV has twelve, at 2.24 (1), 2.38 (2), 2.45 (1), 2.51 (2), 2.66 (2), 2.69 (2), 2.82 (1) and 2.89 (1). The values of the valence of the four kinds of atoms calculated by equation 3 are 3.52, 4.70, 4.60, and 6.29, respectively, which indicate that of the 58 atoms in the unit cube thirty-four (2 MnI, 8 MnII, and 24 MnIII) are the low-valent kind found in the A6 structure, and twenty-four (MnIV) are the high-valent kind.[21]

The configuration of the twelve ligands about the small MnIV atom is that of an approximately regular icosahedron. The thirteen-cornered and sixteen-cornered coördination polyhedra about MnI, MnII, and MnIII are appropriate to axial ratios slightly greater than unity.

Tungsten, in addition to the A2 structure, which gives $R(1) = 1.299$ Å. with $v = 5.78$, crystallizes also as the only representative of another cubic structure, A15, with 8 atoms (2 WI and 6 WII) in a unit cube 5.04 Å. on edge. WI has as ligands 12 WII at 2.816 Å., leading to $v = 5.22$, and WII has fourteen ligands, 2 WII at 2.519, 4 WI at 2.816, and 8 WII at 3.085, leading to $v = 2 \cdot 1.35 + 4 \cdot 0.43 + 8 \cdot 0.16 = 5.70$. We accordingly conclude that both kinds of atoms in the A15 structure are normal, with valence approximately 5.78. The somewhat low values of v suggest that $R(1)$ might be increased by about 0.010 Å.

It is interesting to note that there are strings of tungsten atoms WII in the A15 crystals with each atom between two very near neighbors: the interatomic distance 2.519 Å. leads to the bond number $n = 1.35$.

Uranium also has, in addition to the A2 structure, which gives $R(1) = 1.421$ Å. with $v = 5.78$, a unique structure,[22] A20 (α-uranium), in which each atom has the following ligands: 2.76 (2); 2.85 (2), 3.27 (4), and 3.36 (4). These distances correspond, respectively, to the bond numbers 1.36, 0.96, 0.19, and 0.14, which lead to $v = 5.96$, in excellent agreement with expectation. It is interesting to note that in this structure the four strong bonds use most of the bond-forming power of the atoms (4.64), leaving only 1.32 for the eight weak bonds; and also that the two strongest bonds, as in tungsten (A15), bind the atoms together into straight strings extending through the crystal. This structural feature may be significant with respect to the uranyl ion, UO_2^{++}.

The valence assumed for copper and its congeners, 5.44, is the number of unpaired electrons possible for eleven electrons occupying 8.22 orbitals[1] (the 2.44 stable non-bonding and 5.78 bonding orbitals). Similarly the valence 4.44 is assumed for zinc, cadmium, and mercury, and 3.44 for gallium and its congeners. The remaining 0.88 p-orbital seems to become stable at group IV of the periodic table: we use $v = 4$ for germanium and grey tin, but for white tin and lead the value $v = 2.44$ is indicated.

Zinc crystallizes in a deformed A3 structure with large axial ratio, causing the six equatorial neighbors (at 2.660 Å.) to be nearer than the six neighbors in adjacent planes (at 2.907 Å.). The bond numbers are 0.54 and 0.21, respectively, leading to $R(1) = 1.249$ Å.

Cadmium has a similar structure, with distances 2.973 (6) and 3.287 (6), and bond numbers 0.57 and 0.17, leading to $R(1) = 1.43$ Å.

Mercury has a structure obtained by compressing the cubic close packed structure along a three-fold axis, causing the six equatorial distances (3.463 Å.) to become greater than the six others (2.999 Å.). The values of n are 0.11 and 0.63, respectively, leading to $R(1) = 1.440$ Å. The increasing weakness of the six longer bonds in the sequence zinc, cadmium, mercury is noteworthy.

Gallium has a unique structure,[23] in which each atom has one nearest neighbor, at 2.437 ± 0.010 Å., and six more distant ligands, at 2.706 (2), 2.736 (2), and 2.795 (2). With $v = 3.44$ the bond numbers are 1.21, 0.43, 0.38, and 0.31, and the single-bond radius is 1.245 Å. The strong bond is accordingly somewhat stronger than a single covalent bond, and it is proper to describe the structure, as has been done, as a metallic packing of Ga–Ga diatomic complexes.

Indium, with the tetragonal A6 structure, has coördination 3.242 (4), 3.370 (8), the bond numbers with $v = 3.44$ being 0.39 and 0.24, respectively, and the single-bond radius 1.497 Å.

The A1, A2, and A3 structures for **thallium** agree in giving 1.712 Å. for R(CN12), and, with $v = 3.44$, 1.549 Å. for $R(1)$.

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(20) A. J. Bradley and J. Thewlis, *Proc. Roy. Soc.* (London), **A115**, 456 (1927); SB II, 756; SB III, 2.

(21) Hume-Rothery and Bradley have mentioned that the α-manganese structure can be explained only by assuming that the atoms are of different sizes (*J. Inst. Metals*, **11**, 252, 257 (1944)).

(22) C. W. Jacob and B. E. Warren, THIS JOURNAL, **59**, 2588 (1937); SB VI, 1.

(23) A. J. Bradley, *Z. Krist.*, **91**, 302 (1935); SB III, 1.

Grey tin, with the diamond structure (A4), has effective atomic radius 1.399 Å., which may be taken as $R(1)$ because of the presumption from the structure that the valence is 4. This valence does not, however, apply to white tin: from the coördination 3.016 (4), 3.175 (2) for this metallic form the assumption $v = 4$ leads to $R(1) = 1.483$ Å., which is so much greater than the expected value 1.399 Å. as to eliminate the possibility of quadrivalence.[24] The alternative valence 2.44 leads to bond numbers 0.48 and 0.26 and single-bond radius 1.412 Å. This is not unreasonable, although from comparison with indium, thallium, and lead a value of about 1.46 Å. might be predicted for $R(1)$ for tin with $v = 2.44$. It is likely that in white tin the atoms have an average metallic valence between 2.44 and 4; the value $v = 3$, for example, would lead to the reasonable result $R(1) = 1.441$ Å. Because of uncertainty about the intermediate valence, the values for valence 2.44 are given in the table, together with those for $v = 4$ from grey tin.

The evidence for the existence of the reported third modification of tin is very weak. The hexagonal crystals which are formed by tin in the presence of mercury[25] have a simple structure, with atoms at the points of a hexagonal lattice,[26] with lattice constants[27] $a_0 = 3.198$ Å. and $c_0 = 2.980$ Å. for the alloy with 4.9% mercury. Neglecting the effect of the small number of atoms of mercury (which differ little in size from the atoms of tin), we calculate the value $R(1) = 1.401$ Å. from the coördination 2.980 (2), 3.198 (6) and the valence $v = 2.44$. Hence in this alloy tin has its lower valence.

It may be mentioned that the possibility of bivalence of tin in grey tin and the mercury alloy, suggested by the bipositive oxidation state of the element in many of its compounds, is ruled out because it leads to too small a value of $R(1)$—smaller than that for quadrivalent tin, whereas a larger value would be expected as the result of the appropriation of much of the *s* orbital by the unshared pair.

Lead, with the A1 structure, must have the low valence 2.44, which leads to $R(1) = 1.538$ Å.; the assumption $v = 4$ would give $R(1) = 1.603$ Å., which is much too large.

Bismuth is intermediate in the transition from a metallic to a normal covalent structure: each atom shows the effect of its normal tricovalence by having three nearest neighbors, at 3.10 Å.; and it has also three near neighbors at the larger distance 3.47 Å. The respective bond numbers 0.80 and 0.20 lead to $R(1) = 1.52$ Å. For antimony the values are 2.87 (3), 3.37 (3); $n = 0.87, 0.13$; $R(1) = 1.417$ Å.; and for arsenic 2.51 (3), 3.15 (3); $n = 0.92, 0.08$; $R(1) = 1.244$ Å. It is not unlikely that the value for arsenic is too large.

The values of $R(1)$ given in the table for electronegative atoms are their normal covalent single-bond radii[28] (except for boron, discussed below). The possibility that the radius 0.74 Å. of Schomaker and Stevenson[29] should be used for nitrogen in the metallic nitrides should be borne in mind.

A reliable radius for boron can be calculated from the data for the hexaborides and carbon boride. In CaB_6 each boron atom has five boron neighbors, at 1.716 Å.[30] On the assumption that two electrons are transferred from the calcium atom to the boron framework, we calculate $n = 0.67$ and $R(1) = 0.806$ Å. A similar calculation for ErB_6, with B–B = 1.699 Å. and three electrons transferred,[31] gives $n = 0.70$ and $R(1) = 0.803$ Å. The larger B–B distances for other hexaborides[31] indicate that part of the bond-forming power is used in bonds to the metal atoms; the above values of $R(1)$ must be considered maximum values. In boron carbide,[32] B_4C, each boron atom forms six bonds, the average B–B distance being 1.77 Å. With $n = 1/2$, this leads to $R(1) = 0.795$ Å. We accept the value 0.80 Å. for $R(1)$ of boron.

In applying the metallic radii in the discussion of the structure of a metal or intermetallic compound either the observed distances may be used with the single-bond radii to calculate the bond numbers, the sums of which may then be compared with the expected valences, or the distances may be compared with the sums of radii for suitable coördination numbers, such as CN12. The correction to be added to R(CN12) to give the radius for another coördination number, the va-

TABLE II

CORRECTION TO BE ADDED TO R(CN12)

Coördination number	Correction	Coördination number	Correction
1	−0.324	9	−0.038
2	− .234	10	− .024
3	− .181	11	− .011
4	− .143	12	0.000
5	− .114	13	+0.010
6	− .090	14	.020
7	− .070	15	.029
8	− .053	16	.037

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[24] The indication from interatomic distances that less than 4 bonding electrons per atom are operating in white tin has been recognized by W. Hume-Rothery, "The Structure of Metals and Alloys," The Institute of Metals Monograph and Report Series No. 1, p. 26 (1936).

[25] N. A. Puschin, *Z. anorg. allgem. Chem.*, **36**, 201 (1903).

[26] C. von Simson, *Z. physik. Chem.*, **109**, 183 (1924); SB I, 570.

[27] S. Stenbeck, *Z. anorg. allgem. Chem.*, **214**, 16 (1933). This structure has recently been verified by Mr. A. M. Soldate of these Laboratories (personal communication).

[28] Ref. 3, Chap. V.

[29] V. Schomaker and D. P. Stevenson, THIS JOURNAL, **63**, 37 (1941).

[30] L. Pauling and S. Weinbaum, *Z. Krist.*, **87**, 181 (1934).

[31] M. Stackelberg and F. Neumann, *Z. physik. Chem.*, **B19**, 314 (1932).

[32] G. S. Zhdanov and N. G. Sevast'yanov, *Compt. rend. acad. sci., U. R. S. S.*, **32**, 432 (1941); H. K. Clark and J. L. Hoard, THIS JOURNAL, **65**, 2115 (1943).

lence remaining constant, is given in Table II, as calculated by equation 3.

An Example: Cementite.—As an example of the use of the radii we choose the very important substance cementite, Fe_3C, the orthorhombic crystals of which appear in white cast iron and as one phase of the eutectoid pearlite in steel. In cementite[33] the iron atoms are in reasonably close packing, each having twelve iron neighbors at the average distance 2.62 Å. (FeI) or eleven at the average distance 2.58 Å. (FeII), in each case ± 0.08 Å. Each carbon atom occupies a position at the center of a trigonal prism of six iron atoms, with the Fe–C distance 2.01 ± 0.01 Å.

The radius of C for CN6, 0.82 Å., and that of Fe for CN13 and 14, 1.270 and 1.280 Å., indicate Fe–C distances 2.09 and 2.10 Å., somewhat larger than observed, and Fe–Fe distances 2.54 to 2.56 Å., somewhat smaller than observed. But the radii of iron for CN13 and 14 would be expected to apply to bonds with bond numbers $v/13$ and $v/14$, where $v = 5.78$; and it is expected that the bonds with carbon are stronger—namely, about $n = {}^2/_3$, since carbon is quadrivalent and has CN6 in this structure.

Indeed, if the bond numbers are calculated from the observed distances, the following results are obtained

C: 6 Fe at 2.01 Å., $n = 0.76$; $\Sigma n = 4.56$.
Fe I: 2 C at 2.01 Å., $n = 0.76$;
12 Fe at 2.62 Å. (av.), n (av.) $= 0.33$; $\Sigma n = 5.48$.
Fe II: 2 C at 2.01 Å., $n = 0.76$;
11 Fe at 2.58 Å. (av.), n (av.) $= 0.38$; $\Sigma n = 5.70$.

The bonds from iron atoms to carbon atoms are seen to be about twice as strong as those from iron to iron.

This calculation yields values of Σn in good agreement with the valence v of iron, 5.78, but somewhat larger than 4 for carbon. It seems not unlikely that the structure is under a slight strain, the Fe–C bonds being compressed a bit and the Fe–Fe bonds stretched a bit. If the Fe–C bonds are assigned the bond number 0.67, the FeI–FeI and FeI–FeII bonds the number 0.37, and the FeII–FeII bonds the number 0.43, the valences are exactly right and the following interatomic distances are predicted

Fe—C: 2.04 Å.
FeI—FeI: 2.59
FeI—FeII: 2.59
FeII—FeII: 2.55

The calculated Fe–C distance is 0.03 Å. larger than that observed, and the average Fe–Fe distance, 2.57 Å., is 0.03 Å. smaller than the observed average. It is not unreasonable to expect the same deformation (with opposite sign) for each of six Fe–C bonds as for the opposing seventeen much weaker Fe–Fe bonds (the bond numbers would equate six Fe–C to ten Fe–Fe bonds, and the additional factor would result from the well-known increase in stiffness of bonds with decrease in interatomic distance, as expressed, for example, in Badger's rule[34]); accordingly there is complete agreement between the calculation and experiment, and the conclusion can be reached that the carbon atoms in cementite are forced into holes slightly smaller (by 0.03 Å. in radius) than those into which they would fit exactly, and that the framework of iron atoms suffers a consequent small expansion.

Another Example: AuSn.—From among the many other intermetallic compounds which might be used as a second illustration, AuSn is chosen to show how the consideration of metallic valence and use of the radii contribute to the explanation of the choice of a suitable structure by a compound.

AuSn has the nickel arsenide structure, B8, with abnormally small axial ratio ($c/a = 1.278$, instead of the normal value 1.633). Each tin atom is surrounded by six gold atoms, at the corners of a trigonal prism, with Au–Sn = 2.847 Å.; and each gold atom is surrounded by six tin atoms, at the corners of a flattened octahedron, and two gold atoms, at 2.756 Å., in the opposed directions through the centers of the two large faces of the octahedron.

We expect gold to have valence 5.44, and tin 4 (or a smaller value). The Au–Sn bonds contribute equally to the two kinds of atoms; hence the extra valence of gold must find expression in Au–Au bonds. With the B8 structure (but not with the rather similar sodium chloride structure, B1) this can be achieved by compressing the structure along the c axis until the gold atoms are brought to the distance from one another suitable to the excess valence; that is, to the Au–Au distance corresponding to bond number $n = \frac{1}{2}(5.44 - 4) = 0.72$. With $R(1) = 1.336$, this distance is calculated by equation 3 to be 2.758 Å., in essentially exact agreement with observation.

The use of the values of $R(1)$ and equation 3 with the observed distances leads to the bond numbers 0.72 for Au–Au and 0.65 for Au–Sn, and hence to $v = 5.34$ for gold and 3.90 for tin, in satisfactory agreement with the normal valences of these metals.

It should not be thought that the structure of every intermetallic compound can be treated so simply; the discussion of such structural features as the transfer of electrons between atoms, the occurrence of strained bonds, the significance of relative atomic sizes, and the electron–atom ratio (Hume-Rothery ratio) must, however, be postponed to later papers.

The Dependence of the Radii on Atomic Number

In Figs. 2, 3 and 4 the single-bond metallic radii are plotted against atomic number, together

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(33) S. B. Hendricks, *Z. Krist.*, **74**, 534 (1930); A. Westgren, *Jernkontorets Ann.*, 457 (1932); H. Lipson and N. J. Petch, *J. Iron Steel Inst.*, **142**, 95 (1940).

(34) R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934).

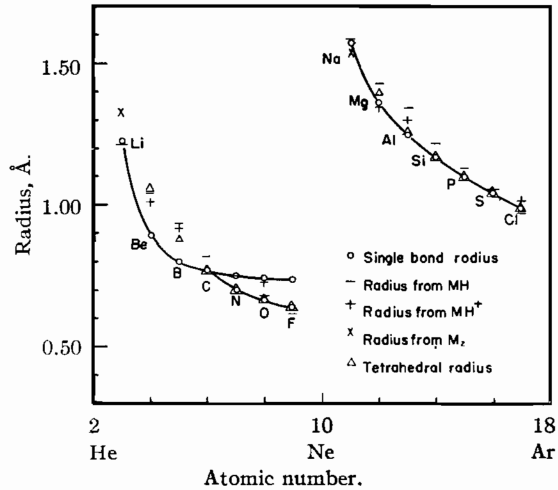

Fig. 2.—Covalent radii of the elements of the two short periods.

with values of covalent radii obtained from the observed interatomic distances in non-metallic substances. It is shown by the following discussion that these radii are very closely related; this investigation hence supports the thesis that the metallic bond is the resonating covalent bond.

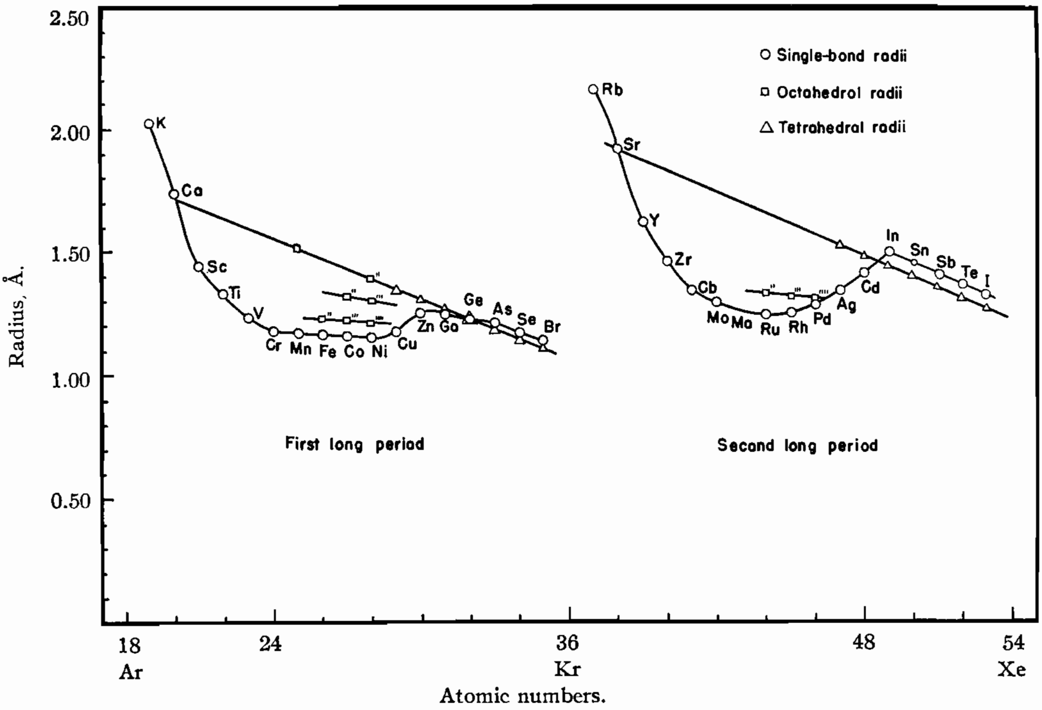

Fig. 3.—Covalent radii of the elements of the two long periods.

The radii for the elements of the two short periods are shown in Fig. 2. The metallic radii for the elements sodium to silicon lie on a common smooth curve with the normal covalent radii silicon to chlorine. Also the curve of the metallic radii lithium to carbon is continued smoothly by the Schomaker–Stevenson radii[29] for nitrogen, oxygen, and fluorine (the radii effective in normal covalent bonds, as in hydrazine, hydrogen peroxide, and the fluorine molecule, and to be used in other bonds with a correction for partial ionic character). The reasons for the deviation of the other set of normal covalent radii[35] of nitrogen, oxygen, and fluorine, the tetrahedral radii,[35] and the effective radii in diatomic hydrides (obtained by subtracting the normal hydrogen radius 0.30 Å. from the spectroscopic value of the interatomic distance) cannot be given with certainty; presumably the nature of the s–p hybridization is one of the important factors.

The curve of single-bond metallic radii for the elements of the first long period has a characteristic appearance (Fig. 3) which must be attributed in the main to variation in the type of bond orbital. The rapid decrease from potassium to chromium results from increase in bond strength due to increasing s–p and d–s–p hybridization. The linear section of the curve from chromium to nickel substantiates the assumption that the same bonding orbitals (hybrids of 2.56 $3d$ orbitals, one $4s$ orbital, and 2.22 $4p$ orbitals) are effective throughout this series. The increase in radius from nickel to copper is attributed not directly to decrease in valence (which has been corrected for by the calculation of the single-bond radii), but to the change in nature of the

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(35) M. L. Huggins, *Phys. Rev.*, **28**, 1086 (1926); L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934); Ref. 3.

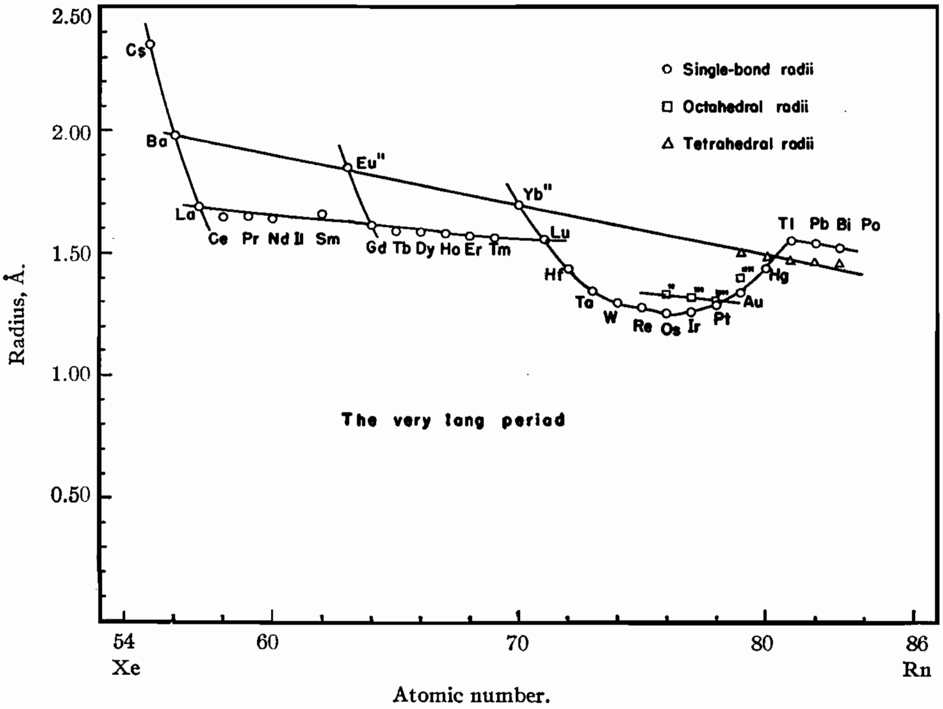

Fig. 4.—Covalent radii of the elements of the very long period.

bond orbitals, which in copper are hybrids of 2.22 $3d$ orbitals, one $4s$ orbital, and 2.22 $4p$ orbitals: the decreased contribution of the d orbitals causes the bond strength of the hybrid orbitals[36] to decrease from 2.981 to 2.967, with a further decrease to 2.874 at zinc.

After rising at copper and zinc, the curve of metallic radii approaches those of the normal covalent radii and tetrahedral covalent radii (which themselves differ for arsenic, selenium, and bromine because of the difference in character of the bond orbitals, which approximate p orbitals for normal covalent bonds and sp^3 orbitals for tetrahedral bonds). The bond orbitals for gallium are expected to be composed of 0.22 d orbital, one s orbital, and 2.22 p orbitals, and hence to be only slightly stronger than tetrahedral bonds, as is indicated by the fact that $R(1)$ is smaller than the tetrahedral radius.

It is interesting that a straight line drawn through the tetrahedral radii passes through the metallic radius for calcium; this suggests that the metallic bonding orbitals for calcium are sp orbitals, and that those for scandium begin to involve d-orbital hybridization.

The octahedral d^2sp^3 covalent radii for Fe^{II}, Co^{III}, and Ni^{IV} are seen to lie on a straight line parallel to and just 0.06 Å. above the line of the metallic radii. This is reasonable in consideration of the decreased contribution of d orbitals to the bonding. A roughly linear relation is found to hold between the radius (corrected to atomic number 28) and number of d orbitals taking part in bond formation, as is shown in Fig. 5.

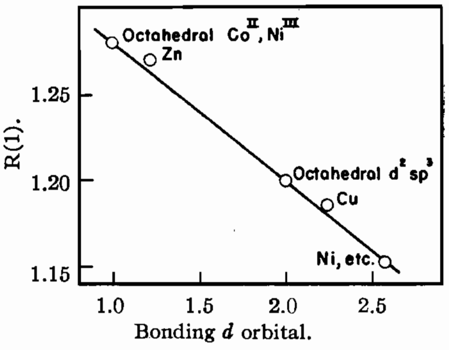

Fig. 5.—The dependence of single-bond radius on the number of bonding d orbitals.

The anomalously large radius[37] shown by manganese in hauerite, MnS_2, which has the pyrite structure, and in the similar substances $MnSe_2$ and $MnTe_2$ may now be accounted for in a satisfactory way. The magnetic properties of the crystals show that the five $3d$ orbitals of manganese are occupied by unshared electrons. The effective radius of manganese, 1.56 Å., corrected to 1.51 Å. for the resonance of four bonds among six positions, lies, as it should, very near the sp radius line.

The spectroscopic values[38] of interatomic dis-

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[36] As calculated by use of the angular wave functions: L. Pauling, THIS JOURNAL, **53**, 1367 (1931); Ref. 3, Chap. III.

[37] Pauling and Huggins, ref. 35; F. Offner, *Z. Krist.*, **89**, 182 (1934); N. Elliott, THIS JOURNAL, **59**, 1958 (1937); ref. 3, Sec. 23d.

[38] From the summary given by G. Herzberg, "Molecular Spectra and Molecular Structure. I. Diatomic Molecules," Prentice-Hall, Inc., New York, N. Y. 1939.

TABLE III

EFFECTIVE RADII OF TRANSITION METALS IN DIATOMIC HYDRIDES

	Fe	Co	Ni	Cu	Zn			
$r_e - 0.30$	1.176	1.243	1.175	1.163	1.295			
$R(1)$	1.165	1.157	1.149	1.173	1.249			
				Ag	Cd	In		
				1.318	1.462	1.552		
				1.339	1.413	1.497		
				Au	Hg	Tl	Pb	Bi
				1 224	1.441	1.570	1.539	1.509
				1.336	1.440	1.549	1.538	1.52

tances in diatomic hydrides of transition metals provide interesting evidence of the constancy in type of the bond orbitals of an atom except when the occupancy of orbitals by unshared electrons requires a change in hybridization. The effective radii (the observed distance minus 0.300 Å., for hydrogen) are for a number of metals within 0.02 Å. of the single-bond radii (Table III). The high value for cobalt and the low value for gold are hard to understand; the high values for zinc and cadmium, and perhaps also for indium, may be due to the occupancy of all *d* orbitals by unshared pairs.

There are few features of the curve for the second long period which differ enough from those of the first long period to require separate discussion. The curve does not have a linear segment in the neighborhood of ruthenium: this fact and the similar behavior of the hardness,[39] compressibility,[40] elasticity,[40] and related properties of the metals indicate clearly that the normal valence and bond type do not remain constant in the series molybdenum to palladium and tungsten to platinum, as they do in the series chromium to nickel; instead, the strength of the bond orbitals, and presumably also the valence, continue to increase somewhat until nearly the middle of each transition, at ruthenium and osmium, and then begin gradually to decrease. This effect is not a great one—the magnetic evidence and the evidence of hydride formation (to $PdH_{0.6}$) indicate that palladium and platinum, like nickel, contain 0.6 unpaired electron per atom; and the application of the relation shown in Fig. 5 leads to about 2.75 bonding *d* orbitals for ruthenium and osmium,[41] 2.6 for iridium and rhodium, and 2.3 for palladium and platinum. These numbers, and especially the numbers of bonding electrons, are, however, so uncertain that a change of valence values from those for the elements of the first long period is not yet justified.

The metallic radius for indium differs from that of gallium by being greater than the tetrahedral radius; it lies nicely on a straight line passing through the normal covalent radii of antimony, tellurium, and iodine. This suggests that the metallic radius for tin might also lie on this curve, which would be achieved by assigning the intermediate valence 3.2 to white tin. The corresponding point is indicated by a small circle in Fig. 3.

The very long period is closely similar to the second long period, except for the interpolation of the rare-earth metals. It is interesting that a straight line can be passed through the points for barium, the two bivalent rare-earth metals, and the tetrahedral radii of the heavier elements.

The Dependence of Metallic Radius on Formal Charge.—A question of interest in the discussion of intermetallic compounds is that of the effect on its metallic radius of transferring an electron to or from an atom. A reasonable method of calculating the single-bond radius of an element of one of the long periods which has gained or lost an electron may be proposed: the radius is that determined by one of the straight lines shown in the figures, or by a similar line; namely, the line appropriate to the electronic structure of the atom. For example, if an atom of gold were to lose an electron it would achieve the configuration of a neutral platinum atom; its radius would then be 1.280 Å.; that is, the radius of platinum, 1.290 Å., corrected by the amount indicated by the octahedral radius line, −0.010 Å. If an atom of calcium were to gain an electron, its radius would be that of scandium, 1.439 Å., plus a correction of about 0.02 Å., giving 1.46 Å.

The proper treatment of elements of the short periods is uncertain. The equality of the tetrahedral radius and normal covalent radius for the electronegative elements indicates that for them no charge correction is needed. For the electropositive elements the same method as for the long periods may be satisfactory, with use of a line with slope about −0.05.

The Use of the Metallic Radii

The considerations presented in this paper have in some degree elucidated such complex elementary metallic structures as those of α- and β-manganese. They may also be applied with value to intermetallic compounds; the results which are yielded and the discussion of their

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(39) O. Winkler, *Z. Elektrochem.*, **49**, 221 (1943).

(40) W. Köster, *ibid.*, **49**, 233 (1943).

(41) The surprising stability of uni-negative rhenium, the complexes of which are undoubtedly covalent, may be related to the especial strength of the bonds formed by the neutral osmium atom.

significance to the great problem of the nature of the metallic state will be communicated later.

Acknowledgment.—The work reported in this paper is part of a series of studies of metals and alloys being carried on with the aid of a grant from the Carbide and Carbon Chemicals Corporation.

Summary

An equation has been formulated to express the change in covalent radius (metallic radius) of an atom with change in bond number (or in coördination number, if the valence remains constant), the stabilizing (bond-shortening) effect of the resonance of shared-electron-pair bonds among alternative positions being also taken into consideration. This equation has been applied to the empirical interatomic-distance data for the elementary metals to obtain a nearly complete set of single-bond radii. These radii have been compared with the normal covalent radii, tetrahedral radii, and octahedral radii of the elements; their evident close relationship strongly supports the idea that the interatomic forces in metals are for the most part due to covalent bonds resonating among the available interatomic positions.

It is found that chromium atoms, manganese atoms, and tin atoms exist in metals in two forms, a small, high-valent form and a larger, low-valent form. The two kinds of manganese atoms coexist in α-manganese and in β-manganese.

In many metals each atom is attached to some of its neighbors by strong bonds and to others by much weaker bonds. An extreme case is β-tungsten, in which there are straight strings of strongly bonded atoms. Similar strings are also present in the α-uranium structure.

The use of the radii is illustrated by the discussion of two compounds, cementite and AuSn.

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The Ratio of Valence Electrons to Atoms in Metals and Intermetallic Compounds*

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It is shown that the numbers of valence electrons assigned to the γ-alloys, β-manganese and alloys with similar structure, and α-manganese by a new system of metallic valences agree closely with the electron numbers calculated for complete filling of important Brillouin polyhedra for these structures.

I. INTRODUCTION

WHEREAS chemical valence theory has provided a satisfactory systematization of the formulas of most organic and inorganic compounds, the intermetallic compounds have continued to present a puzzling problem. Some intermetallic compounds, such as Mg_2Sn, have formulas that can be correlated with the customary valences of the elements involved. Many others, however, seem to show in their formulas no correlation with chemical valence: examples are $NaCd_2$, KHg_{13}, Cu_5Zn_8, $Cu_{31}Sn_8$, Cu_9Al_4, Fe_5Zn_{21}. Added interest is given to the problem by the fact that the last four of these compounds, with formulas that seem to show little relation to one another, are sufficiently similar in their properties, and different from other intermetallic compounds, to indicate that they are to be classified together.

Only in recent years has progress been made in attacking the problem presented by these intermetallic compounds; at the present time we may say that, although there are a number of puzzling questions that remain unanswered, the beginning of a theory of the stability and other properties of the substances has been formulated.

Let us first consider, as an example, the copper-zinc system of alloys.[1,]** The ordinary yellow brass of commerce is restricted in composition to the first (copper-rich) phase of the system. This phase, which has the face-centered cubic structure characteristic of copper, is followed successively, as the zinc content is increased, by the β-phase (body-centered cubic),

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* Contribution from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, No. 1163.

** References are listed in the bibliography at the end of the paper.

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γ-phase (with a complex cubic structure), ϵ-phase (close-packed hexagonal, with axial ratio c/a less than $(8/3)^{\frac{1}{2}}$), and the η-phase (close-packed hexagonal, with c/a greater than $(8/3)^{\frac{1}{2}}$, terminating in pure zinc). The α- and η-phases are regarded as primary solid solutions in the parent metals, but the intermediate phases have compositions that can be described approximately by relatively simple chemical formulas, CuZn for the β-phase, Cu_5Zn_8 for the γ-phase, and $CuZn_3$ for the ϵ-phase.

In other systems of binary alloys similar phases are found. The simple structure characteristic of the β-phase, with two atoms in a cubic unit cell, at positions 000 and 1/2 1/2 1/2, is shown by the compounds AgZn, AgCd, AuZn, AuCd, and CuBe. The compounds Cu_3Al and Cu_5Sn, with different formulas, also have structures related to the body-centered structure for pure metals. In 1926, even before complete x-ray investigations of these compounds had been published,[2] Hume-Rothery[3] suggested that the β-phases CuZn, Cu_3Al, and Cu_5Sn are analogous in structure. He further pointed out that if valences of 1, 2, 3, and 4 are assigned to metals of groups I, II, III, and IV of the periodic table, a constant ratio 3/2 of valence electrons to atoms is displayed by these β-phase compounds (CuSn, $(2+1)/2=3/2$; Cu_3Al, $(3+3)/4=3/2$; Cu_5Sn, $(5+4)/6=3/2$). This observation led him to conclude that certain metal structures are stabilized by the possession of a definite ratio of valence electrons to atoms, this ratio being equal to 3/2 in the case of the arrangement characteristic of the β-phase. In the course of the next few years this rule was extended by various investigators, chiefly Westgren and Phragmén[4] and Bradley and Thewlis.[5] They showed that in a large number of different alloy systems the β-, γ-, and ϵ-phases appear at or near electron-to-atom ratios of 3/2, 21/13, and 7/4, respectively, calculated with the usual valence values for the elements. In some systems they found, instead of the β-phase, a complex structure similar to β-manganese appearing at the ratio 3/2 (for example, Ag_3Al).

In order to bring β-phases such as FeAl and CoAl into correspondence with the rule it was necessary to assign the valence of zero to the transition elements manganese, iron, cobalt, and nickel and to their congeners, the palladium and platinum metals. In spite of this element of arbitrariness the Hume-Rothery rule has served to organize and to simplify a large amount of data relative to alloy systems.[6] The known examples of the Hume-Rothery phases and intermetallic compounds of similar structure, including the β-manganese structure, are listed in Table I. Not all of the compounds shown here have the electron-atom ratio demanded by the Hume-Rothery rule.

The γ-alloys are compounds with complex formulas, the cubic unit of structure containing 52 atoms or a multiple of 52 atoms. For these alloys the Hume-Rothery ratio is a constant at 21/13, with two exceptions, $Li_{10}Pb_3$ at 22/13 and $Li_{10}Ag_3$ at 13/13. The evidence is accordingly strong that the electron-atom ratio is important in stabilizing these structures. It seems likely that it is also important for β-manganese, with 20 atoms per unit cube, and also for the ϵ-structure. The β-phase structure, however is so simple, consisting of atoms placed at the points of a body-centered cubic lattice, that it might well be expected that factors other than the electron-atom ratio, such as the relative sizes of the atoms, would be determinative in the selection of this structure, and it is accordingly not surprising that nearly half of the β-phase intermetallic compounds listed in Table I show Hume-Rothery ratios different from 3/2.

The β- and ϵ-phases are not unlike their component metals in properties such as luster, malleability, and electrical resistivity. The γ-phase, however, shows striking differences: it is brittle and is associated with sharp maxima in electrical resistivity[7] and diamagnetic susceptibility.[8]

The theoretical significance of the Hume-Rothery rule and the quantum mechanical explanation of the curious properties of the γ-alloys have been discussed by Jones.[9] Jones' treatment is based upon the study of the effect of the periodic potential of a lattice in which electrons are moving in producing bands or zones of energy levels.[10, 11] It was found that the energy of the electron moving in a periodic field may be a discontinuous function of its momentum, and L. Brillouin[12] recognized that the points of discontinuity correspond to Bragg reflection of the electrons from crystallographic planes of the crystal. The geometrical conditions for this sort of perturbation can be described in a space which is at the same time momentum space for the electron and reciprocal-lattice space for the crystal; perturbations occur when the momentum vector terminates on polyhedral surfaces. We shall call these polyhedra Brillouin polyhedra and the zones of energy levels between the polyhedral surfaces Brillouin zones.[13] The Brillouin polyhedra can be described by assigning to the faces the crystallographic indices of the planes which by Bragg reflection of the electron produce the perturbation that concentrates the energy levels into zones.

Jones pointed out that the energy discontinuities produced in this way are large only for planes from which the electrons are reflected strongly; that is, for planes with a large structure factor for electrons. Usually these are also planes which give strong x-ray reflections, although in special cases, when the relative scattering powers of atoms of two elements for slow electrons are considerably different than for x-rays, this criterion may not be valid. Jones observed that the physical properties shown by the γ-alloys are those which would be expected for a metallic crystal with a completely filled or nearly completely filled Brillouin zone. He noted that the first two strong x-ray reflections shown by γ-brass, Cu_5Zn_8, those from the forms {330} and {411}, determine a Brillouin polyhedron of volume $45/a_0^3$ (a_0 being the edge of the unit cube), which leads to occupancy by 90 electrons per unit cell of 52 atoms. The Hume-Rothery ratio of 21/13 corresponds to 84 electrons per 52 atoms; accordingly the zone is $84/90=93.5$ percent filled. This might be considered sufficient to explain the filled-zone properties of γ-brass, and it was indeed supposed by Jones that the number of electrons required to fill a zone is somewhat less than the volume of the Brillouin polyhedron. The argument for this, however, is not very clear, and, in particular, there is no reason to expect the stabilization to occur exactly at 84/52, in place of 90/52. In a similar treatment of alloys with the β-manganese structure, containing 20 atoms per cubic unit cell, Mott and Jones[9] found that there is a Brillouin polyhedron containing 32.4 electrons per unit cell of 20 atoms. Since the Hume-Rothery ratio is 3/2 this zone is $30/32.6=92$ percent filled. In the consideration of the β-phase alloys Mott and Jones[9] found that the first strong reflection from the body-centered cubic lattice, {110}, gives a Brillouin polyhedron (constituting the first Brillouin zone) that contains 4 electrons per atom, so that the Hume-Rothery ratio 3/2 represents only a partial (75 percent) filling. This is in agreement with the highly metallic character of this phase, the alloys being malleable and good conductors of electricity, and having normal magnetic properties. Mott and Jones pointed out that a sphere inscribed in the {110} Brillouin polyhedron contains 1.480 electrons per atom, which is essentially equal to the customary Hume-Rothery ratio, and they suggested that, in this instance, stabilization occurs when the spherical surface of the momentum sphere first touches the Brillouin polyhedron; that is, at values of the momentum for which Bragg reflection first appears, in certain directions.

TABLE I. Hume-Rothery phase.

Phase	β		β-Mn		γ		ϵ	
Type in Strukturbericht	*B*2 and *L*20		*A*13		*D*81, 82, 83, 84			
Character	body-centered cubic		complex cubic		complex cubic		hexagonal close packed $c/a<(8/3)^{\frac{1}{2}}$	
Atoms per unit cell (minimum)	2		20		52		2	
	Compounds	H-R ratio	Compounds	H-R ratio	Compounds	H-R ratio	Compounds	H-R ratio
Compounds formed, with Hume-Rothery ratio electrons: atoms	CuZn	3/2	β-Manganese	0	Cu_5Zn_8	21/13	$CuZn_3$	7/4
	AgZn	3/2			Cu_5Cd_8	21/13	$CuBe_3$	7/4
	AgCd	3/2	Ag_3Al	3/2	Ag_5Zn_8	21/13	$CuCd_3$	7/4
	AuZn	3/2	Au_3Al	3/2	Ag_5Cd_8	21/13	$AgZn_3$	7/4
	AuCd	3/2	Cu_5Si	3/2	Au_5Zn_8	21/13	$AgCd_3$	7/4
	Cu_3Ga	3/2	$CoZn_3$	3/2	Au_5Cd_8	21/13	$AuZn_3$	7/4
	Cu_5Sn	3/2			Au_5Hg_8	21/13	Cu_3Sn	7/4
	BeCu	3/2			Cu_9Al_4	21/13	Cu_3Ge	7/4
	MgAg	3/2			Cu_9Ga_4	21/13	Ag_3Sn	7/4
	AlFe	3/2			Cu_9In_4	21/13	Au_3Sn	7/4
	AlCo	3/2			Ag_9Al_4	21/13	Au_5Al_3	7/4
	AlNi	3/2			$Cu_{31}Sn_8$	21/13	$FeZn_7$	7/4
	$AlCu_3$	3/2			$Ag_{31}Sn_8$	21/13		
	LiHg	3/2			Fe_5Zn_{21}	21/13		
	LiAg	1.0			Co_5Zn_{21}	21/13		
	LiTl	2.0			Ni_5Zn_{21}	21/13		
	BeCo	1.0			Rh_5Zn_{21}	21/13		
	BePd	1.0			Pd_5Zn_{21}	21/13		
	MgHg	2.0			Pt_5Zn_{21}	21/13		
	MgTl	2.5			Ni_5Cd_{21}	21/13		
	CaTl	2.5			$Cu_7Zn_4Al_2$	21/13		
	SrTl	2.5			$Li_{10}Pb_3$	22/13		
	AlNd	3.0			$Li_{10}Ag_3$	13/13		
	PdCu	0.5						
	TlSb	4.0						
	TlBi	4.0						

II. A NEW SYSTEM OF METALLIC VALENCES

The Hume-Rothery valences described above have the values zero for manganese, iron, cobalt, and nickel, one for copper, two for zinc, three for gallium, etc. For the metals from copper on these values correspond to the assumption that all electrons outside of a completely filled 3*d* sub-shell are valence electrons. A new valence system for the transition metals was proposed in 1938[14] and has been recently applied in the discussion of values of interatomic distances in metals and intermetallic compounds.[15] This system of valences depends primarily on the interpretation of values of the saturation magnetic moment of ferromagnetic metals. It represents an alternative interpretation of these magnetic moment data to that given by Mott and Jones, Slater, and other investigators. The previous interpretation may be illustrated by the consideration of nickel. The saturation magnetic moment of nickel is 0.61 Bohr magnetons per atom. Nickel has atomic number 28, and it might be expected that it would have a completed 3*d* sub-shell, with no outer electrons. The value 0.61 magnetons for the magnetic moment is explained by saying that there is a transfer of 0.61 electrons per atom from the 3*d* sub-shell to a bonding Brillouin zone, formed by 4*s* electrons, which contribute little to the magnetic properties, and that the deficiency of 0.61 electrons in the 3*d* sub-shell is responsible for the magnetic properties. (On this basis the Hume-Rothery valence of nickel might well be expected to be 0.6 instead of 0.) The observed saturation magnetic moment of cobalt, 1.71 Bohr magnetons, is similarly accounted for by the assumption that essentially the same number of electrons, 0.71 per atom, are used as binding electrons in a 4*s* Brillouin zone, leaving a deficiency of 1.71 in the 3*d* sub-shell. The moment observed for iron, however, offers some difficulty, in that its value, 2.22 magnetons, would indicate, on a straightforward extension of the argument, that only 0.22 electrons per atom were involved in the metallic binding. Because the mechanical properties seemed difficultly reconcilable with this assumption, Slater[16] arbitrarily assumed, instead, that the Hund rules are no longer applicable to iron and that the magnetic moment for the partially filled 3*d* sub-shell is not to be calculated in the usual way, as the difference between the maximum occupancy of the sub-shell, 10, and the number of electrons present.

The alternative explanation proposed in 1938 for these values is that the 9 orbitals, five 3*d*, one 4*s*, and three 4*p*, per atom are to be hybridized and divided into three classes. The first class of hybrid orbitals is the stable bonding orbitals, the number of which is approximately 5.78 per atom. The second class of orbitals, stable atomic orbitals, presumably 3*d* orbitals, is present to the extent of about 2.44 per atom. The third class, 0.78 per atom, consists of unstable orbitals that are not utilized except at and beyond the subgroup IV*b* of the periodic table. With these assumptions the sequence of metals potassium, calcium, scandium, titanium, and vanadium use, respectively, 1, 2, 3, 4, and 5 electrons per atom in forming bonds, their metallic valences being then equal to the maximum normal chemical valences of the elements. If only 5.78 bonding orbitals are available, chromium would be considered to form 5.78 bonds, and to retain 0.22 electrons per atom in the stable atomic orbitals. Manganese and iron would similarly contain 5.78 bonding electrons per atom, with 1.22 and 2.22 unpaired electrons occupying the stable atomic orbitals; this, then, accounts for the observed saturation magnetic moment of 2.22 for iron. A similar explanation applies also to the alloys of iron and chromium and of iron and vanadium, for which experimental values are indicated in Fig. 1.

When the effective atomic number becomes a little greater than the value for iron, however, the stable atomic orbitals are occupied by one electron per orbital, and further electrons can enter this set of orbitals only by becoming paired; accordingly, the magnetic moment begins to fall, as is indicated by the experimental data. The magnetic moment drops to the value 1.7 for cobalt and 0.6 for nickel, and to zero at a point 60 percent of the way between nickel and copper.

The numbers 5.78 and 2.44 were obtained in 1938 by the analysis of these magnetic data. It is seen from Fig. 1 that the experimental points are not precisely represented by straight lines with slope +1 and −1, and that, accordingly, there is some uncertainty in the construction of these lines and, hence, in the number of bonding orbitals and the number of stable atomic orbitals deduced from them. The full lines in Fig. 1 are those selected in 1938. The dashed lines, which

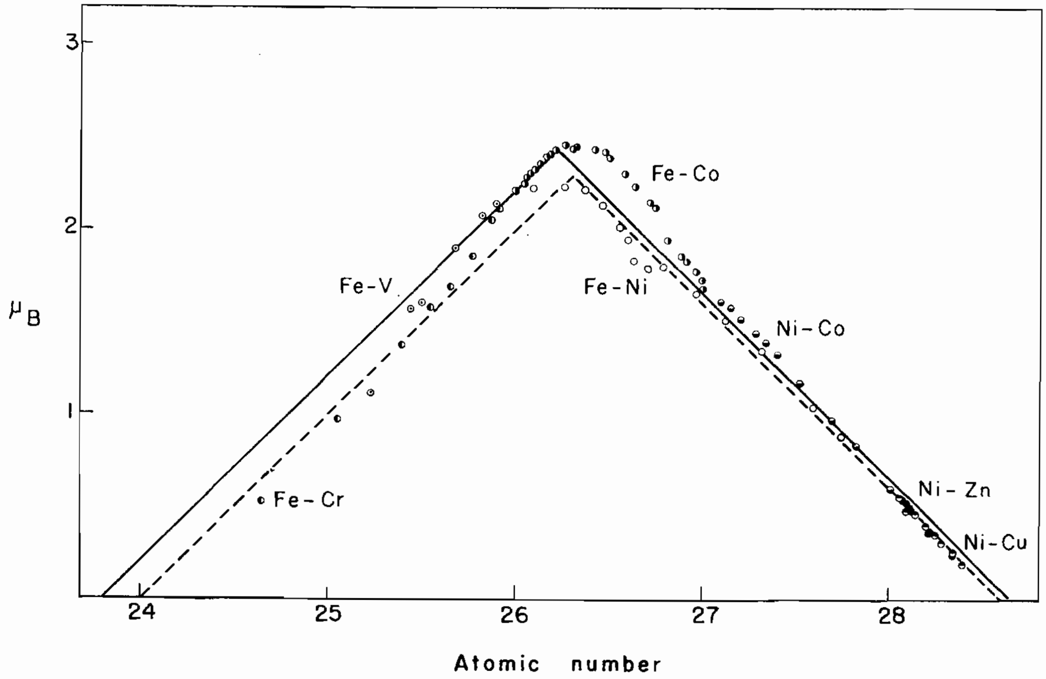

FIG. 1. Experimental values of saturation magnetic moment, in Bohr magnetons per atom, for ferromagnetic metals and alloys, as function of average atomic number.

may be considered to represent the data about as well, correspond to 6 bonding orbitals per atom and 2.30 atomic orbitals per atom. It is not possible to obtain satisfactory agreement with the experimental points by the use only of integral numbers of orbitals per atom.

In the papers referred to above it is pointed out that the mechanical properties of the transition elements and the distances between atoms in metals and intermetallic compounds are well accounted for by these considerations. In the following sections of the present paper a discussion is given of the number of valence electrons by the Brillouin polyhedron method, and it is shown that the calculations for the filled-zone alloys such as the γ-alloys provide further support for the new system of metallic valences.

Let us review the calculation of the number of electrons in successive Brillouin zones. The calculation has as its starting point a distribution of free electrons. In a volume V to which the electrons are restricted the most stable pair of electrons occupies the lowest energy levels, with nearly zero kinetic energy, and correspondingly long wave-lengths. As the number of electrons in the metal increases, continually higher energy levels are occupied until finally there occur electrons with wave-lengths having the value corresponding to a Bragg reflection at 90° incidence from a crystallographic plane with the largest interplanar spacing present in the crystal. The value of the wave-length is found from the Bragg equation $n\lambda = 2d \sin\theta$ to be equal to $2d_{hkl}$, for $n=1$ and $\sin\theta = 1$.

A very simple calculation can be made of the number of electrons with energy less than this value at which strong perturbation begins. The volume in phase space corresponding to energy values equal to or less than this critical value is $(4/3)\pi p^3_{\max} V$. There is one quantized state per volume h^3 in phase space, and two electrons occupy each quantized level; hence, the number of electrons is $2/h^3 \cdot (4/3)\pi p^3_{\max} V$. This equation can be simplified by replacing $p_{\max}$ by its value as given by the deBroglie expression, $p_{\max} = h/\lambda_{\min}$, which is in the case under consideration equal to $h/2d_{hkl}$. The number of electrons contained within this momentum sphere then becomes $N = \pi V/3d_{hkl}^3$. In a cubic crystal the interplanar spacing d_{hkl} is equal to $a_0/(h^2+k^2+l^2)^{\frac{1}{2}}$. If we

TABLE II. X-ray reflection data for γ-brass (Cu_5Zn_8) and calculated electron densities.

			Number of electrons per unit cell		
		Square of structure amplitude		Valence electrons	
hkl	Σh^2	S^2	Brillouin polyhedron	(H-R)	(P)
110	2	0.1			
200	4	0.0			
211	6	0.1			
220	8	0.0			
310	10	0.1			
222	12	7.2	72		
321	14	1.1			
400	16	0.0			
330	18	78.3	108 } 90	84	—
411	18	31.7	97.2		
420	20	0.5			
332	22	8.4	148		
422	24	5.5	144		
510	26	3.3	(194)		
431	26	0.5			
521	30	0.7			
440	32	2.2	(256)		
433	34	0.5			
530	34	0.8			
600	36	24.0	432 } 255.60	—	250.88
442	36	8.4	291.60		
611	38	3.4	(326)		
532	38	1.5			
620	40	0.1			
541	42	0.1			
622	44	1.3			
631	46	8.0			

introduce this expression and replace V by a_0^3, we find that the number of electrons contained within the momentum sphere per cubic unit cell is

$$N=\frac{\pi}{3}(h^2+k^2+l^2)^{\frac{3}{2}}.$$

The number of electrons in a Brillouin zone is that given by the volume in momentum space represented by a polyhedron with faces corresponding to the crystallographic indices of the perturbing crystallographic plane and circumscribed about the minimum sphere. The volume of the Brillouin polyhedron is accordingly somewhat larger than that of the minimum sphere; it can be determined by geometrical calculation.

III. THE GAMMA-ALLOYS

The structure of γ-brass was determined by Bradley and Thewlis.[5] This structure may be derived from a unit consisting of 27 body-centered cubes, containing altogether 54 atoms, by removing two of the atoms, at 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ of the large cube, and slightly rearranging the remaining 52 atoms. Since this structure is essentially a superstructure of $A2$ (in the nomenclature of the Strukturbericht) it would be expected that only a few of the crystallographic planes would reflect strongly. This expectation is borne out by observation, as can be seen from Table II, where the intensities of reflection for crystallographic planes out to $\Sigma h^2=h^2+k^2+l^2=46$ are given. (These values are calculated for γ-brass, Cu_5Zn_8, from the structure reported by Bradley and Thewlis; the calculated values of the stronger reflections are in excellent agreement with the observed values.)

The first set of strong reflections occurs at $\Sigma h^2=18$. As was stated above, Jones found the Brillouin polyhedron defined by the corresponding forms {330} and {411} to have the volume $45/a_0^3$, giving an electron density of 90 electrons per unit cell. The next set of strong reflections occurs at $\Sigma h^2=36$. We have found it possible to construct a Brillouin polyhedron defined by the corresponding forms {600} and {442}. This polyhedron, shown in Fig. 2, has a volume of $(9^3/5-18)/a_0^3=127.800/a_0^3$, enclosed by its 30 faces, leading to an electron density of 255.600 electrons per unit cell. The new metallic valences 5.44 for copper and 4.44 for zinc lead to 250.88 electrons per unit cell (containing 4 molecules of Cu_5Zn_8), in very close agreement with the value calculated for the second Brillouin polyhedron. The fill of the Brillouin polyhedron is 250.88/255.6 = 98.5 percent, and accordingly this calculation gives considerably better explanation of the filled-zone properties of the alloys than the Jones treatment, where a fill of only 84/90 = 93.5 percent was obtained.

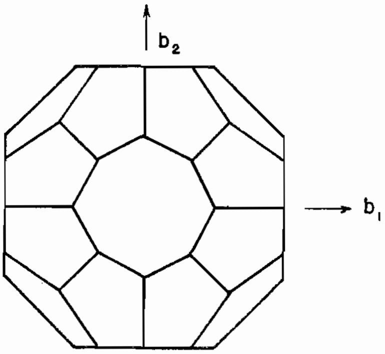

FIG. 2. The Brillouin polyhedron for forms {442} and {600}, an important one for γ-brass and other γ-alloys.

TABLE III. X-ray reflection data for β-manganese structure (Ag_3Al) and calculated electron densities.

			Number of electrons per unit cell		
				Valence electrons	
hkl	Σh^2	Calculated intensity	Brillouin polyhedron	(H-R)	(P)
221	9	86	32.4	30	—
310	10	48			
311	11	26			
222	12	0.8			
320	13	0.7			
321	14	7			
400	16	0.02			
322	17	0.02			
410	17	0.7			
330	18	0.01			
411	18	2.1	$\left.\begin{matrix}97.21\\111.11\end{matrix}\right\}96.13$	—	96.60
420	20	4			
421	21	0.3			
332	22	1.3			
422	24	1.6			
430	25	2.3			
431	26	20			
510	26	4			
333	27	0.05			
511	27	4			

Inasmuch as the inscribed sphere corresponds to only 226 electrons per unit cube, it seems likely that the density of energy levels in momentum space has become small at 250.88, possibly small enough to provide a satisfactory explanation of the filled-zone properties. However, there exists the possibility that the Brillouin polyhedron is in fact completely filled by valence electrons. If there are 255.6 valence electrons per 52 atoms at the composition Cu_5Zn_8, and if the valence of copper is one greater than the valence of zinc, then it is possible to determine values of the metallic valences of these elements from the assumption that the Brillouin polyhedron is filled. These values are found to be 5.53 for copper and 4.53 for zinc. The accuracy of the determination of the metallic valences from magnetic properties is not great enough to exclude these values; in fact, the valence for copper calculated by the assumption that the full line in Fig. 1 is to be accepted is 5.44 and that calculated from the assumption that the dashed line is to be accepted is 5.60, so that the value 5.53 given by the Brillouin-polyhedron calculation for γ-brass lies within these limits. It may accordingly be said that the Brillouin-polyhedron calculation for γ-brass provides substantiation of the new set of metallic valences.

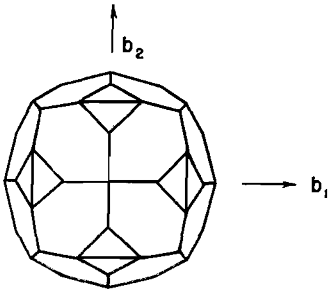

FIG. 3. The Brillouin polyhedron {411} {420}, for β-manganese, Ag_3Al, and $CoZn_3$.

It may be noted that the Brillouin polyhedron used in this calculation corresponds to the only strongly reflecting planes in the entire range $26 \leqslant \Sigma h^2 \leqslant 46$. Thus the Brillouin polyhedron is, in effect, isolated from interference by any neighboring crystallographic planes.

It is interesting to note that the same electron number, 250.88 electrons per unit cell, is found not only for the compounds similar in composition to Cu_5Zn_8 (Cu_5Cd_8, Ag_5Zn_8, Ag_5Cd_8, Au_5Zn_8, Au_5Cd_8, Au_5Hg_8) but also for other γ alloys involving the metals of the *B* subgroups of the periodic table, such as Cu_9Ga_4, Cu_9In_4, $Cu_{31}Sn_8$, and $Ag_{31}Sn_8$. In fact, it can be easily shown that the constancy of the electron-atom ratio for all of these compounds, with the compositions as given here, holds for any set of valences in which the successive elements in the periodic table differ in valence by either +1 or −1. The Hume-Rothery valences correspond to an increment in valence of +1 with increase in atomic number and the new valences to an increment of −1.

The γ-phase is homogeneous in the copper-zinc system over the range of compositions of 60 to 69 atomic percent of zinc. These limits correspond to 251.68 and 247.00 electrons per unit cell, respectively. It was found by Lane[17] that at room temperature the diamagnetic susceptibility of γ-brass is approximately a linear function of the zinc content over the range 60 to 67 weight percent (59–65 atomic percent) increasing from 0.25×10^{-6} to 0.80×10^{-6} in this interval. He also found that the magnetic susceptibility of alloys with about 60 atomic percent zinc, corresponding closely to the composition Cu_5Zn_8, changes very little with temperature from 0 to 400°C, whereas that of the samples containing larger amounts of zinc decreases rapidly with increasing temperature, the values for all alloys being 0.3×10^{-6} at approximately 800°C. It seems likely that the alloys with a filled Brillouin zone behave normally with respect to their diamagnetic properties, whereas abnormally large diamagnetism results from a small defect in the zone.

In the copper-tin system the γ-phase is homogeneous between 20.8 and 22.3 atomic percent tin. This corresponds to a change from 250.43 to 248.09 electrons per unit cell, using the valences 5.44 and 2.44 for copper and tin, respectively. If we adopt the slightly higher values 5.53 and 2.53 suggested by the values required for a completed polyhedron in γ-brass, we obtain 254.81 and 252.77, corresponding to 99.85 and 98.9 percent filling of the polyhedron.

Whereas the compounds such as Cu_9Ga_4 with gallium and its congeners give similar agreement with the Brillouin-polyhedron calculations, the corresponding compounds Cu_9Al_4 and Ag_9Al_4, which have the same numbers of electrons according to the Hume-Rothery treatment, lead to only 243.84 electrons per unit cell with the new valences. The compounds M_6Zn_{21}, M_6Cd_{21}, and M_6Hg_{21}, with M = Fe, Co, Ni, Rh, Pd, or Pt, similarly show with the new valences the low value 244.28 electrons per unit cell. It seems probable that in these compounds, involving a metal of the transition group and a metal of the ascending branch of the transition group, in which the metallic valence can be increased by the removal of an electron, the phenomenon of electron transfer occurs, some electrons being removed from the zinc atoms and assigned to the iron atoms (in Fe_6Zn_{21}). The valence of the iron atom is not changed by its negative charge, whereas that of the zinc atom is increased by the removal of electrons, and accordingly added stability of the compounds can be achieved in this way. To produce a filled zone about $\frac{1}{4}$ electron must be removed from each zinc atom in Fe_6Zn_{21} and 1 electron added to each iron atom. A similar transfer of electrons from copper to aluminum produces a filled Brillouin zone for the compound Cu_9Al_4.

IV. THE BETA-MANGANESE STRUCTURE

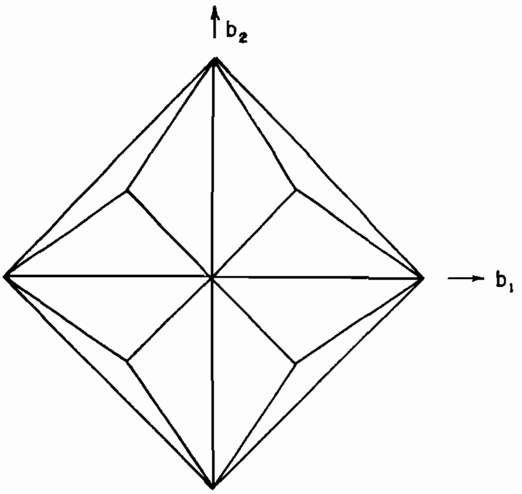

FIG. 4. The Brillouin polyhedron {442}, for α-manganese.

The β-modification of metallic manganese, stable at higher temperatures, has a rather complex cubic structure[18] containing 20 atoms in the unit cube. Westgren and Bradley[19] found that the compound Ag_3Al has an x-ray diffraction pattern substantially identical with that of β-manganese. They discussed the possibility that the 20 atomic positions per unit cube in the

TABLE IV. X-ray reflection data for α-manganese and calculated electron densities.

			Number of electrons per unit cell	
hkl	Σh^2	S^2	Brillouin polyhedron	Valence electrons (P)
110	2	0		
200	4	0		
211	6	0		
220	8	2		
310	10	0		
222	12	5		
321	14	2		
400	16	54		
330	18	217	108 } 90	
411	18	242	97.2	
420	20	0		
332	22	125	148 } 134	140 (Mg_3Al_2)
422	24	52	144	
431	26	31		
510	26	13	194	
521	30	5		
440	32	3		
433	34	6		
530	34	3		
442	36	17	291.60	293.76
600	36	1		
532	38	9		
611	38	6		
620	40	4		
541	42	2		
622	44	35		
631	46	5		
444	48	275		

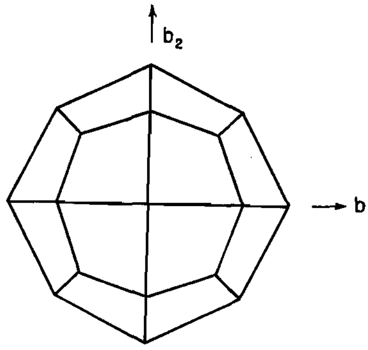

FIG. 5. The Brillouin polyhedron {422}. for $Mg_{17}Al_{12}$.

β-manganese structure are occupied by silver and aluminum atoms distributed essentially at random. This statistical distribution was verified by the x-ray data for Ag_3Al by Fagerberg and Westgren[20] and was also extended to Au_3Al and Cu_5Si by them. The data of these investigators for Ag_3Al are reproduced in Table III. It is seen that the first strong x-ray reflections are those from the forms {221} and {310}, which were used by Mott and Jones to set up a Brillouin polyhedron containing, as was mentioned above, 32.4 electrons per unit cell, in fair correspondence with the 30 electrons required by the Hume-Rothery ratio 3/2.

The new values of the metallic valences lead to 96.60 electrons per cell for Ag_3Al and Au_3Al. In the region $16 \leqslant \Sigma h^2 \leqslant 24$ there are only two strongly reflecting forms, {441} and {420}. These give separate Brillouin polyhedra containing 97.21 and 110.0 electrons, respectively; they combine to give a truncated polyhedron, shown in Fig. 3, which contains 96.13 electrons per unit cell. This value is in good agreement with the value 96.60 calculated from the metallic valences. It might be mentioned, however, that a somewhat larger value might be expected from the metallic valences, since presumably the conditions are satisfactory for the phenomenon of electron transfer to occur.

The compound Cu_5Si, which with the older valences has the same calculated electron number as Ag_3Al, leads with the new system to a different electron density, 104 electrons per unit cell.

It was reported by Fagerberg and Westgren[20] that the compound $CoZn_3$ also crystallizes with the β-manganese structure. The electron number calculated from the valences 5.78 for cobalt and 4.44 for zinc is 95.50 electrons per unit cell, which is only 0.7 percent less than required to fill the Brillouin polyhedron.

A notable shortcoming in the earlier system was the failure to provide a consistent treatment for β-manganese itself, because of the arbitrary assignment of zero valence to manganese and the other transition elements. In the new system of metallic valences the transition metals in general have the valence 5.78, but a detailed examination of the interatomic distances[15] led to the conclusion that two essentially different kinds of manganese atoms are present in β-manganese, 8 atoms in the unit cube with valence 5.78 (or 6) and 12 with valence 4, leading to 94.24 (or 96) electrons per unit cell. We accordingly conclude that the stabilization of the β-manganese structure for β-manganese itself as well as for the compounds Ag_3Al and Au_3Al results in part from the filling of the Brillouin polyhedron.

V. THE ALPHA-MANGANESE STRUCTURE

α-Manganese, like β-manganese, has physical properties of brittleness and low electrical conductivity that indicate a filled-zone structure. It could not be treated under the old system of valences, because of the zero valence assigned to the element. The structure of α-manganese is very complicated, the unit cell containing 58 atoms arranged compactly together.[21]

The x-ray data for α-manganese as reported by Preston are given in Table IV. It is seen that there is a pair of strong reflections with $\Sigma h^2 = 18$, leading to a Brillouin polyhedron containing 90 electrons per unit cube. Another pair of strong reflections occurs with $\Sigma h^2 = 22$ and 24, which together produce a truncated polyhedron containing 134 electrons. Then there occurs the reflection {442}, which leads to 291.60 electrons per unit cell (see Fig. 4). It may be noted that this polyhedron is related to that discussed above for the γ-alloys; with α-manganese, however, the {600} reflection has very small intensity, and accordingly is not considered to truncate the {442} polyhedron.

It was pointed out by Bradley and by Hume-Rothery[22] that the nature of the α-manganese structure suggests that there are manganese atoms present of two different sizes, and a study of interatomic distances[15] led to the conclusion that of the 58 atoms in the unit cell 24 have the normal valence 5.78 (or 6) and 34 a lower valence of about 4 or 4.5. The actual values indicated for the different kinds of manganese of lower valence are 2 MnI, 3.52; 8 MnII, 4.70; 24 MnIII, 4.60. The electron number calculated with valences 5.78 and 4 is 274.72, whereas that calculated for the valences 5.78, 3.52, 4.70, and 4.60, suggested by the interatomic distances, is 293.76. It is seen that, to within the uncertainty of the valence values, the electron number is such as to correspond to the filling of the Brillouin polyhedron {442}.

Only one intermetallic compound has so far been reported to have the α-manganese structure. This is the compound with approximate formula Mg_3Al_2, found by Laves, Löhberg, and Rahlphs[23] to have a structure with 58 atoms in the unit cell. These investigators suggested that the formula is $Mg_{17}Al_{12}$, the larger magnesium atoms then being analogous to the large low-valent manganese atoms in α-manganese, and the smaller aluminum atoms analogous to the smaller high-valent manganese atoms in this structure. The electron number for $Mg_{17}Al_{12}$ is 140 electrons per unit cell. This does not correspond very closely to the content of the Brillouin polyhedron, which is 134 for the {332} polyhedron truncated by {422} (Fig. 5). These polyhedra independently contain 148 and 144 electrons per unit cell, respectively.

VI. THE BETA ALLOYS

The β-alloys are different in nature from the γ-alloys and the α-manganese and β-manganese structures discussed above, in that they are not complex structures, but are simple, being based upon the body-centered arrangement. β-Brass, for example, has either a disordered structure, above 480°K, the copper and zinc atoms in essentially equal number being distributed largely at random over the points of a body-centered cubic lattice, or an ordered structure, below 300°K, with copper and zinc at the positions 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, respectively, of the cubic unit. Moreover, the physical properties of β-brass are not those that indicate a filled zone structure.

It seems likely that the assumption of the β-brass structure is determined mainly by factors other than the ratio of valence electrons to atoms. Nevertheless, it is a fact that the ratio of valence electrons to atoms calculated with the Hume-Rothery valence is 3/2 for more than one-half of the intermetallic compounds reported to have this structure, and it seems likely that stabilization is due in part to this ratio.

For CuZn the number of valence electrons in the unit cube is 3, in case that the older valences of 1 and 2 are accepted for copper and zinc, respectively, and 9.88 with the newer valences 5.44 and 4.44. The Brillouin polyhedra for the body-centered cubic arrangement contain 4, 8, 12, ··· electrons per unit cell, whereas those for the $B2$ structure, corresponding to an ordered arrangement of atoms at 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, contain 2, 4, 6, 8, 10, 12, ··· electrons per unit cell. In either case the Hume-Rothery number of valence electrons, 3, does not correspond to a Brillouin zone. On the other hand, an ordered arrangement of atoms with different scattering powers for electrons in the positions 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ would cause a perturbation of energy levels such as to tend to stabilize a structure with 10 valence electrons per unit cell. In case that the scattering powers for electrons of the two atoms were not very greatly different, the resultant perturbation would not be great enough to separate the Brillouin zone from the succeeding zone, and the alloy would retain metallic properties; the perturbation would, however, have the effect of depressing the energy levels occupied by the 10 electrons per unit cell, and would accordingly tend to stabilize the ordered structure for the alloy.

It has been found by x-ray investigation that many of the β-alloys have an ordered structure sufficiently pronounced to produce x-ray reflections involving the difference in scattering powers of the atoms at 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. For these alloys the stabilization of ten electrons per unit cell would be expected, as discussed above. When the alloy changes from an ordered to a disordered phase on increase in temperature, there might still remain sufficient short-range order to produce this stabilization to some extent, even though not enough to give rise to x-ray reflections, the atoms having much smaller scattering powers for x-rays than for the slow electrons in the lattice. Similarly, stabilization of the alloy

CuZn would be expected, because the scattering powers of the two atoms for slow electrons in the lattice are probably considerably different, even though the scattering powers for fast electrons and for x-rays are very nearly the same.

VII. THE SIGNIFICANCE OF THE BRILLOUIN-POLYHEDRON CALCULATIONS

It is seen from the above considerations that there is what seems to be significant agreement between the electron numbers filling important Brillouin polyhedra and the number of valence electrons provided by the new system of metallic valences for the γ-alloys, β-manganese and alloys of similar structure, and α-manganese. There is also agreement, somewhat more approximate, between the electron numbers given by other Brillouin polyhedra and those provided by the older valence system. The agreement in each case can hardly be accidental, since the Brillouin polyhedra correspond to the planes giving the strongest x-ray reflections. It seems likely that both series of electron numbers are significant, but an understanding of their significance may not be obtained until a more penetrating theory of the structure of metals and alloys has been developed.

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A resonating-valence-bond theory of metals and intermetallic compounds

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The resonating-valence-bond theory of metals discussed in this paper differs from the older theory in making use of all nine stable outer orbitals of the transition metals, for occupancy by unshared electrons and for use in bond formation; the number of valency electrons is consequently considered to be much larger for these metals than has been hitherto accepted. The metallic orbital, an extra orbital necessary for unsynchronized resonance of valence bonds, is considered to be the characteristic structural feature of a metal. It has been found possible to develop a system of metallic radii that permits a detailed discussion to be given of the observed interatomic distances of a metal in terms of its electronic structure. Some peculiar metallic structures can be understood by use of the postulate that the most simple fractional bond orders correspond to the most stable modes of resonance of bonds. The existence of Brillouin zones is compatible with the resonating-valence-bond theory, and the new metallic valencies for metals and alloys with filled-zone properties can be correlated with the electron numbers for important Brillouin polyhedra.

INTRODUCTION

The difficult problem of the electronic structure of metals has in recent years been tackled mainly by molecular-orbital (one-electron-orbital) methods. This attack has led to a reasonably satisfactory understanding of some metallic properties, such as electrical conductivity, but not of others, including interatomic distances (density), hardness and other mechanical properties, and the relative stability of alternative atomic arrangements. A decade ago (1938) I pointed out that the resonating-valence-bond concept of metals permits a straightforward explanation to be given not only of the hardness, melting-point, and related properties of the transition metals but also of their ferromagnetic saturation moments, which lead to the assignment of metallic valences such as 5·78 for iron and 5·44 for copper, in place of the numbers 0·2 to 0·6 for iron and 1 for copper assumed in the usual molecular-orbital treatment. It was suggested that these valence numbers result from the hybridization of the nine stable outer orbitals (five nd, one $(n+1)s$, and three $(n+1)p$) of a transition atom into 5·78 good bond orbitals (resembling the six d^2sp^3 orbitals of the central atom in an octahedral complex), 2·44 stable atomic orbitals (largely d in character, and responsible for the magnetic moment), and 0·78 'unstable' orbital, with no obvious use.

In the course of the further investigation of resonating valence bonds in metals the nature and significance of this previously puzzling 'unstable' orbital have been discovered, and it has become possible to formulate a rational theory of metallic valence and of the structure of metals and intermetallic compounds.

THE FUNDAMENTAL STRUCTURAL FEATURE OF A METALLIC SYSTEM: THE 'METALLIC ORBITAL'

Let us consider lithium as an example. In the usual treatment of this metal a set of molecular orbitals is formulated, each of which is a Bloch function built from the $2s$ orbitals of the atoms, or, in the more refined cell treatment, from $2s$ orbitals that are slightly perturbed to satisfy the boundary conditions for the cells. These molecular orbitals correspond to electron energies that constitute a Brillouin zone, and the normal state of the metal is that in which half of the orbitals, the more stable ones, are occupied by two electrons apiece, with opposed spins.

A roughly equivalent valence-bond theory would result from allowing the $2s$ electron of each lithium atom to be involved in the formation of a covalent bond with one of the neighbouring atoms. The wave function for the crystal would be

$$\psi = \sum_{i=1}^{M} a_i \psi_i, \tag{1}$$

in which†

$$\psi_i = 2^{-\frac{1}{2}N} \sum_{R} (-1)^R \left[\{(2N)!\}^{-\frac{1}{2}} \sum_{P} (-1)^P \, Pa(1)\,\beta(1)\,b(2)\,\alpha(2)\ldots \right] \tag{2}$$

is the wave function representing one of the M ways of distributing the valence bonds among the interatomic positions in the metal such that each atom forms one bond.

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† See Slater (1931); for the meaning of the symbols see Pauling & Wilson (1935).

If the functions ψ_i are equivalent and orthogonal a_i will equal $M^{-\frac{1}{2}}$, and the energy of the normal state can be written as

$$W = W_{\text{bond}} + W_{\text{resonance}}, \tag{3}$$

in which $W_{\text{bond}} = \int \psi_i^* H \psi_i \, d\tau$ is the energy of any one of the valence-bond structures ψ_i and

$$W_{\text{resonance}} = \sum_{i=1}^{M} \sum_{j \neq i} a_i a_j K_{ij} = 2 \sum_{j=2}^{M} K_{1j} \tag{4}$$

is the resonance energy, K_{ij} being the resonance integral $\int \psi_i^* H \psi_j \, d\tau$ between two valence-bond structures i and j.

It is this resonance energy that would be in the main responsible for the difference in energy of the crystal and the gas of diatomic molecules $\mathrm{Li_2}$. But the heat of formation of $\mathrm{Li_2}$ molecules from atoms is only 6·6 kcal./g.-atom, whereas that of the metal is 39 kcal./g.-atom. It seems unlikely, by comparison for example with the analogous case of Kekulé-like resonance in aromatic molecules, that the great difference, 32·4 kcal./g.-atom, could result from the synchronized resonance, of type $\left\{\begin{array}{ccc} \mathrm{Li{-}Li} & \mathrm{Li} & \mathrm{Li} \\ & | & | \\ \mathrm{Li{-}Li} & \mathrm{Li} & \mathrm{Li} \end{array}\right\}$, requiring two or more bonds to shift simultaneously. A much greater amount of resonance stabilization† can be achieved by resonance of the sort $\left\{\begin{array}{ccc} \mathrm{Li{-}Li} & \mathrm{Li{-}Li^-} \\ & \quad\;\; | \\ \mathrm{Li{-}Li} & \mathrm{Li^+\;Li} \end{array}\right\}$, in which one bond resonates independently from one position to another, through the process of electron transfer (Pauling 1948*a*).

However, this uninhibited resonance, involving the conversion of atoms into ions (or the transfer of ionic charges to atoms), *requires that the atom receiving a bond have an orbital available for its reception. It is the possession of this extra orbital* (*the metallic orbital*), *in addition to the orbitals required on the average for occupancy by unshared*

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† A simple calculation may serve to illustrate this point. Let the $2N$ atoms in a lithium crystal containing N bonds (atomic arrangement A 2) be divided into classes A and B, at 000 and 1/2 1/2 1/2, respectively, in the unit cube. Let each atom be forming one bond. The total number of structures representing the eight bond positions for each atom A is 8^N. But only the fraction $(7/8)^7$ of these are, on the average, acceptable to a given atom B (the chance of its receiving a bond in any one position and not in others being $8/8\,(7/8)^7$); and hence the number of ways of placing bonds between adjacent atoms in the A 2 structure is

$$8^N(7/8)^{7N} = (7^7/8^6) \;\; \simeq 3{\cdot}14^N.$$

The number 3·14 is a measure of the coefficient of the resonance integral for synchronous resonance.

If $\mathrm{Li^+}$ and $\mathrm{Li^-}$ ions (the latter bicovalent) are also present, their *a priori* probabilities in class A are 1 and 28, respectively, with geometrical mean $2{\cdot}7^{\frac{1}{2}}$ (the ions must be present in pairs), which corresponds to 8 for neutral atoms. A calculation similar to that above, on the assumption that there is no energy difference between Li Li and $\mathrm{Li^+\,Li^-}$, leads to $(7^7/8^6)^N(1+7^{\frac{1}{2}}/2)^N$ for the number of ways of placing the bonds and hence to the number $(7^7/8^6)\,(1+7^{\frac{1}{2}}/2) = 3{\cdot}14 \times 2{\cdot}32$ as the measure of the coefficient of the resonance integral for uninhibited resonance. This result, containing the factor 2·32, indicates the importance of uninhibited resonance.

The relative weights $8 : 2{\cdot}7^{\frac{1}{2}}$ for Li and $\mathrm{Li^+}$ ($= \mathrm{Li^-}$) correspond to 43 % neutral atoms and 28·5 % each of anions and cations. Calculations based on minimizing the energy of the system also indicate similar values for the ratio of atoms to anions and cations. The rule of essential electrical neutrality (Pauling 1948*b*) would require that only the singly-charged ions need be considered.

electron pairs and bonding electrons, by all or many of the atoms in a condensed phase that permits the uninhibited resonance of valence bonds that gives rise to metallic properties.

HYBRIDIZATION OF BOND ORBITALS IN THE ALKALI METALS

In the molecule Li_2 the bond involves a hybrid atomic orbital $as+bp$ formed from the $2s$ orbital and one of the much less stable $2p$ orbitals. It is shown below that the amount of p character of this bond orbital (equal to b^2, with $a^2+b^2=1$) is small, being about 8 %. On the other hand, if each of the atoms in metallic lithium requires a bond orbital and a metallic orbital and the two are equivalent they will be $2^{-\frac{1}{2}}(s+p)$ and $2^{-\frac{1}{2}}(s-p)$, with 50 % p character. The analysis of energy quantities supports this conclusion.

It has been suggested (Pauling 1931; Pauling & Sherman 1937) that the bond-forming power of an orbital can be taken as proportional to its concentration in the bond direction, as measured by the value of its radial factor (normalized to 4π). The square of this quantity, the bond strength S, is approximately proportional to the bond energy. This postulate is equivalent to assuming that the off-diagonal matrix element H'_{sp} for $s-p$ hybridization is equal to S_sS_p, the diagonal elements being $H_s^0-\kappa S_s^2$ and $H_p^0-\kappa S_p^2$, in which H_s^0 and H_p^0 are the corresponding s and p atomic energies for the two bond electrons and κS_s^2 and κS_p^2 are the bond energies. S_s and S_p have the values 1 and $3^{\frac{1}{2}}$, respectively, and κ is a proportionality factor. The bond energy for formation of the most stable hybrid bond is then given by the lowest root (with changed sign) of the secular equation

$$\begin{vmatrix} -\kappa-W & 3^{\frac{1}{2}}\kappa \\ 3^{\frac{1}{2}}\kappa & H_p^0-3\kappa-W \end{vmatrix} = 0, \tag{5}$$

in which H_s^0 has been taken as the origin for energy. Solution of this equation gives

$$-\frac{W}{\kappa}=\frac{1}{2}\left[\left\{\left(\frac{H_p^0}{\kappa}\right)^2-4\frac{H_p^0}{\kappa}+16\right\}^{\frac{1}{2}}+4-\frac{H_p^0}{\kappa}\right]. \tag{6}$$

The quantities $-W$ (the bond energy D_e of the Li_2 molecule) and H_p^0 (twice the difference in energy of the states $2p\,^2P$ and $2s\,^2S$ of Li) are known from spectroscopic data, and hence their ratio $\rho=-W/H_p^0$ is known. It is found from equation (6) that

$$\kappa = H'_s=\frac{\rho(\rho+1)}{4\rho+1}H_p^0. \tag{7}$$

The ratio b/a is the ratio of matrix elements in one row of the secular equation:

$$\frac{a}{b}=-\frac{\kappa+W}{3^{\frac{1}{2}}\kappa}. \tag{8}$$

The energy values and the derived quantities for the diatomic molecules of the alkali metals are given in table 1. It is seen that the amount of p character is calculated to lie between 5 and 14 %.

TABLE 1. BOND ENERGIES AND HYBRIDIZATION OF BOND ORBITALS IN DIATOMIC MOLECULES OF ALKALI METALS

molecule	$D_e = -W$	H^0_p	ρ	$\kappa = H'_s$	b/a	amount of p character (%)
Li_2	26·8†	85·0†	0·316	15·6†	0·41	14·0
Na_2	17·9	97·0	0·185	12·2	0·27	6·8
K_2	11·8	74·6	0·158	8·4	0·24	5·5
Rb_2	11·2	73·0	0·153	8·0	0·23	5·0
Cs_2	10·4	67·1	0·155	7·4	0·24	5·5

† The energy quantities in columns 2, 3 and 5 are in kcal./mole of diatomic molecules.

An independent estimate of the amount of p character of these bonds can be made with use of the assumption that a linear extrapolation of the low-lying vibrational energy levels (as indicated by the Morse potential function) will lead to the energy level of the atomic state involved in the bond. The equation

$$D^*_0 = \frac{\omega_e^2}{4\omega_e x_e} - \tfrac{1}{2}\omega_e \tag{9}$$

for the linearly extrapolated energy of dissociation leads with use of the spectroscopic values for ω_e and $\omega_e x_e$ to the values of D^*_0 given in column 4 of table 2. The ratio of the difference between this value and the actual energy of dissociation D_0 into atoms in the normal spectroscopic state and the p-s separation for two atoms (H^0_p, column 3 of table 1) is then the amount of p character in the bond orbitals. The values found in this way lie between 7·2 and 8·6 %, and are thus in approximate agreement with those found by the first method.

TABLE 2. HYBRIDIZATION OF BOND ORBITALS AS INDICATED BY LINEAR EXTRAPOLATION OF VIBRATIONAL ENERGY LEVELS

molecule	ω_e	$\omega_e x_e$	D^*_0	D_0	$D^*_0 - D_0$	amount of p character (%)
Li_2	351·4	2·59	33·6†	26·3†	7·3†	8·6
Na_2	159·2	0·726	24·7	17·7	7·0	7·2
K_2	92·64	0·354	17·1	11·7	5·4	7·3
Rb_2	57·8	0·14	17·0	11·1	5·9	8·1
Cs_2	41·99	0·08	16·0	10·4	5·6	8·3

† In kcal./mole.

It is interesting to see, by comparison of the values in column 2 of table 1 (actual bond energy) and column 5 (calculated energy of pure s bonds) that this small amount of p character increases the bond energy by as much as one-half.

The results of the application of equations (7) and (8) to the metals themselves are given in table 3. The assumption is made that the bond-resonance energy depends on the bond strength S in the same way as the bond energy itself. The bond energy W is replaced by the heat of sublimation W_c. It is found that the calculated amount of p character is much greater than for the diatomic molecules. The calculated values, lying between 26 and 41 %, are, however, not so large as the 50 %

expected for the simple model discussed above. It seems likely that, whereas the two bond orbitals in the bicovalent anions M^- have 50 % p character, the occupied bond orbital in the neutral atoms has less than 50 % p character and the metallic orbital more. This difference in hybridization would decrease the value of the resonance integral but increase the atomic energy, and would result in the usual compromise that minimizes the total energy of the system.

TABLE 3. RESONANCE ENERGY AND HYBRIDIZATION OF BOND ORBITALS IN ALKALI METALS

metal	$-W_c$	ρ_c	κ_c	κ_c/κ	b/a	amount of p character (%)
Li	78·0†	0·918	32·0‡	2·05	0·83	41
Na	51·8	0·533	25·3	2·07	0·61	27
K	39·6	0·531	19·5	2·32	0·60	26
Rb	37·8	0·518	18·7	2·34	0·59	26
Cs	37·6	0·560	18·1	2·45	0·62	28

† Heat of sublimation in kcal./mole of bonds (2 g.-atoms of metal).

‡ Calculated energy of resonating s bonds in kcal./mole.

The ratio κ_c/κ given in column 5 of table 3 is the ratio of the energy of resonating s bonds to static s bonds. The values found, lying between 2·05 and 2·45, indicate that the energy of metallic resonance is indeed great, being as large as the bond energy (for fixed bonds). The increase by a factor of about 3 in the energy of the system accompanying the condensation of diatomic molecules to the crystalline metal can be divided into two factors; one of these, approximately 2, is due to resonance energy, and the other, approximately $\frac{3}{2}$, is due to change in hybridization, which is itself, to be sure, the result of the resonance energy in causing the p-s separation to bear a smaller ratio to the (resonating) bond energy.

The results of a simpler calculation for the alkaline-earth metals are given in table 4. The second column ($-W_c$) contains the heats of sublimation to atoms in the normal state $s^2\,{}^1S$. If the atoms are bicovalent, however, their hypothetical bond-forming state would be the configuration sp, with energy $\frac{1}{4}\{3(^3P)+(^1P)\}$ (that is, the weighted mean of the triplet and singlet states for the configuration sp), in case that the occupied bonding orbitals had 50 % p character (the metallic orbital being a pure p orbital), or would be a state with somewhat higher energy, in case that the metallic orbital had some s character, as in the alkali metals. If it is assumed, by analogy with the alkali metals, that the p character of the occupied bond orbitals lies midway between the values 50 and $66\frac{2}{3}$ %, corresponding respectively to a pure p metallic orbital and a metallic orbital equivalent to the occupied bond orbitals, the bond-forming state has energy $7/6H_p^0$, and the bond energy relative to this state becomes $7/6H_p^0-W_c$. Values of this quantity are given in the fourth column of the table.

It is interesting that the bond energy relative to the bond-forming state of the atoms shows the same monotonic trend for the alkaline-earth metals as for the alkali metals. The irregularity in the heats of sublimation at magnesium is due to the high energy of the bond-forming state of the atom, and not to any extraordinary property of the bonds themselves. The much larger bond energies of the alkaline-earth metals (by a factor of 2 for Be/Li and about 3 for the other pairs) is due mainly to a difference in character of the hybrid bond orbitals. If the alkaline-earth bond energies are divided by 3·88, the value of S^2 for *sp* bond orbitals with 41·7 % *s* character, as assumed above, there are obtained the values for the energy of resonating *s* bonds given in column 5 of table 4. The next column contains values of the ratio of this quantity κ'_c to the corresponding quantity for the alkali metals. These values are reasonable, in comparison with the ratio of single-bond radii— 1·38 for Be/Li, but somewhat smaller for the other pairs.

TABLE 4. ENERGIES OF RESONATING BONDS IN ALKALINE-EARTH METALS

	$-W_c$	H_p^0	$-W_c+\frac{7}{6}H_p^0$	κ'_c	κ'_c/κ_c
Be	75†	79·4‡	168‡	43‡	1·34
Mg	36·3	83·5	133·7	34·5	1·36
Ca	47·8	58·0	116·5	30·0	1·54
Sr	47	55·2	111	28·6	1·53
Ba	49	48·1	105	27·3	1·51

† The heat of sublimation in kcal./mole. ‡ In kcal./mole.

METALLIC RESONANCE AND METALLIC VALENCY

The straightforward way in which metallic valency can now be discussed may be illustrated by the example tin, which is more versatile in its behaviour than its congeners germanium and lead).

Tin has fourteen electrons outside of its krypton-like core. These may occupy the nine orbitals in the following three most stable ways (atomic electrons are indicated by spin vectors, bonding electrons by dots, the metallic orbitals by open circles):

		4*d*					5*s*	5*p*		
Sn A	$v = 4$	⇅	⇅	⇅	⇅	⇅	•	•	•	•
Sn B	2	⇅	⇅	⇅	⇅	⇅	⇅	•	•	○
Sn C	0	⇅	⇅	⇅	⇅	⇅	⇅	⇅	○	○

Sn A has the maximum possible valency, 4. Because of their greater stability, it is essentially the *d* orbitals that are occupied by the five unshared electron pairs. The four bonding electrons occupy the four remaining orbitals, which may conveniently be considered to be hybridized to sp^3 tetrahedral bond orbitals. There is no extra orbital to serve as the metallic orbital, and so this quadrivalent tin would not, alone, form a metallic phase. Instead (Pauling 1947) it forms the essentially non-metallic variety of tin, grey tin, which has the diamond arrangement, each atom being surrounded tetrahedrally by four neighbours, to which it is attached by non-resonating single bonds.

The metallic form of tin, white tin, consists largely of the bivalent atoms Sn B, which have a metallic orbital. In white tin each atom has co-ordination number 6, and the bonds resonate among the alternative positions. It is the energy of this resonance which in the main compensates for the difference in bond energy between four bonds and two; some stabilization of bivalent tin also results from the fact that in it two electrons occupy essentially the 5*s* orbital, which has lower energy than the 5*p* orbitals.

White tin, to which the valency 2·44 has been assigned (Pauling 1938), does not contain bivalent Sn B alone, but also some Sn A. It seems likely that these two kinds of tin atoms occur in the ratio 3 : 1, leading to the average valency 2·5, a value in essential agreement with that suggested before.

Thus in general the non-integral metallic valencies shown by the transition elements are to be interpreted as averages, corresponding to resonance of each atom among two or more electronic structures with integral valencies. The relative weights of the different structures would be for a given metallic phase such as to minimize the energy of the system. A simple treatment involving consideration of the energy quantities involved, and especially of the resonance energy as affected by the ratio of metallic orbitals to atoms, permits the conclusion to be drawn that a 3 : 1 ratio of a lower-valent form with a metallic orbital and the higher-valent form without this orbital is reasonable; but deviations from this ratio are to be expected, and tin in its various alloys might show any valencies from 2 to 4. The zero-valent form Sn C has no virtues, and presumably does not make a contribution in any alloy of tin, but the analogous forms of certain other metals, with valency 4 less than the maximum, are important.

Similar valence structures A, B, etc., may be written for gallium, zinc, and copper and their congeners:

		3*d*					4*s*	4*p*		
Ga A	$v = 5$	⇅	⇅	⇅	⇅	•	•	•	•	•
Ga B	3	⇅	⇅	⇅	⇅	⇅	•	•	•	○
Ga C	1	⇅	⇅	⇅	⇅	⇅	⇅	•	○	○
Zn A	$v = 6$	⇅	⇅	⇅	•	•	•	•	•	•
Zn B	4	⇅	⇅	⇅	⇅	•	•	•	•	○
Zn C	2	⇅	⇅	⇅	⇅	⇅	•	•	○	○
Zn D	0	⇅	⇅	⇅	⇅	⇅	⇅	○	○	○
Cu A	$v = 7$	⇅	⇅	•	•	•	•	•	•	•
Cu B	5	⇅	⇅	⇅	•	•	•	•	•	○
Cu C	3	⇅	⇅	⇅	⇅	•	•	•	○	○
Cu D	1	⇅	⇅	⇅	⇅	⇅	•	○	○	○

These tend to be combined to produce effective metallic valencies of 3·5 for gallium, 4·5 for zinc, and 5·5 for copper (and their congeners), but other valencies are also shown by these versatile metals.

Pivoting valence-bond resonance

In ordinary covalent molecules and crystals the co-ordination number of an atom is equal to its covalency, because the resonance energy of synchronized resonance is not great enough to overcome the additional repulsive energy between non-bonded atoms. However, in an electron-deficient substance, with extra orbitals permitting uninhibited resonance, the resonance energy often becomes great enough to stabilize a structure with increased ligancy (co-ordination number)—the ligancy then usually increasing to a value greater than the number of orbitals.†

It is of interest to note that *in order for a given atom to increase its ligancy beyond its covalency it is not necessary that this atom have an extra orbital: it is instead sufficient for the atoms that surround it to have extra orbitals.* The valence bonds of the central atom may then resonate among their alternative positions by pivoting about the central atom.

It is this sort of pivoting resonance that permits the 25 % contribution of Sn A to white tin, in which each atom has ligancy 6. Other examples are AuSn (Pauling 1947), in which each tin atom is surrounded by a trigonal prism of gold atoms, and Mg_2Sn, with the fluorite structure (Pauling 1923), in which each tin atom is surrounded by a cube of magnesium atoms. The interatomic distances show that in each case the tin is quadrivalent, and its four bonds are permitted to resonate among the six or eight positions by use of the metallic orbitals of the gold or magnesium atoms. Resonance of this sort also characterizes many carbides, such as cementite, in which each carbon atom is surrounded by six iron atoms.

The stable atomic orbitals

We now interpret the ferromagnetic saturation moments as indicating that as many as seven hybrid orbitals have such a nature (concentration in bond directions, permitting large overlapping with orbitals of adjacent atoms) as to make them useful as bond orbitals (including the metallic orbital), and that the remaining two orbitals, essentially d in character, are available for occupancy by unshared electrons. These orbitals are of such a nature as to lead to positive rather than negative exchange integrals (small in magnitude, however), thus causing the parallel orientation of spins of adjacent atoms that leads to ferromagnetism.

Often, however, one or more additional d orbitals are used as atomic orbitals. This occurs as the result of the stabilizing influence of certain configurations of the atomic electrons and of certain molecular or crystal structures requiring only a smaller valency (smaller number of bond orbitals than seven). Thus *chromium*, with six outer electrons, might have any valency from 6 to 1, the non-valence electrons occupying the atomic orbitals. By Hund's rule of maximum multiplicity for a partially filled subgroup these $6-v$ atomic electrons would remain unpaired, and would require one $3d$ orbital apiece. If conditions were such as to favour a large valency the element would have its maximum valency 6. If they were to favour a small valency we might at first expect two electrons to occupy the two stable atomic orbitals, leading to $v = 4$. However, if three d orbitals combine with sp^3 to produce seven most satisfactory bond orbitals, only $2{\cdot}14d$ orbitals would be required to produce five bond orbitals (for $v = 4$ and the metallic orbital) with the same hybrid character, or 1·71 to produce four. Hence by the change to a lower valency another d orbital is released for use as a stable atomic orbital, and a third electron might well occupy it. Indeed, the energy stabilizing the atomic state of maximum multiplicity is three times as great for the quartet configuration d^3 as for the triplet configuration

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† V. Schomaker, private communication; also Conference on the Chemical Bond, Paris, 15 April 1948.

d^2, and hence there is good reason to expect the lower-valent state of chromium to have three atomic electrons and valency 3. Both sexivalent and tervalent chromium exist, as forms of the elementary metal, with the structures A2 and A3, respectively. In addition to the evidence of the interatomic distances (Pauling 1947), the value 3 for the valency of the low-valent state is supported by the value 3 magnetons found for the magnetic moment of chromium alloyed with gold† (so far as I know, the saturation moment of A3 chromium has not been reported).

Manganese by a similar argument would be expected to have the metallic valencies 6 and 4, as observed (Pauling 1947). The corresponding valencies 6 and 5 for *iron* do not occur as distinct modifications of the elementary substance, but instead both contribute, in ratio 78 : 22, to the average valency 5·78 shown for α-iron by the ferromagnetic saturation moment 2·22. It may be pointed out that the quinquevalent state of iron is not expected to be so stable as the lower-valent states of chromium and manganese because the decrease in valence by 1 would liberate only 0·43 of a d orbital, and the introduction of an additional atomic electron would hence weaken the bond orbitals by decreasing their d character.‡

Cobalt in its normal metallic form involves resonance between the two following sexivalent structures, in the ratio 35 : 65, as indicated by the saturation moment 1·71 magnetons:

		3*d*					4*s*	4*p*		
Co A	$v = 6$	↑	↑	↑	•	•	•	•	•	•
Co B	6	⇅	↑	•	•	•	•	•	•	○

The contribution of Co A is presumably limited to 35 % by the destabilizing effects of absence of a metallic orbital and decreased d character of the bond orbitals, which oppose the stabilizing effect of the quartet atomic state. In the same way *nickel* involves resonance between the two following structures, in the ratio 30 : 70 (saturation moment 0·61):

		3*d*					4*s*	4*p*		
Ni A	$v = 6$	⇅	↑	↑	•	•	•	•	•	•
Ni B	6	⇅	⇅	•	•	•	•	•	•	○

The decrease in the contribution of A from 35 % (for cobalt) to 30 % is presumably due in the main to the smaller amount of resonance stabilization for the triplet state than for the quartet state.

We have thus concluded from the foregoing arguments that the high-valent states of metallic chromium, manganese, cobalt, and nickel are all sexivalent states, with only iron having the slightly lower valency 5·78, in contradiction to the assumption previously made (Pauling 1938), in ignorance of a sound theory of the nature of metals, that the valency 5·78 applies to all the transition elements. The ferromagnetic data indicate that in alloys of iron and cobalt the average valency remains about 5·78 from 0 to 25 % cobalt (the moment increasing linearly from 2·22 to 2·48), and then increases to 6 at about 50 % Co (the moment remaining roughly constant

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† Personal communication from Professor P. Néel.

‡ The quinquevalent state with a pure p metallic orbital would have somewhat more d character in the bond orbitals.

at 2·48), and thereafter remains 6 (the moment decreasing rapidly). The detailed discussion of the electronic structure of these alloys in terms of Fe A, Fe B, Co A and Co B is complicated, and requires consideration also of the ions Fe^+ A, Fe^- A, etc.

THE STABILITY OF STRUCTURES IN RELATION TO BOND NUMBER

The factors that determine the choice of one from among alternative crystal structures of a metal or intermetallic compound have not been well understood. In the resonating-valence-bond theory of metals a very important energy quantity contributing to the stability of the systems is the energy of resonance of bonds among interatomic positions. It is clear that some modes of resonance would make larger contributions to the energy than others, and that in particular a simple ratio of number of bonds to number of positions would be exceptional. The simplest ratios, in order, are $\frac{1}{2}$, $\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{4}$, $\frac{3}{4}$, etc. We are thus led to the principle that *a special stability is associated with bond numbers* $\frac{1}{2}$, $\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{4}$, $\frac{3}{4}$, etc.†

For example, tin, with $v = 2{\cdot}5$, crystallizes with a unique atomic arrangement, in which each atom has six ligates, four at 3·016 Å and two at 3·175 Å. These distances have been used (1947) in assigning the bond numbers 0·48 and 0·26 to these bonds. It is clear that these bond numbers can be taken as $\frac{1}{2}$ and $\frac{1}{4}$, and that the choice of the structure and the value of its axial ratio (which determines the relative lengths of the two kinds of bonds) are the result of the effort of the tin atom to use its valency 2·5 in the formation of stable bonds with simple fractional bond numbers.

Zinc and cadmium have the A 3 structure, but with abnormally large axial ratio (1·856 for zinc) instead of the value 1·633 corresponding to close packing. From the distances 2·660 Å (for six bonds) and 2·907 Å (for the other six) the bond numbers 0·54 and 0·21 have been deduced. If the axial ratio were normal each of the twelve bonds formed by a zinc atom with $v = 4{\cdot}5$ would have bond number $\frac{3}{8}$. The assumption of the distorted structure permits a split into two classes with the more stable bond numbers $\frac{1}{2}$ and $\frac{1}{4}$ (or, probably, $\frac{1}{6}$, with the average valency of zinc equal to 4).

A similar explanation can be given of the occurrence of other unusual structures, shown by mercury, gallium, indium, β-tungsten, β-uranium, α-manganese, and β-manganese. There is, of course, a close relation between the principle of the stability of simple fractional bond numbers and the filling of the Brillouin polyhedra corresponding to strong perturbations of the wave functions for the resonating valence bonds, discussed below.

Because of the occasional occurrence of a difference in hybridization of the bond orbitals involved in bonds of different classes, leading to a difference in single-bond radius, the determination of the bond numbers from experimental values of the bond lengths involves some uncertainty.

A NEW SYSTEM OF METALLIC RADII

The interpretation of experimental values of interatomic distances for metals in terms of bond numbers, with use of the equation

$$R_n = R_1 - 0{\cdot}300 \log_{10} n, \tag{9a}$$

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† The importance of half bonds (with $n = \frac{1}{2}$) has been emphasized by Rundle (1947).

has permitted considerable progress to be made, but has been hampered by uncertainty as to whether or not a significant change in the single-bond metallic radius of an element accompanies a change in its valence. The system described here is designed to eliminate this difficulty by permitting the prediction of the metallic radius for any element in any valence state.

This system is based on the observations (Pauling 1947) that a linear relation between single-bond radius and atomic number holds for bonds of constant hybrid character, and that for an element the single-bond radius is (at least approximately) linearly dependent on the *d* character of the *dsp* hybrid bond orbitals.

The values of $R_1(sp^3)$, the single-bond radius for sp^3 bonds, for the iron-transition elements are given by the equation

$$R_1(sp^3) = 1{\cdot}825 - 0{\cdot}043z, \tag{10a}$$

in which $z = Z - 18$ is the number of outer electrons in the neutral atom (outside of the argon shell). This equation represents the straight line in figure 3 of Pauling (1947).

The value 1·165 Å for iron with valence 5·78 is an average for 78 % of sexivalent iron, with seven d^3sp^3 orbitals, and 22 % of quinquevalent iron, with d^2sp^3 orbitals (in each case including one metallic orbital); this value hence corresponds to 39·7 % *d* character, and with the assumed linear relation leads to 1·138 Å for d^3sp^3 orbitals (42·9 % *d* character). Similarly the value 1·162 Å for sexivalent cobalt with 39·5 % *d* character (average of 65 % d^3sp^3 and 35 % d^2sp^3, calculated from the magnetic moment) leads to 1·138 Å for the d^3sp^3 radius, and the value 1·137 Å is found for nickel from the sexivalent single-bond radius 1·154 Å for 40·0 % *d* character (70 % d^3sp^3 and 30 % d^2sp^3).

The essential equality of these three values suggests† that 1·138 Å may be taken as R_1 for d^3sp^3 orbitals for all the elements of the first long period:

$$R_1(d^3sp^3) = 1{\cdot}138. \tag{10b}$$

Equations (10*a*) and (10*b*) and the assumed linear relation between R_1 and the amount of *d* character (δ) lead to the equation

$$R_1(\delta, z) = 1{\cdot}825 - 0{\cdot}043z - (1{\cdot}600 - 0{\cdot}100z)\,\delta. \tag{10c}$$

The radii for pure *p* bonds are about 0·030 Å larger than for sp^3 bonds:

$$R_1(p) = R_1(sp^3) + 0{\cdot}030. \tag{10d}$$

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† The treatment adopted here must be considered as an approximation, inasmuch as it involves neglect of factors that without doubt have some effect on the interatomic distances. Among these factors is the difference in the ability of single unshared electrons and electron pairs to compete with bonding electrons for the stable orbitals. It is not unlikely that the radius 1·165 for iron corresponds to an amount of *d* character larger than the assumed 39·7 %, because of the promotion of the atomic electrons to orbitals with less than 100 % *d* character. Moreover, it is likely, from the results of the analysis of the energy quantities for the alkali metals, that the metallic orbital has less *d* character than the bond orbitals, instead of the same amount as assumed. The contribution of the ionic aspects of the atoms, with one bond more or less than normal, has also not been considered explicitly. Incorporation of these effects in the treatment of interatomic distances would make the system much more complicated, without greatly changing the conclusions derived from its application.

Application of equation (10*c*) to the observed single-bond radii of *scandium*, *titanium* and *vanadium* (1·439, 1·324, 1·224 Å) leads to 20, 27 and 35 % of *d* character, respectively (table 5). The gradual increase presumably results from the increasing stability of the 3*d* orbitals relative to 4*s* and 4*p*.

TABLE 5. SINGLE-BOND RADII AND AMOUNT OF *d* CHARACTER FOR TRANSITION ELEMENTS

Sc	Ti	V	Cr	Mn	Fe	Co	Ni
1·439 (3)	1·324 (4)	1·224 (5)	1·176 (6, 3)	1·171 (6, 4)	1·165 (5·78)	1·162 (6)	1·154 (6)
20	27	35	39	40·1	39·7	39·5	40·0
Y	Zr	Cb	Mo	Tc	Ru	Rh	Pd
1·616 (3)	1·454 (4)	1·342 (5)	1·296 (6)	1·271 (6)	1·246 (6)	1·252 (6)	1·283 (6)
19	31	39	43	46	50	50	46
Lu	Hf	Ta	W	Re	Os	Ir	Pt
1·557 (3)	1·442 (4)	1·343 (5)	1·304 (6)	1·283 (6)	1·260 (6)	1·265 (6)	1·295 (6)
19	29	39	43	46	49	49	44

The observed single-bond radius for both sexivalent and tervalent *chromium* is 1·177 Å, which corresponds to 39·0 % *d* character. This might result for sexivalent chromium from a large (42 %) contribution of the set of orbitals d^2sp^3 (without a metallic orbital), or for a disproportion in the d^3sp^3 set, with the metallic orbital having more than the average amount of *d* character. In tervalent chromium three of the orbitals (presumably largely *d*) are occupied by the three atomic electrons, and the d^2sp^3 set remaining for the three bonds and the metallic orbital may produce the hybrid character that is most stable.

For *manganese* the quadrivalent single-bond radius 1·163 Å corresponds to 40·1 % *d* character. The sexivalent single-bond radius is the same, to within the accuracy (about 0·010 Å) of its determination from the interatomic distances in the crystals (β-manganese and α-manganese) in which sexivalent and quadrivalent manganese occur together.

The metals of the first ascending branch

If the assumption is made that the bond orbitals and one metallic orbital (except for the state with maximum valence, which has no metallic orbital) have the same hybrid character, values of the radii for the various pure valence states of the metals of the first ascending branch, from copper to germanium, can be calculated by use of equations (10*c*) and (10*d*). These values are given in table 6. There are also given the values interpolated for resonance between the state of maximum valency (with no metallic orbital) and the next state (with valency two less, and with a metallic orbital) in the ratio 25 : 75, the number of orbitals being included in the calculation as a weight factor.

For *copper* the predicted value of R_1 for the hybrid state with valency 5·5 is 1·172 Å. This is in nearly exact agreement with the observed value, $R_{(\mathrm{CN}12)} = 1{\cdot}276$ Å, which corresponds to $R_1 = 1{\cdot}174$ for $v = 5{\cdot}50$, and hence supports this value for the valency of copper in the elementary metal.

Zinc in the elementary metal has six ligates at 2·660 Å and six at 2·907 Å. If the strong bonds are assumed to have bond number $n = \frac{1}{2}$, the value of R_1 is 1·240 Å. This is close to the value 1·229 Å predicted for Zn B, with $v = 4$. If this quadrivalent zinc alone is represented, the weak bonds have $n = \frac{1}{6}$, and the value of R_1 calculated with the correction $-0{\cdot}300 \log \frac{1}{6} = 0{\cdot}234$ is 1·220 Å, again in good agreement with the predicted value. On the other hand, if there were 25 % contribution of Zn A, making $n = \frac{1}{4}$ for the long bonds, the value of R_1 would be 1·273 Å, which is much larger than the predicted radius for $v = 4{\cdot}5$, 1·214 Å. We hence conclude that elementary zinc is pure quadrivalent Zn B, and that the six strong and six weak bonds have bond numbers $\frac{1}{2}$ and $\frac{1}{6}$, respectively. The strong bonds formed by each atom involve resonance of three valencies among six positions, and the weak bonds involve resonance of one valency among six positions.

TABLE 6. METALLIC RADII OF ELEMENTS OF THE ASCENDING BRANCHES

	Cu	Zn	Ga	Ge
A	1·138 (7)	1·176 (6)	1·206 (5)	1·223 (4)
B	1·185 (5)	1·229 (4)	1·266 (3)	1·253 (2)
C	1·227 (3)	1·309 (2)	1·296 (1)	
D	1·352 (1)			
	1·172 ($5\frac{1}{2}$)	1·214 ($4\frac{1}{2}$)	1·248 ($3\frac{1}{2}$)	1·244 ($2\frac{1}{2}$)

	Ag	Cd	In	Sn
A	1·303 (7)	1·343 (6)	1·377 (5)	1·399 (4)
B	1·353 (5)	1·400 (4)	1·442 (3)	1·434 (2)
C	1·396 (3)	1·485 (2)	1·477 (1)	
D	1·528 (1)			
	1·340 ($5\frac{1}{2}$)	1·384 ($4\frac{1}{2}$)	1·423 ($3\frac{1}{2}$)	1·423 ($2\frac{1}{2}$)
			1·456 ($2\frac{1}{2}$)	

	Au	Hg	Tl	Pb
A	1·303 (7)	1·345 (6)	1·387 (5)	1·430 (4)
B	1·351 (5)	1·403 (4)	1·460 (3)	1·540 (2)
C	1·393 (3)	1·490 (2)	1·540 (1)	
D	1·520 (1)			
	1·338 ($5\frac{1}{2}$)	1·388 ($4\frac{1}{2}$)	1·419 (4)	1·506 ($2\frac{1}{2}$)
		1·418 ($3\frac{1}{2}$)	1·439 ($3\frac{1}{2}$)	
			1·477 ($2\frac{1}{2}$)	
			1·497 (2)	

In the complex structure of *gallium* each atom has seven neighbours, at four different distances, 2·437 (1), 2·706 (2), 2·736 (2) and 2·795 Å (2). These were previously interpreted, with the assumed valency 3·44, as corresponding to bond numbers 1·21, 0·43, 0·38 and 0·31, respectively, leading to the single-bond radius 1·245 Å, and the value 1·251 Å would have been obtained if the valency had been taken as 3·50. The close agreement of this value with the predicted value 1·248 for valency 3·50 (table 6) thus supports this valency for elementary gallium.

If it is assumed that the valency $3\frac{1}{2}$ is divided among one single bond, four $\frac{1}{2}$-bonds, and two $\frac{1}{4}$-bonds the corresponding values of R_1 are 1·219, 1·263, 1·278 and 1·217 Å. The first and last values correspond to orbitals with 16 % *d* character, and the others to sp^3 orbitals. This suggests that the 0·25 *d* orbital provided by the 25 % contribution of Ga A is divided among the $1\frac{1}{2}$ orbitals of the single bond and two $\frac{1}{4}$-bonds, giving 16·7 % *d* character to them.

The observed interatomic distance 2·446 Å for *germanium*, with the diamond structure, was used as a fixed point in formulating equation (9*a*), the valency 4 being assumed. Germanium seems to be quadrivalent in all of its intermetallic compounds. A representative one is Mg_2Ge, with the Mg_2Sn (fluorite) structure. The germanium atom is surrounded by eight magnesium atoms, and its four valences undergo pivoting resonance among the eight positions, leading to half bonds.

The radii of the heavier transition metals

For the palladium-transition metals we write the equations

$$R_1(sp^3) = 2{\cdot}001 - 0{\cdot}043z, \tag{11a}$$

$$R_1(d^3sp^3) = 1{\cdot}303, \tag{11b}$$

$$R_1(\delta, z) = 2{\cdot}001 - 0{\cdot}043z - (1{\cdot}627 - 0{\cdot}100z)\,\delta, \tag{11c}$$

$$R_1(p) = R_1(sp^3) + 0{\cdot}035. \tag{11d}$$

The corresponding equations for the platinum-transition metals are

$$R_1(sp^3) = 1{\cdot}850 - 0{\cdot}030z, \tag{12a}$$

$$R_1(d^3sp^3) = 1{\cdot}303, \tag{12b}$$

$$R_1(\delta, z) = 1{\cdot}850 - 0{\cdot}030z - (1{\cdot}276 - 0{\cdot}070z)\,\delta, \tag{12c}$$

$$R_1(p) = R_1(sp^3) + 0{\cdot}110. \tag{12d}$$

Equations (11*a*) and (12*a*) are based upon the values 1·399 and 1·430 for $R_1(sp^3)$ for tin and lead, respectively, with slopes as indicated by the tetrahedral radii for the heavier elements. The value 1·430 for quadrivalent lead was obtained by adding to the radius for quadrivalent tin the difference 0·031 Å between the Mg-Pb distance in Mg_2Pb and the Mg-Sn distance in Mg_2Sn. The simple form of equations (11*b*) and (12*b*) was assumed in analogy with (10*b*), and the equal values of the constant were obtained from the observed distances for silver and gold, both assumed to have valence $5\frac{1}{2}$.

Revised values† of the single-bond radii for the elements molybdenum to palladium and tungsten to platinum are given in table 5. These differ from those previously published (Pauling 1947) in that the valency is assumed‡ to be 6 instead of 5·78. The course of the radii for these sequences differs from that in the sequence chromium to nickel in that the contraction shown in the preceding sequences continues, a minimum being reached at ruthenium and osmium. It is likely that this further contraction beyond molybdenum and tungsten is due to the appropriation of an amount of *d* character greater than 42·9 % (for d^3sp^3 orbitals) by the bond

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† The value for technetium is from Mooney (1948):

$$\text{Tc-Tc} = 2{\cdot}706\,(6),\ 2{\cdot}738\,(6);\ R_1(\text{CN }12) = 1{\cdot}361\,\text{Å}.$$

‡ Possibly slightly different valencies should be assumed, especially for ruthenium and osmium, and a small change may be required when reliable magnetic data become available.

orbitals, probably at the expense of both the atomic orbitals (occupied by unpaired electrons) and the metallic orbital. The effect decreases at palladium and platinum, with atomic orbitals mainly occupied by pairs of electrons, which tend to cause them to retain 100 % d character. It is seen from table 5 that the amounts of d character calculated by application of equations (11c) and (12c) show a reasonable trend, and are almost exactly the same for the two series of elements. The d character is equal to that for d^3sp^3 bonds at molybdenum and tungsten, and reaches its maximum of 50 % at ruthenium, rhodium, osmium, and iridium.

The metals of the silver and gold ascending branches

Values of the single-bond radii for the metals of the series silver to tin and gold to lead are also given in table 6, as calculated by equations (10c) and (11c) for the pure valence states A, B, C and D and for certain intermediate valencies, corresponding to resonance among these states.

The values for *silver* and *gold* with $v = 5\frac{1}{2}$ agree closely with the experimental values, 1·340 and 1·337 Å, respectively, upon which the equations were in part based.

For *cadmium* the observed interatomic distances 2·973 (6) and 3·287 Å (6) indicate bond numbers $\frac{1}{2}$ and $\frac{1}{6}$, respectively, as for zinc, and lead to the values 1·397 and 1·410 Å for R_1, in good agreement with the value 1·400 Å given in the table for $v = 4$. Bond number $\frac{1}{4}$ for the longer bonds would lead to $R_1 = 1{\cdot}463$, in disagreement with the value 1·384 for $v = 4\frac{1}{2}$. Hence we conclude that in the elementary metal cadmium, like zinc, is quadrivalent.

Mercury, with interatomic distances 2·999 (6) and 3·463 (6), appears to have valency $3\frac{1}{2}$. With bond numbers $\frac{1}{2}$ and $\frac{1}{6}$, respectively, these distances lead to $R_1 = 1{\cdot}410$ and 1·498, the latter being much too large for $v = 4$ ($R_1 = 1{\cdot}403$), whereas bond numbers $\frac{1}{2}$ and $\frac{1}{12}$ lead to $R_1 = 1{\cdot}410$ and 1·408, in approximate agreement with the value 1·418 for $v = 3\frac{1}{2}$. The decrease in valency from cadmium to mercury conforms to a general trend toward smaller metallic valencies with increasing atomic number in a group of elements.

In *indium* each atom has four ligates at 3·242 and eight at 3·370 Å. The first of these distances leads with $n = \frac{1}{4}$ to $R_1 = 1{\cdot}440$, a reasonable value in comparison with $R_1 = 1{\cdot}442$ for $v = 3$ (table 6). However, the eight longer bonds must have $n < \frac{1}{4}$, so that the valency is less than 3. With $n = \frac{3}{16}$ for these bonds their value of R_1 is 1·446, the weighted average of this value and that for the shorter bonds, 1·456, agreeing exactly with the value for $v = 2\frac{1}{2}$ in table 6; the valency of indium in the elementary metal is hence indicated to be $2\frac{1}{2}$.

In grey *tin* the distances 3·016 (4) and 3·175 (2) lead with $n = \frac{1}{2}$ and $\frac{1}{4}$ to $R_1 = 1{\cdot}418$ and 1·407, respectively, in approximate agreement with the interpolated value 1·423 for $v = 2\frac{1}{2}$. The distances 2·980 (2) and 3·198 (6) for γ-tin (containing a small amount of mercury), with $n = \frac{1}{2}$ and $\frac{1}{4}$, similarly give $R_1 = 1{\cdot}400$ and 1·418.

Thallium, with R (CN 12) = 1·712 Å, seems to be approximately bivalent. With $n = \frac{1}{6}$ the value 1·478 is found for R_1, slightly smaller than that in table 6 for $v = 2$, 1·497. The value R (CN 12) = 1·746 Å for *lead* gives $R_1 = 1{\cdot}512$ for $v = 2$, and $R_1 = 1{\cdot}542$ for $v = 2\frac{1}{2}$; comparison with the values in table 6 suggests that the valency lies between these limits. The conclusions for thallium and lead are uncertain because of uncertainty in the radii for pure *p* bonds. The value of the constant in equation (11*d*) is indicated not only by the single-bond radius for bismuth but also by the distances in the diatomic hydrides (M-H distance minus 0·300 = 1·570 for TlH, 1·539 for PbH, 1·509 for BiH; table III of Pauling 1947). By decreasing these radii by 0·03 Å exact agreement would be obtained for both thallium and lead with valency 2.

INTERATOMIC DISTANCES IN INTERMETALLIC COMPOUNDS

The discussion of interatomic distances is less simple for intermetallic compounds than for pure metals; among the complicating factors are the partial ionic character of bonds, the transfer of electrons, with consequent changes in valency, and the preferential use of the valencies of an atom in the formation of strong bonds rather than weaker ones. These factors, which of course participate in minimizing the energy of the system, usually operate to decrease the interatomic distances. Their effects may be illustrated by some examples.

In a discussion of cementite, Fe_3C, it was pointed out (Pauling 1947) that the observed interatomic distances, Fe-C = 2·01 Å and Fe-Fe = 2·62 Å (average), differ from those predicted from the valencies and radii of iron and carbon, Fe-C = 2·04 Å and Fe-Fe = 2·59 Å, by ± 0·03 Å, and that the lack of agreement might indicate that the structure is under some strain, compressing the Fe-C bonds and stretching the Fe-Fe bonds. An alternative and in some ways preferable explanation is that, in order to form as strong bonds as possible with the carbon atoms, the two corresponding orbitals of the iron atoms undergo a change in hybridization with increase in the amount of *d* character and decrease of the iron radius by 0·03 Å, and that a compensating decrease in the amount of *d* character (by one-half as much) occurs in the four orbitals involved in forming Fe-Fe bonds, accompanied by an increase in radius by 0·015 Å. The same explanation has been advanced (Pauling & Soldate 1948) for the observed shortening of the Fe-Si distances in the cubic crystal FeSi; and in addition it has been suggested that in this crystal the valency of silicon is used entirely in forming bonds with iron, the Si-Si separation of 2·76 Å, which indicates bond number 0·20, being assumed rather to be a non-bonded contact required by the geometry of the atomic arrangement.

The substance FeB, which may serve as another example, forms orthorhombic crystals (Bjurström 1933) in which each boron atom has two boron ligates at 1·77 Å and six iron ligates at 2·15 ± 0·03 Å. These distances correspond to half bonds, for which the calculated distances are 1·78 and 2·15 Å, respectively, and the covalency of boron is hence indicated to be 4. We might thus be led to assume that, in order to allow the formation of the maximum number of strong bonds (involving boron) permitted by the number of bonding orbitals of the boron atom, an electron is transferred from iron to boron. An alternative explanation is that the B-Fe bonds have bond number $\frac{1}{3}$, the iron radius being decreased by 0·11 Å by an increase in *d* character of the two iron orbitals involved in these bonds, and the boron atom remaining tervalent. Such a large decrease in the iron radius seems unlikely, however, and it is instead probable that both effects operate, there being a smaller change in hybridization and also some electron transfer in this crystal.

Each iron atom in FeB has six boron ligates, six iron ligates at 2·64 Å, and four iron ligates at 2·94 Å, corresponding to valency about 5·5.

The interpretation of simple structures of intermetallic compounds is made difficult by the metrical relations between non-equivalent interatomic distances that prevent them from independently assuming the values corresponding to their bond type. The B 32 structure, shown by LiGa and several other compounds of elements of groups I and III *b* of the periodic table, consists of two interpenetrating diamond arrangements: each atom is surrounded by four atoms of the same kind and four of the other kind, at the tetrahedral corners of a cube, and there is thus only one bond distance (2·68 Å in LiGa) for three kinds of bonds (Li-Li, Li-Ga and Ga-Ga), which hence are expected to be strained. Nevertheless the bond number calculated from this distance for the strongest bonds (Ga-Ga) should be approximately correct.

Several investigators have suggested that in the B 32 substances the alkali metal loses its valence electron to the III *b* metalloid, which then acts as a fourth-group element, and forms four single bonds with its four similar neighbours. However, this structure would lead to interatomic distances much smaller than those observed—to 2·53 Å for LiGa, for example, instead of 2·68 Å. The corresponding Ga-Ga bond number, 0·57, calculated by equation (9), suggests instead that the bonds are half bonds, or perhaps $\frac{5}{8}$-bonds. Presumably the lithium atom uses its valence electron in forming bonds with gallium atoms (four Li-Ga $\frac{1}{4}$-bonds), the Li-Li contacts being essentially non-bonded. The valency of gallium is 3 (for Ga-Ga half bonds) or $3\frac{1}{2}$ (for $\frac{5}{8}$-bonds).

The compound PtTl (Zintl & Harder 1935) illustrates the phenomenon of the increase in valency of an element (thallium) in response to a change in its environment. This substance forms hexagonal crystals, the unit containing 3 Pt, 1 Tl I, and 2 Tl II, with ligation as follows: Pt, 4 Pt at 2·803 Å, 2 Tl I at 2·803 Å, and 4 Tl II at 2·83 Å; Tl I, 6 Pt at 2·803 Å; Tl II, 6 Pt at 2·83 Å. The Pt-Pt distance corresponds to $n = 0{\cdot}44$, calculated by equation (9) with $R_1 = 1{\cdot}295$. Presumably platinum has its normal valency 6, which is used in forming Pt-Tl bonds except for the amount used in the Pt-Pt bonds. The bond number $n = 0{\cdot}44$ would lead to 4·24 as the average valency of thallium in this compound; it is likely, however, that the Pt-Pt bonds are half bonds, and that the valency of thallium is 4—twice that for the elementary substance. The predicted value of R_1 for quadrivalent thallium is 1·419 Å, and the calculated bond numbers for Pt-Tl I and Pt-Tl II are 0·71 and 0·64, respectively. The small differences between these values and the value $\frac{2}{3}$ corresponding to the assumed valencies and between 0·44 and $\frac{1}{2}$ for the Pt-Pt bonds may be attributed to a change in hybridization of the orbitals of platinum, in response partially to the requirement of the structure that the Pt-Pt and Pt-Tl I distances be equal and partially to the effort to use better bond orbitals (with more *d* character) for the stronger Pt-Pt bonds than for the weaker Pt-Tl bonds.

There are many interesting problems involving solid solutions that might be discussed by use of the new system of radii. Of these I select one pointed out to me by Mr E. C. Ellwood, of King's College, Newcastle-upon-Tyne. The solid solution of zinc in aluminium, with the Al structure, extends from 0 to 66 atomic % zinc. On cooling below 365° C the phase containing approximately 40 at. % zinc separates into two phases, both of which are solid solutions with the Al structure; at 275° C one phase (α) contains only 17 at. % zinc, and the other (α') contains 59 at. % zinc. The values of the lattice constants indicate that the effective radius of zinc is smaller in the α' phase than in the α phase.

An explanation that may be suggested of these facts is that solid solutions of a quadrivalent metal (zinc) in a tervalent metal (aluminium) tend to be unstable because of the difficulty of saturating the valency of isolated quadrivalent atoms by bonds to its lower-valent ligates. With zinc as the solute an increase in free energy at the lower temperatures would accompany the separation into the zinc-poor α phase, in which the versatile zinc atoms tend to assume the valency 3 (less stable, however, for them than their normal valency) in order to fit into the aluminium structure, and the zinc-rich α' phase, in which the concentration of zinc atoms is great enough to permit the extra valency of zinc to be satisfied through the formation of Zn-Zn bonds.

BRILLOUIN ZONES AND THE RESONATING-VALENCE-BOND THEORY

In the customary treatment of metals it is shown that the interaction of the metallic electrons with the atomic nuclei (and their strongly bound electrons) arranged in a crystallographic array leads to perturbations of the energy that can be described as the concentration of the one-electron energy levels into Brillouin zones. It is interesting that the same concentration into Brillouin zones results from the resonating-valence-bond theory, and, moreover, the successive zones (Brillouin polyhedra) contain the same numbers of electrons as given by the one-electron molecular-orbital theory.

Instead of formulating the wave function for a crystal as a sum of functions describing various ways of distributing the electron-pair bonds among the interatomic positions, as was done in the first section of this paper, let us formulate it in terms of two-electron functions describing a single resonating valence bond. A bond between two adjacent atoms a_i and a_j may be described by a function $\phi_{ij}(1,2)$ in which 1 and 2 represent two electrons and the function ϕ_{ij} may have the simple Heitler-London form

$$\phi_{ij}(1,2) = C\{\phi_i(1)\phi_j(2)+\phi_j(1)\phi_i(2)\}\{\alpha(1)\beta(2)-\beta(1)\alpha(2)\}, \qquad (13)$$

with ϕ_i and ϕ_j the appropriately hybridized bonding orbitals of atoms a_i and a_j and α and β the one-electron spin functions, or it may include ionic terms or have a still more complex form. The ϕ_{ij} could then be used in building antisymmetrized functions corresponding to the various possible valence-bond structures for the crystal. This procedure would lead to essentially the same results as those given by equations (1) and (2). However, a convenient approximation is made by neglecting the resonance energy of the bonding pairs of electrons with one another, and considering only the bond energy and the resonance energy of each bond among its alternative positions, without correlating its resonance with that of other bonds. The wave function for the crystal (not antisymmetrized) may then be written as

$$\psi(1,2,\ldots,2N) = \Phi_1(1,2)\Phi_2(3,4), \tag{14}$$

in which each of the functions Φ_k is a two-electron function representing a valence bond resonating through the crystal. The total energy, in this approximation, is the sum of the resonating-bond energies:

$$W = \Sigma W_k. \tag{15}$$

The form of the functions Φ_k may be closely similar to that of the molecular orbitals used in the simple theory of metals. If there are M interatomic positions in the crystal which might be occupied by any one of the N electron-pair bonds, then the M functions ϕ_{ij} may be combined into the M mutually orthogonal linear aggregates that approximate the solutions of the wave equation with inclusion of the interaction terms representing resonance. This combination can be effected with use of Bloch factors:

$$\Phi_k(1,2) = C\phi_{\mathbf{r}}(1,2)\,\mathrm{e}^{2\pi i\mathbf{P}_k\cdot\mathbf{r}/h} \tag{16}$$

Here $\mathbf{r}$ is the radius vector from the origin to a point R in the crystal, $\phi_{\mathbf{r}}$ is the electron-pair-bond function in the region near R, $\mathbf{P}_k$ is the momentum vector corresponding to the three quantum numbers k (the density of states being calculated in the usual way), h is Planck's constant, and C is the normalizing factor.

When the momentum vector $\mathbf{P}_k$ has such magnitude and orientation as to correspond to Bragg reflexion from an important crystallographic plane (with large structure factor for slow electrons) strong interaction between the resonating bond and the rest of the crystal will occur, leading to the displacement of energy levels and the formation of Brillouin zones. The striking agreement between the number of bonding electrons given by the new system of metallic valencies and the number of electrons contained in an important Brillouin polyhedron for the γ-alloys, α-manganese, β-manganese, and some other metallic substances with properties indicating filled zones (brittleness, low electrical conductivity) has been discussed in an earlier paper (Pauling & Ewing 1948).

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The Dependence of Bond Lengths in Intermetallic Compounds on the Hybrid Character of the Bond Orbitals

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The observed bond lengths in some intermetallic compounds can be made compatible with those in the constituent metals by consideration of the possibility of distributing the *d* character unequally among the bond orbitals of an atom.

I met Paul Ewald forty-one years ago, not long after I had arrived in Munich to work in Arnold Sommerfeld's Institute of Theoretical Physics (April 1926). When I visited Ewald in his laboratory in Stuttgart he was hard at work, with C. Hermann, on the preparation of the first volume of the *Strukturbericht*. He asked me what I thought about the structure of calcium carbide. A reported structure determination placed the carbon atoms in groups of four, at the corners of a regular tetrahedron with edge 1·62 Å. Ewald asked if I thought that there was any chance that this structure determination could be correct. I answered that in my opinion the structure was unlikely, but could not be ruled out as impossible, because the strain energy of the six bent bonds in the tetrahedron might be no greater than the instability of two carbon–carbon triple bonds, relative to six unstrained single bonds (110 kcal.mole^{-1}). This question, and others that he asked, impressed me strongly as to the amount of care and thought that Ewald was devoting to the task of writing this important volume.

Another matter that we discussed was the extent to which knowledge of the sizes of atoms could be used as the basis of a decision about the correctness or incorrectness of a reported structure determination. Although Bragg (1920), Huggins (1926), and Goldschmidt (1926) had published tables of atomic radii, there were still great doubts as to their general applicability and reliability. As late as 1928 it was possible for a well-trained investigator (in Sommerfeld's Institute) to consider his structure determination to be acceptable and worth publication even though it placed atoms of two elements, zirconium and silicon, only 0·59 Å apart, only twenty per cent as far from one another as the average of the smallest interatomic distances in the crystals of the two elementary substances (Seyfarth, 1928). By 1936, when the second volume of the *Strukturbericht* was published, there had been developed enough confidence in the reliability of atomic radii to permit this reported structure to be described as very unlikely.

In 1922, when I began my graduate work in the California Institute of Technology, I started to collect the information about interatomic distances from the literature, and to make an effort to formulate a system of bond lengths. I had become interested in metals and alloys in 1920, and I was especially interested in making a structure determination of an intermetallic compound. This interest resulted in the assignment of the fluorite structure to Mg_2Sn, and to the observation that the distance between magnesium atoms and tin atoms in magnesium stannide (in the compound) is 2·94 Å, somewhat smaller than the average of the observed magnesium–magnesium distance and tin–tin distance in the elements, with either allotrope of tin (Pauling, 1923).

Goldschmidt (1926) grouped metals and covalent crystals together, and Bernal (1929) pointed out that many properties of metals indicate that metallic bonds are closely similar to covalent bonds. I developed this idea further (Pauling, 1938), and formulated a set of metallic radii in 1947, with use of the empirical equation

$$D(n) = D(1) - 0{\cdot}600\ \text{Å} \log n \qquad (1)$$

for the dependence of interatomic distance on the bond number n.

The set of metallic radii and the equation permit the reasonably satisfactory discussion of observed interatomic distances in many intermetallic compounds. In some crystals, however, the simple application of the radii and the equation leads to disagreement with observation.

Also, for some elementary metals, such as with the *A*2 structure (cubic body-centered), there has been uncertainty about how to divide the total valence of the atom between the non-equivalent bonds, and consequent uncertainty in the value of the single-bond radius of the metal.

A way to overcome some of these difficulties can be developed on the assumption that in metals and intermetallic compounds the nonequivalent bond orbitals in an atom may have different hybrid character, such as to correspond to suitable values of R_1, the single-bond radius of the atom. A set of empirical equations giving the single-bond radius as a function

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of the hybrid character of the orbital and the atomic number of the element, formulated nearly twenty years ago (Pauling, 1949), includes the following three, which show, for metals of the three long periods, the single-bond radius as a function of z, the number of electrons beyond the corresponding noble-gas structure, and δ, the amount of d character of the bond orbital:

First long period (iron-transition metals):

$$R_1(\delta,z)=1{\cdot}825-0{\cdot}043z-(1{\cdot}600-0{\cdot}100z)\delta \quad (2a)$$

Second long period (palladium-transition metals):

$$R_1(\delta,z)=2{\cdot}001-0{\cdot}043z-(1{\cdot}627-0{\cdot}100z)\delta \quad (2b)$$

Third long period (platinum-transition metals):

$$R_1(\delta,z)=1{\cdot}850-0{\cdot}030z-(1{\cdot}276-0{\cdot}070z)\delta . \quad (2c)$$

As a first example of the application of these equations we may evaluate the single-bond radius for tungsten from the observed bond lengths in β-tungsten* and α-tungsten. In β-tungsten the two tungsten atoms of the first kind form twelve bonds with neighboring W_{II} atoms, with the length 2·822 Å. The valence of 6 requires that the bonds be half bonds, if we assume that no electron transfer occurs between the two kinds of tungsten atoms. Each W_{II} atom forms four of these bonds with the neighboring W_I atoms, two bonds to W_{II} at 2·543 Å, and eight bonds to W_{II} at 3·092 Å. Of the valence 6 of W_{II}, two valence units are used in forming the bonds to W_I. The two short bonds, at 2·543 Å, may be assumed to have $n=1$. The other eight bonds formed by W_{II} accordingly have $n=\frac{1}{4}$. With use of equation (1), the value of R_1 found for the W_I–W_{II} bonds is 1·321 Å, and the corresponding value of the amount of d character, given by equation (2c), is 40·8%. The corresponding values of R_1 and δ for the bonds of the other two kinds are 1·273 Å, 46·6%, and 1·365 Å, 35·6%. The weighted average of the amount of d character is 41·0%, which corresponds to the average value $R_1=1{\cdot}319$ Å.

In α-tungsten each atom is surrounded by eight atoms at 2·741 Å and six atoms at 3·165 Å. We may answer the question as to how the total valence 6 is to be divided among the fourteen bonds by assuming that the amount of d character varies with bond length in the same way as for β-tungsten. This assumption leads to the bond numbers 0·60 for the eight stronger bonds and 0·20 for the six weaker bonds. Application of equations (1) and (2c) then gives 1·304 Å, 42·8% and 1·373 Å, 34·7%, average amount of d character 41·1%. This amount of d character corresponds to the average $R_1=1{\cdot}318$ Å, in excellent agreement with the value 1·319 Å from the β form. I think that this value should replace the older values 1·299 Å (Pauling, 1947) and 1·304 Å (Pauling, 1949, 1960), which were obtained by more arbitrary methods of interpreting the observed bond lengths.

A similar method may be used to interpret the observed bond lengths for other $A2$ metals. For vanadium, niobium, and tantalum we may assume that the total valence is divided among the stronger and weaker bonds in the same ratio as for tungsten; the stronger bonds then have $n=0{\cdot}50$ and the weaker bonds have $n=0{\cdot}167$. In vanadium the eight strong bonds at 2·622 Å correspond to $R_1=1{\cdot}221$, $\delta=35{\cdot}4\%$, and the six weak bonds at 3·028 Å to $R_1=1{\cdot}281$, $\delta=30{\cdot}0\%$, average $\delta=34{\cdot}3\%$, leading to $R_1=1{\cdot}233$ Å (older value 1·224 Å). The corresponding values for niobium are 2·858 Å, $R_1=1{\cdot}339$ Å, $\delta=39{\cdot}7\%$, 3·300 Å, $R_1=1{\cdot}417$, $\delta=32{\cdot}8\%$, average $\delta=38{\cdot}3\%$, giving the single-bond radius 1·354 Å (older value 1·342 Å); and for tantalum 2·860 Å, 1·340, 38·9%, 3·302 Å, 1·418, 30·5%, average $\delta=37{\cdot}2\%$, single-bond radius 1·356 Å (older value 1·343 Å).

From among the many intermetallic compounds that might be used to illustrate the procedure, I select Nb_3Sn, which is of a special interest because of its high superconducting transition temperature (18·05°K). This compound has the β-tungsten structure, with tin atoms in the W_I positions and niobium atoms in the W_{II} positions. Each tin atom has twelve niobium neighbors, at 2·957 Å. Each niobium atom has four tin neighbors, two niobium neighbors at 2·645 Å, and eight niobium neighbors at 3·239 Å. The small interatomic distance strongly indicates that the tin atom is quadrivalent, with pivoting resonance of its four bonds among the twelve positions, leading to bond number $\frac{1}{3}$ for the tin–niobium bonds. I assume that the shorter Nb–Nb bonds are single bonds, with $n=1$. To achieve the valence 5 for niobium the longer Nb–Nb bonds must have $n=0{\cdot}208$. With use of the single-bond radius 1·405 Å for quadrivalent tin and of equations (1) and (2b), R_1 for niobium in the niobium–tin bonds is found to have the value 1·266, corresponding to $\delta=42{\cdot}6\%$. For the stronger and weaker niobium–niobium bonds the corresponding values are 1·322, 41·2%, and 1·415, 32·9%. The average value of δ is 39·8%, somewhat larger than the value for elementary niobium, 38·3%. Similarly, the single-bond radius of niobium in the compound, 1·338 Å, is somewhat smaller than that for the element, 1·354 Å.

The tetragonal crystal WSi_2 (Zachariasen, 1927) may serve as another example. Each silicon atom forms five bonds with surrounding silicon atoms at 2·633 Å and five bonds with tungsten atoms at the same distance. Each tungsten atom forms ten bonds with silicon atoms at 2·633 Å and four bonds with tungsten atoms at 3·214 Å. Application of equation (1) with single-bond radii of silicon and tungsten taken as 1·173 and 1·315 Å, respectively, leads to bond numbers corresponding to valences 4·67 for silicon and 6·16 for tungsten. These values of the valence are too large; the valence of silicon may be taken as 4 (with pivoting resonance of the bonds among the ten positions), and that of tung-

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* It is possible that a small amount of oxygen is necessary to stabilize the β-tungsten structure (see, *e.g.* Moss & Woodward, 1959). A consideration of the effect of this oxygen might lead to a small revision in the values of the single-bond radii and amounts of d character.

sten as 6, which with equation (1) would lead to bond lengths an average of 0·027 Å larger than those observed. If the assumption is made that the two kinds of bond orbital of the tungsten atom have different amounts of *d* character, we may assign the values $n=0{\cdot}333$ to the silicon–silicon bonds (as given by equation (1) and the single-bond radius of silicon), $n=0{\cdot}467$ to the silicon–tungsten bonds, and $n=0{\cdot}333$ to the tungsten–tungsten bonds. The values of R_1 and δ for the bond orbitals of tungsten involved in the bonds to silicon atoms are 1·262 Å and 47·7%, and for the bonds to tungsten atoms 1·464 Å and 24·1%, respectively. The average value of δ, 42·5%, corresponds to $R_1=1{\cdot}306$ Å for the tungsten atom, which is 0·012 Å less than for the element.

A similar discussion of transition-metal bond lengths has been reported for FeSi and other silicides with the *B*31 structure (Pauling & Soldate, 1948), and Co_2Al_9 (Pauling, 1951).

In the above discussion the effect of difference in electronegativity of unlike atoms on bond length (usually a decrease) has been ignored. There is the possibility also of a small change in bond length between unlike atoms, such as of a metal and a metalloid, that reflects the difference in the nature of the overlapping orbitals, in addition to the effects of partial ionic character and of electron transfer. I believe that a thorough analysis of this problem, with consideration of the present great amount of experimental information about bond lengths in metals and intermetallic compounds, would now permit the formulation of a table of metallic radii reliable to 0·001 Å and a set of structural principles that would allow bond lengths and lattice constants to be predicted to within about 0·1%.

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Laves Structures, $MgCu_2$, $MgZn_2$, $MgNi_2$

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It is in some measure demonstrated that the formation of A–B and B–B contacts provides the energy for the compression of the A atoms and permits AB_2 phases with radius ratios so much larger (up to 1·67) than the ideal (1·225) to adopt the $MgCu_2$ type structure. At radius ratios somewhat lower than the ideal, the B atoms are insufficiently compressed for A–B and A–A contacts to form. This is probably a consequence of there being twice as many B atoms as A atoms, and it results in fewer known Laves phases with radius ratios below the ideal value than above it.

There have been many reviews and discussions of the crystal chemistry of the Laves phases (among the more recent see Berry & Raynor, 1953; Laves, 1956; Elliott & Rostoker, 1958; Bardos, Gupta & Beck, 1961; Dwight, 1961; Nevitt, 1963) but none of these explicitly discuss what we find to be their most remarkable features:

(i) Phases adopt structures which result mainly from the geometrical facility of packing together two components in the proportion AB_2 if the ratio of their radii, r_A/r_B, is 1·225, *when the actual size ratios of the components may differ greatly* (values from 1·05 to 1·67) *from the ideal value.*

(ii) Structural compression in the Laves phases may amount to more than 35% in unit-cell volume compared with the sums of the elemental volumes. Such large compressions might be expected in structures of phases with strong A – B interactions, but scarcely in those of the ideal Laves structures which, on the hard sphere atomic model, have only A – A and B – B contacts.

Space filling models based on the concept of incompressible atoms (Laves, 1956; Parthé, 1961) are of no assistance in understanding these features, but the problem can be discussed in terms of a model which allows compression of the A (or B) atoms to establish

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The Metallic Orbital and the Nature of Metals*

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In 1938 it was noticed (L. Pauling, *Phys. Rev.* **54,** 899, 1938) that about 0.72 of the nine outer *spd* orbitals per atom of a transition metal remain unoccupied by bonding electrons, unpaired ferromagnetic electrons, or unshared electron pairs. In 1948 this 0.72 orbital per atom was identified (L. Pauling, *Nature* (*London*) **161,** 1019, 1948; *Proc. Roy. Soc. A* **196,** 343, 1949) as required for the unsynchronized resonance that confers metallic properties on a substance, and it was named the metallic orbital. A statistical theory of unsynchronized resonance of covalent bonds in a metal with atoms restricted by the electroneutrality principle to forming bonds only in number $v - 1$, v, and $v + 1$, with v the metallic valence, has now been developed. This theory leads directly to the value 0.70 ± 0.02 for the number of metallic orbitals per atom, in reasonable agreement with the empirical value, and to the conclusion that M^+, M^0, and M^- occur in the ratios near 28 : 44 : 28. It leads also to the conclusions that stability of a metal or alloy increases with increase in the ligancy and for a given value of the ligancy is a maximum for valence equal to half the ligancy. These results with consideration of the repulsion of unshared electron pairs on adjacent atoms go far toward explaining the selection of different structures by different elemental metals and intermetallic compounds.

Introduction

Mike Sienko's interest in the question of the nature of the structural features that confer metallic properties on a substance (*1*) has stimulated me to renew my interest in this question.

Forty six years ago, on the basis mainly of empirical arguments, I formulated a description of the interatomic forces in metals (*2*) that had some novel features. I pointed out that according to this view the metallic bond is very closely related to the ordinary covalent (shared-electron-pair) bond: some of the electrons in each atom in a metal are involved with those of neighboring atoms in an interaction described as covalent-bond formation, with the bonds resonating among the available positions in the usual case that the number of positions exceeds the number of bonds. Moreover, all or most of the outer electrons of the atom, including for the transition elements the *d* electrons, take part in bond formation.

One of the reasons for my having attacked this problem in 1938 was that I was thoroughly dissatisfied with the claim of some physicists that only the *s* electrons were involved in the cohesion of the transition metals: the observed magnetic properties were said to show that the bonding in Ni involves 0.61 *s* electrons per atom, that in Co involves 0.71, that in Fe involves 0.22, and that in Cu involves 1 (the *d* shell for copper having its full complement of 10 electrons). The physical properties of these

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* Dedicated to Dr. M. J. Sienko.

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metals seemed to me to show clearly that the bonds involve interaction of a larger number of electrons. I knew, of course, that the quadrivalence of carbon is not based on the normal state $2s^2 2p^2$ of the carbon atom, but requires $s \rightarrow p$ promotion of one electron, to give the configuration $2s2p^3$, and it seemed possible to me that the cobalt atom in the metal might be promoted from its normal configuration $3d^7 4s^2$ to $3d^5 4s 4p^3$, with nine unpaired electrons which might enter into the formation of as many as nine covalent bonds.

I feel now that I was influenced to some extent by my knowledge that in 1926 Goldschmidt had formulated a set of "atomic" radii that represented reasonably well the interatomic distances in both covalent crystals and metals (*3*). I was also impressed by a discussion of the properties of metals by Bernal, who, however, rejected the idea that covalent bonds are present in metals (*4*). Bragg also rejected this idea (*5*).

The Discovery of the Metallic Orbital

In order to explain the observed saturation ferromagnetic moment of Fe, $2.22\mu_B$, I assumed that the Fe atom in the metal has two kinds of $3d$ orbitals: 2.22 "atomic" (contracted) orbitals, and 2.78 bonding $3d$ orbitals, which can hybridize with $4s$ and $4p$ to form bond orbitals. Thus 2.22 of the 8 outer electrons could occupy the atomic orbitals to provide the ferromagnetic moment, with the other 5.78 outer electrons forming 5.78 covalent bonds.

At that time I was handicapped by my remembering a misinterpretation that I had made of some results obtained in 1932 by one of my students, Ralph Hultgren (*6*). He had begun to make a thorough study of sets of equivalent *spd* hybrid bond orbitals, and soon found that he could not handle the computational problem in those precomputer days. I pointed out that the best hybrid orbitals have cylindrical symmetry about the bond direction and suggested that he assume cylindrical symmetry for his orbitals. With this assumption he treated several sets of equivalent orbitals, and found that the bond strength decreased rapidly for more than six orbitals. Only much later was it found that this decrease does not occur when the requirement of cylindrical symmetry is not imposed. In 1938, however, it seemed reasonable to assume that the number of bonding electrons remained constant at 5.78 from Cr to Ni.

With this assumption, and with 3.22 other orbitals available for occupancy by odd electrons or electron pairs, the ferromagnetic moment would be predicted to rise to a maximum of $3.22\mu_B$ at Co and then to decrease steadily with slope -1 to 0 for the alloy $Zn_{78}Ga_{22}$. This prediction agrees only in part with observation: the values of μ_B for alloys Fe–Co, Co–Ni, and Ni–Cu (Fig. 1) reach a rounded-off maximum of about 2.50 and then decrease to 0 at $Ni_{44}Cu_{56}$.

The obvious conclusion to be reached is that there are *three* kinds of *spd* orbitals: hybrid bond orbitals, contracted *d* orbitals, and about 0.70 other orbitals. In 1938 I considered this 0.70 unstable orbital per atom to be unsuited for either bond formation or

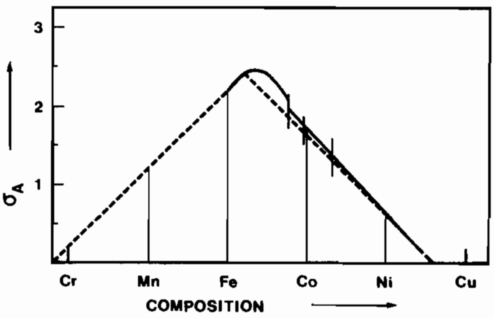


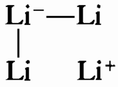
FIG. 1. Comparison of experimental values (solid curves) and predicted values (dashed lines) of the saturation ferromagnetic moment per atom, in Bohr magnetons, for Fe–Co, Co–Ni, and Ni–Cu alloys. The short vertical lines indicate change in crystal structure (from Ref. (*2*)).

occupancy by an "atomic" electron; only 10 years later did I recognize its significance and name it the metallic orbital (*7, 8*).

The argument was originally presented (*7, 8*) with Li as an example. The value of ΔH_f^0 (at 298 K) for the reaction $Li^+ + e^- \rightarrow Li(c)$ is -164 kcal mole^{-1} and that for $Li^+ + e^- \rightarrow Li(g)$ is -126 kcal mole^{-1}. Accordingly we might consider 77% of the binding energy of Li^+ and e^- in lithium metal to result from the formation of normal lithium atoms in the metal, and only 24% to result from the interaction of these atoms with one another. Moreover, the enthalpy change for the reaction $Li(g) \rightarrow \frac{1}{2}Li_2(g)$ is -13 kcal mole^{-1} and that for the reaction $\frac{1}{2}Li_2(g) \rightarrow Li(c)$ is -25 kcal mole^{-1}. If we consider four atoms in a square in a lithium crystal, there are two ways in which the bonds can be drawn to form Li_2 molecules:

$$\begin{array}{cc} Li & Li \\ | & | \\ Li & Li \end{array} \quad \text{and} \quad \begin{array}{c} Li—Li \\ \\ Li—Li \end{array}$$

The energy of the synchronized resonance between structures of this sort would contribute to the stabilization of the crystal, but far greater stabilization would result if there were also unsynchronized resonance to structures such as



$$\begin{array}{cc} Li^-—Li & \\ | & \\ Li & Li^+ \end{array}$$

in which one bond resonates independently from one position to another. The electroneutrality principle permits M^+, M^0, and M^- in a crystal or molecule, but not charges larger than ± 1.

However, this uninhibited resonance requires that the atom receiving a bond (M^+ or M) have an orbital available for its reception (occupied in M^-). *It is the possession of this orbital (the metallic orbital), in addition to the orbitals required for occupancy by unshared electron pairs and bonding electrons, by all or many of the atoms in a condensed phase that permits the unsynchronized resonance of covalent bonds that gives rise to metallic properties.*

Electric Conductivity

The unsynchronized resonance of covalent bonds through a metal provides a simple explanation of their characteristic electric conductivity. The valence bonds resonate from one position to another at electronic frequencies, as determined by the resonance energy, which is comparable in magnitude to the bond energy and is only about an order of magnitude less than the binding energy of a valence electron to the atom. In the presence of an applied electromagnetic field the electrons tend to move in the appropriate direction from atom to atom, as indicated in the diagram of Fig. 2, in which by a succession of shifts by single bonds a negative charge is seen to move toward the anode. In a similar way positive charges (electron holes) can move toward the cathode. The negative temperature coefficient of the electric conductivity is accounted for by the effect of thermal agitation in temporarily lengthening some bonds

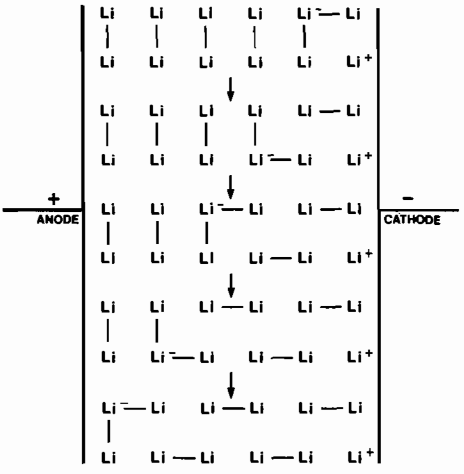


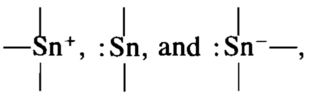
FIG. 2. Diagram illustrating motion of a negative charge (an electron) from the cathode to the anode by successive pivoting resonances of a covalent bond.

and shortening others, thus interfering somewhat with the resonance of the bonds, which takes place less often between nonequivalent positions than between equivalent (equienergetic) positions. This explanation is, of course, compatible with the usual explanation involving the scattering of electron waves by phonons.

An Example: White Tin

Hypoelectronic atoms, with fewer outer electrons than stable outer orbitals, do not provide a test for the metallic orbital, because such an orbital is necessarily available. The metallic orbital was discovered through the analysis of the values of the saturation ferromagnetic moments of the alloys of the hyperelectronic elements, from cobalt to copper, as shown in Fig. 1. Another test is provided by gray and white tin. Gray tin is not metallic; it is instead a metalloid, a semiconductor, with a positive temperature coefficient of its electric conductivity. It has the diamond structure, with each atom forming four covalent bonds, with bond length 2.80 Å. These bonds make use of all four of the stable outer orbitals, $6s6p^3$, leaving no metallic orbital and accordingly not permitting the substance to be a metal.

White tin, on the other hand, has metallic properties. Each atom in the crystal forms six bonds, four with length 3.016 Å and two with length 3.175 Å. When I first made a thorough study of bond lengths in metals (*9*) I interpreted these values as showing the valence to be 2.44; later (*8*) the value was recalculated to be 2.50, and then (*10*) to be 2.56. This value is explained by use of the metallic orbital. The atoms Sn$^+$, Sn, and Sn$^-$ have the structures



$$—\overset{|}{\underset{|}{\mathrm{Sn}}}{}^+,\ :\overset{|}{\underset{|}{\mathrm{Sn}}},\ \text{and}\ :\overset{|}{\underset{|}{\mathrm{Sn}}}{}^-—,$$

with Sn$^+$ and Sn having a metallic orbital and all other stable orbitals used either for bond formation or for occupancy by an unshared pair. (Sn$^-$ has no need for a metallic orbital, because it is prevented by the electroneutrality principle from accepting another electron.) With Sn$^+$ and Sn$^-$ tricovalent and Sn^0 bicovalent, the resultant valence 2.56 is achieved by 28% Sn$^+$, 44% Sn^0, and 28% Sn$^-$. The amount of metallic orbital (Sn$^+$ + Sn^0) is 0.72 per atom, in agreement with the value given by the magnetic moment measurements.

A Comment on the Magnetic Moments

When the magnetic moments were first analyzed (*2*) the conclusion was reached that the metal atoms from Cr to Ni use 5.78 orbitals for bond formation and 2.44 for occupancy by unshared atomic electrons. The deviation of the values 5.78 and 2.44 from integers was not understood; moreover, the slope of the curve of Fig. 1 from Fe$_{72}$Co$_{28}$ to Ni$_{44}$Cu$_{56}$ was not −1, as expected, but was about −1.10. These difficulties were eliminated in 1953, when I pointed out (*11*) that the Zener theory of ferromagnetism (*12*) clarifies our understanding of the phenomena. In this theory the interaction between atomic moments that stabilizes their parallel orientation is the resultant of the polarization of the conduction electrons, some electron pairs becoming decoupled in order that each of the two electrons be able to orient its spin parallel to the spin of the atomic electrons, in accordance with Hund's first rule. This effect is equivalent to converting a shared-electron-pair bond into two one-electron bonds, with the spins of the two electrons then contributing to the ferromagnetic moment. This adds about 11% to the moment. The moment for Fe is $2.22\mu_B$, of which 0.22 is contributed by polarized one-electron bonds and 2.00 is the corrected atomic moment. The total metallic valence of Fe, and also of adjacent elements, thus becomes 6, and the amount of metallic orbital given by the foot of the curve at $Ni_{44}Cu_{56}$ becomes 0.72 per atom.

A Simple Theory of Resonating Covalent Bonds in Metals

The significance of unsynchronized resonance can be assessed by a simple theoretical treatment.

Let us consider a crystal containing N atoms in which each atom has ligancy L and covalence v. The average occupancy of each bond position by a bond is v/L, and the average nonoccupancy is $(L - v)/L$. There are $W = (LN/2)!/\{(L - v)N/2\}!\,(vN/2)!$ ways of distributing $vN/2$ bonds among $LN/2$ positions, with multiple occupancy excluded. The total number of ways $w = W^{1/N}$ in which bonds are arranged around each atom is found with use of Stirling's approximation $x! = (2\pi x)^{1/2}(x/e)^x$ to be

$$w = \frac{L^{L/2}}{v^{v/2}(L - v)^{(L-v)/2}}. \qquad (1)$$

The number of ways in which n bonds are arranged around an atom with average valence v in a crystal involves a binomial coefficient:

Number of structures per atom with n bonds, average valence v

$$= w\,\frac{v^n(L - v)^{(L-n)}\,L!}{L^L\,n!\,(L - n)!} \qquad (2)$$

The number of structures for synchronized resonance is given by Eq. 2 with $n = v$:

Number of structures for synchronized resonance

$$= \frac{v^{v/2}(L - v)^{(L-v)/2}\,L!}{L^{L/2}\,v!\,(L - v)!} \qquad (3)$$

For a metal crystal, with unsynchronized resonance, the electroneutrality principle (*13*) permits the number of bonds per atom to be $v - 1$, v, and $v + 1$, corresponding respectively to M^+, M^0, and M^-. With Eq. 2 we calculate the number of structures with $n = v - 1$ and $v + 1$ to differ from the number with $n = v$ by the factors $(L - v)/(L - v + 1)$ and $v/(v + 1)$, respectively. The numbers of M^+ and M^- must of course be equal. With the assumption that the electrostatic interactions give the mean probability for M^+ and M^- to each, the number of unsynchronized resonance structures is found to be given by the equation:

Number of unsynchronized resonance structures per atom

$$= \frac{v^{v/2}(L - v)^{(L-v)/2}\,L!}{L^{L/2}\,v!\,(L - v)!}\left(\frac{L - v}{L - v + 1} + 1 + \frac{v}{v + 1}\right). \qquad (4)$$

The equation for synchronized resonance with $L = 4$ and $v = 2$ gives $R \ln 3/2$ for the residual entropy of ice (*14*). This value differs by only 1.1% from that given by calculations that do not involve the approximations made in our simple treatment. It is likely that the accuracy of Eq. 4 is also reasonably high.

The Amount of Metallic Orbital

The amount of metallic orbital per atom is given by this theory as $(2v + 1)/(3v + 1)$, for $v = L/2$, with values decreasing from 0.714 for $v = 2$ to 0.684 for $v = 6$, in good agreement with the value 0.72 given by the magnetic moments.

A Comparison of Synchronized and Unsynchronized Resonance

The ratio of the number of structures per atom for unsynchronized resonance to that for synchronized resonance is given by the expression in parentheses in Eq. 4. Its value increases from 2.33 for $L = 6$, $v = 1$ to 2.78 for $L = 16$, $v = 8$, with average about 2.65. The amount of resonance stabilization for unsynchronized resonance is thus far greater than that for synchronized resonance. Accordingly we should expect that *every element with an extra orbital to serve as the metallic orbital should be a metal.*

This expectation is in fact realized, with a single apparent exception. Boron, with three valence electrons and four outer orbitals ($2s2p^3$), is not usually classed as a metal.

Boron

Boron as an element and in some of its high-boron compounds assumes crystalline arrangements in which all or most of the boron atoms are present as icosahedral clusters B_{12}. For example, the unit of structure of the tetragonal form has four B_{12} icosahedra and two other tetraligating B atoms. The ligancy of the icosahedral borons is 6, being accordingly greater than the number of orbitals, as is customary for electron-deficient substances. The average bond number is 0.506.

The calculated number of resonance structures per atom (Eq. 4) is 2.50 for synchronized resonance and 6.25 for unsynchronized resonance. The second number is so much greater than the first that there is no doubt that the structure is one involving unsynchronized resonance, with 28% B^+, 44% B^0, and 28% B^-.

We may now ask why boron does not show the properties of large electric conductivity, high malleability, and high ductility characteristic of metals. The total number of structures per B_{12} icosahedron is $6.25^{12} = 3.55 \times 10^9$ and the number involving interactions between B_{12} groups is only 32.7, smaller by the factor 10^{-8}. Moreover, the usual mechanism of unsynchronized resonance involves pivoting of a bond about one atom (Fig. 2). There are no atoms in the B_{12} groups that have neighbors such as to permit pivoting resonance to transfer a charge from one B_{12} group to another, and the electric conductivity would accordingly be very small. The reported values of the conductivity for various samples of doped and undoped boron have minima usually around 10^{-10} to 10^{-13} ohm^{-1} cm^{-1} at $T \sim 100$ K, but with indication that at lower temperatures the conductivity increases, as is characteristic of metallic conduction.

We may now ask why boron does not crystallize with ligancy 12. The answer is that the bond lengths for Li and Be are large enough that the repulsion of the K-shell electron pairs is so small as to be overcome by the extra resonance energy associated with high ligancy, whereas for B to F this repulsion is large enough to require that the ligancy be kept small, decreasing the number of K-shell contacts.

Some Conclusions about Metal Structures

Some calculated values of the number of resonance structures are given in Table I. It is seen from the values for ligancy 12 that the number of structures per bond is roughly constant from $v = 1$ to $v = 6$, and then decreases rapidly from $v = 7$ to $v = 11$. Also the number of resonant structures per bond increases rapidly from 4.17 at $L = 6$ to 34.91 at $L = 16$. It is found that the following equation holds reasonably well for $v \leq L/2$ g with L not greater than 12:

$$\text{Number of resonance structures per bond} = 0.90\,L^2,\ v \leq L/2. \quad (5)$$

The resonance energy stabilizing a metal can be taken to be proportional to the number of resonating structures per atom. (This number is less by 1 than the number of structures, in that there is no resonance energy for a single structure, but we may ignore this correction in our approximate treatment.) *Accordingly the most stable atomic arrangement, in the absence of conflicting effects, should be that in which the atoms have the maximum ligancy.* If the atoms are all equivalent this arrangement

TABLE I

NUMBER OF RESONANCE STRUCTURES FOR UNSYNCHRONIZED RESONANCE

		Number	
L	v	Per atom	Per bond
6	3	6.25	4.17
8	4	11.38	5.69
10	5	21.00	8.40
12	6	39.19	13.06
14	7	73.73	21.07
16	8	139.65	34.91
18	9	265.89	59.09
12	1	5.19	10.38
12	2	11.39	11.39
12	3	19.97	13.31
12	4	29.21	14.61
12	5	36.44	14.58
12	6	39.19	13.06
12	7	36.44	10.41
12	8	29.21	7.30
12	9	19.97	4.44
12	10	11.39	2.28
12	11	5.19	0.94

has $L = 12$, as found in cubic and hexagonal closest packing, A1 and A3. These arguments show why 80% of all metals crystallize with closest packing, $L = 12$.

About 24% of all metals crystallize in the body-centered arrangement A2 (some metals have more than one modification). In this arrangement the ligancy L may be said to lie somewhere between $L = 8$ and $L = 14$, in that each atom has 8 neighbors at one distance and 6 others at a distance 15% greater, which is short enough to count as a position for a bond, but with smaller probability than the shorter positions. I have in the past considered the effective ligancy in A2 to be about 10, but it might be as great as 12 in contributing to the resonance stabilization in a statistical treatment.

With atoms of two different sizes arrangements are known for which the smaller atoms have $L = 12$ and the larger ones have $L = 13$, 14, 15, 16, or even larger values. Our statistical analysis explains why many alloys crystallize with these arrangements, which are stabilized by the large values of the resonance energy, as given by Eq. (4). Manganese is an example of an element that crystallizes in arrangements of this sort, involving two different kinds of manganese atoms, with different valences and different sizes.

Metal Arrangements with Smaller Ligancy

From Table I we see that the amount of resonance stabilization is small if the valence v is larger than one-half the ligancy. For a metal with valence v the ligancy should accordingly be equal to or greater than $2v$. The resonance energy increases with increase in the ligancy. There is another interatomic interaction that opposes increase in the ligancy. This is the repulsion that operates between electrons that are not paired with each other (*15*). This repulsion is especially strong between two unshared electron pairs. Unshared electron pairs appear in the outer shells of electrons in the right-hand side of the periodic table, starting with the Cu, Ag, Au column.

All of the metals to the left of Cu, Ag, Au have the A1, A2, or A3 arrangement (including Cu, Ag, and Au) except Mn, mentioned above, and U, which has an unusual structure with $L = 12$. To the right, however, we have a number of metals with values of L less than 12, as predicted by these arguments.

The next elements are Zn, Cd, and Hg. Each of these metals crystallizes with an arrangement such that each atom has six neighbors at one distance and six others at a distance corresponding to bonds about half as strong. The effective ligancy might accordingly be considered to be 9, rather than 12, and the maximum stability would thus be achieved for these elements, which have metallic valence 4.56, about one-half as great, together with a minimization of the repulsion of the unshared electron pairs by keeping the number of contacts as small as possible.

The next metals are Ga, In, and Tl, with metallic valence 3.56. Maximum stability, with minimum ligancy and minimum repulsion of unshared electron pairs, would be expected for ligancy 7. Gallium has an atomic arrangement in which each atom has 7 near neighbors, as expected from the foregoing considerations. Indium has a tetragonal structure in which each atom has 4 near neighbors and 8 more distant neighbors, perhaps representing an effort to achieve ligancy 7. Tl has the A3 structure, indicating that unshared pair repulsion is less important for it than for its lighter congeners.

Of the next elements, Ge, Sn, and Pb, Sn, and Ge (at high pressure) have metallic phases with $L = 6$, as discussed above, and Pb has the Al structure.

Our consideration of Eq. 5 accordingly accounts in a general way for the atomic arrangements of most of the metals, in addition to providing a criterion for metallic character.

Interatomic Distances

In 1947 I formulated the equation

$$D(n) - D(1) = -0.60 \text{ Å} \log n \qquad (6)$$

for the relation between the difference in bond length for fractional bond number n (between 0 and 1), $D(n)$, and the bond length $D(1)$ for a single bond, taken as the sum of the single-bond metallic radii R_1 for the two atoms (*9*). With use of this equation I formulated sets of single-bond metallic radii R_1 and also of R (ligancy 12). It has become clear in recent years that the system based on Eq. 6 fails when the ligancy is much smaller or larger than 12. In intermetallic compounds with ligancy greater than 12 the bond lengths are shorter than the calculated values, and in those with low ligancy they are longer. Especially striking is the difference of about 0.07 Å between the enneacovalent radii of the transition metals in the organometallic cluster compounds (1.23 Å for cobalt, for example (*16*)), and the single-bond metallic radii (1.162 Å for cobalt (*9*)). There is some evidence that when the nature of the hybrid bond orbitals is essentially the same the value of the single-bond radius does not change. For Fe and Co the enneacovalent radii are 1.24 and 1.23 Å, and the radii for ligancy 6 are 1.23 and 1.22 Å, the same to within their uncertainty of about ±0.01 Å.

I conclude that the 1947 values of the metallic single-bond radii are in error because of the neglect of the increasing stabilizing and bond-shortening effect of resonance. The number of resonance structures over the region of interest can be taken as $0.9\,L^2$, and the energy of resonance stabilization is expected from quantum mechanical principles to be proportional to this number. The decrease in single-bond radius should be proportional to this number. The observed difference for cobalt gives the relation

$$\Delta R_1 = -L^2 \cdot 0.0005 \text{ Å} \qquad (7)$$

This correction of R_1 for ligancy, together with the bond-number equation and a set of values of the new single-bond metallic radii, provides an improved system of correlating interatomic distances not only in metals and alloys but also in other crystals and molecules.

The Metallic Valence of the Heavier Transition Metals

In 1938 I concluded (*2*) from the consideration of the values of their saturation ferromagnetic moments that the elements of the first transition sequence from Cr to Ni have the constant metallic valence 5.78, later revised (*8*) to 6. Despite their lack of ferromagnetism, I assumed (*9*) in 1947 that their heavier congeners Mo to Pd and W to

Pt also have the same metallic valence, 5.78 or 6. Then in 1977 I reconsidered this question (*17*) with consideration of the observed enneacovalence of transition metals in some of their organometallic compounds and concluded that the metallic valence could become as large as 8.3 for Ru–Rh and Os–Ir alloys. This conclusion was reached by an argument based on the observed bond lengths that I now believe to have been misleading.

Values of the reciprocal of the covalent radius for ligancy 12 are shown in Fig. 3. It is seen that the points for each sequence can be represented by three curves. The first curve for each sequence represents the effect of the increase in valence from 2 to 6 and the corresponding increase in binding energy for Ca to Cr, Sr to Mo, and Ba to W. Each of these curves is extrapolated to a maximum at $v = 8.3$, corresponding to nine *spd* orbitals with 0.7 metallic electron. It is seen that for all three sequences the values deviate from the extrapolated curves. From Cr to Ni they are represented by a straight line, interpreted as corresponding to the constant value 6 for the metallic valence.

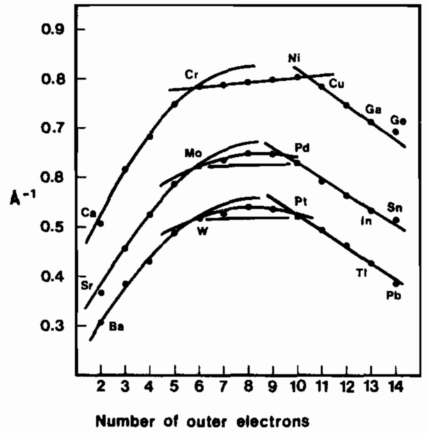


FIG. 3. Curves showing values of the reciprocal of the metallic radius for ligancy 12 of metals of the sequences Ca to Ge, Sr to Sn, and Ba to Pb. The vertical scale has been shifted down for the second and third sequences by 0.1 and 0.2, respectively.

For the other two sequences, however, the curves indicate a continued increase in the valence, although not so great as indicated by the extrapolated curves.

The Valence of Pd and Pt

Information about the structure of Pd and Pt is provided by the paramagnetic susceptibility of the metals, interpreted by the Weiss equation

$$\chi = \frac{C}{T - \Theta} \tag{8}$$

with

$$C = \frac{N\mu^2}{kT}. \tag{9}$$

In Fig. 4 there are shown the lines representing χ^{-1} as a function of T for Ni, Pd, and Pt. It is seen that the slopes, which give the values of C^{-1}, are essentially the same, and that accordingly Pd and Pt have the same number of unpaired electrons as Ni. We accordingly conclude that they have the same valence, 6.

The Curie temperature Θ has the value 680 K for Ni, corresponding to the Zener interaction that tends to keep the electron spins parallel and that below this temperature gives rise to ferromagnetism. For Pd and Pt the values of Θ are negative (−100 K, −650 K). These negative values correspond to a dominating interaction that tends to keep the electron spins antiparallel, and which we may describe as the formation of a weak shared-electron-pair bond. We might accordingly conclude that Pd and Pt have metallic valence slightly greater than 6.

Application of the Theory of Unsynchronized Resonance

We may apply the statistical theory to determine the number of outer electrons involved in bond formation by determining

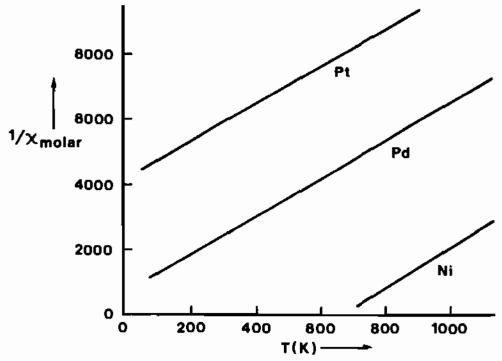


FIG. 4. Curves showing the reciprocal of the molar paramagnetic susceptibility of Ni, Pd, and Pt as a function of the temperature.

the derivative with respect to v of the number of resonating structures per atom (presumably proportional to the stabilizing resonance energy). Values of the increase in the number of resonating structures per atom with $L = 12$ as v increases by unit steps from 0 to 9, obtained by subtracting successive numbers in the third column of Table I, are shown in Fig. 5. It is seen that the value 0 comes at $v = 6.5$, which may be considered the maximum expected metallic valence for ligancy 12.

Here I have ignored the energy of the bond itself and of other contributions to the energy of cohesion of the metal. Some justification for this neglect is provided by some rough calculations (*8*) indicating that for the alkali metals the nonresonating bond energy contributes only about one-third and the resonance energy two-thirds of the cohesion energy.

The Metallic Valences of Tc, Ru, Rh, Re, Os, and Ir

From Fig. 5 we might predict that the values of v for the metals Tc, Ru, Rh, Re, Os, and Ir would be close to 6.5. From Fig. 3 we make the estimates $v = 6.5$ for Tc and Re, 7.0 for Ru and Os, and 6.6 for Rh and Ir. Consideration of the values of the paramagnetic Curie constant in comparison with those for the elements M~~u~~n to Co might permit the determination of more precise values.

The Metallic Orbital and the Band Theory of Metals

It was pointed out in my 1949 paper (*8*) that resonance of electron-pair bonds among the bond positions gives energy bands similar to those obtained in the usual band theory by formation of Bloch functions of the atomic orbitals. There is no incompatibility between the two descriptions, which may be described as complementary. It is accordingly to be expected that the 0.72 metallic orbital per atom would make itself clearly visible in the band-theory calculations for the metals from Co to Ge, Rh to Sn, and Pt to Pb; for example, the decrease in the number of bonding electrons from 4 for gray tin to 2.56 for white tin should result from these calculations. So far as I know, however, no such interpretation of the band-theory calculations has been reported.

Conclusion

Since 1938 there has been recognition of

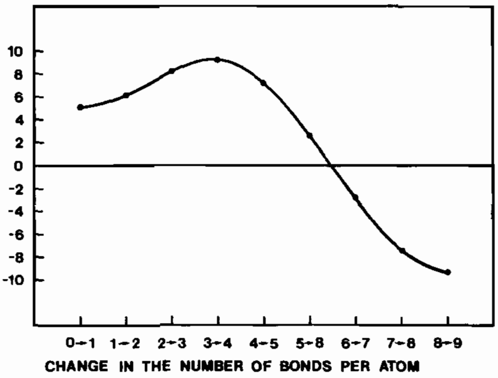


FIG. 5. Increase in the number of resonance structures per atom with unit increase in the average number of bonds formed by an atom; ligancy 12.

the existence of the metallic orbital and of its significance in conferring metallic properties on a substance. The amount of metallic orbital per atom, about 0.72, given by the values of the saturation ferromagnetic moments of the alloys from Fe to Cu agrees well with values from 0.684 to 0.714, average 0.70, given by the statistical theory of unsynchronized resonance of bonds. Also, for the elements Mo to Pd and W to Pt the values of R_{12}^{-1} (Fig. 3) indicate a maximum at 8.3 outer electrons, 0.7 less than the possible number 9 of *spd* orbitals.

The value 0.72 for the number of metallic orbitals per atom corresponds to the distribution 28% M^+, 44% M^0, and 28% M^-, with the electric charges moving from atom to atom with electronic frequencies, as determined by the magnitude of the resonance energy. This distribution is given in a straightforward way by the statistical theory, together with the electroneutrality principle. The statistical theory, described in earlier sections of this paper, provides strong support for the resonating-covalent-bond theory of metals that has been developed over the last 45 years on a largely empirical basis.

Acknowledgments

I thank Dr. Zelek Herman, Mrs. Dorothy Munro, and Mrs. Ruth Reynolds for their help in the preparation of this paper.

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Chemistry

Extension of the statistical theory of resonating valence bonds to hyperelectronic metals

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Contributed by Linus Pauling, August 8, 1985

ABSTRACT **The statistical treatment of resonating covalent bonds in metals, previously applied to hypoelectronic metals, is extended to hyperelectronic metals and to metals with two kinds of bonds. The theory leads to half-integral values of the valence for hyperelectronic metallic elements.**

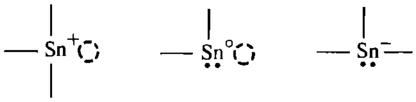
A theory of resonating covalent bonds in metals, developed over the period 1938–1953 (1–3), was recently refined by the formulation of a statistical treatment for hypoelectronic metals (4). We have now extended the statistical treatment to include hyperelectronic metals. This extension has resulted not only in the evaluation of the number of resonance structures for these metals but also in the determination for them of the values of the metallic valence, which have been somewhat uncertain.

In the discussion of hypoelectronic metals in ref. 4, the number of ways of distributing $Nv/2$ bonds among $NL/2$ positions in a crystal containing N atoms with valence v and ligancy L was evaluated. The number per atom is the Nth root of this quantity. Structures for which the number of bonds on any atom is other than $v - 1$, v, or $v + 1$ were then eliminated with use of the binomial distribution function [only the charge states M^+, M^0, and M^- are allowed by the electroneutrality principle (5)]. In this way the following expression for ν_{hypo}, the number of resonance structures per atom for a hypoelectronic metal, was obtained:

$$\nu_{\text{hypo}} = \frac{v^{v/2}(L-v)^{(L-v)/2}L!}{L^{L/2}v!\,(L-v)!} \left(\frac{L-v}{L-v+1} + 1 + \frac{v}{v+1}\right). \quad [1]$$

HYPERELECTRONIC METALS

A requirement for metallic character is that unsynchronized resonance of covalent bonds occur, which means that M^+ and M^0 have an unoccupied orbital available to accept an additional bond, changing them to M^0 and M^-, respectively. M^- does not need the extra orbital, because it cannot change to M^{2-}. A hyperelectronic metal is one in which the number of outer electrons is greater than the number of outer orbitals, not including the metallic orbital. An example is metallic tin, with 14 outer electrons and 9 outer orbitals (6*s*, three 6*p*, five 5*d*). Sn^+ and Sn^0 have five unshared electron pairs, and Sn^- has six. Sn^+ and Sn^- form three covalent bonds, and Sn^0 forms two. Sn^+ and Sn^0 have a metallic orbital, and Sn^- does not. They may be represented as



Here the broken circle represents the metallic orbital.

It is evident that the calculation of the number of resonating structures must be made in a different way from that for hypoelectronic metals, because M^+ and M^- form the same number of bonds and are therefore classed together in the calculation of the number of ways of distributing the bonds. We consider first the valence v of a hyperelectronic metal whose neutral atoms form z bonds and whose ions M^+ and M^- form $z + 1$ bonds. For any atom, with average valence v, the number of structures, b, having n bonds, is, by the assumption used previously (4), proportional to the probability given by the binomial distribution:

$$b(L, v, n) = w' \frac{v^n(L-v)^{(L-n)}L!}{L^L n!\,(L-n)!}. \quad [2]$$

Here w', the proportionality constant, is the total number of structures per atom without constraint as to the number of bonds (in the range 0 to L).

To evaluate the valence, we represent the fractions of M^+, M^0, and M^- by y, x, and y, respectively. The ratio of the number of neutral atoms (M^0) to ions (M^+ and M^-) is then

$$\frac{x}{2y} = \frac{b(L, v, z)}{b(L, v, z+1)} = \frac{(L-v)(z+1)}{v(L-z)}. \quad [3]$$

In addition, we have the following constraints:

$$x + 2y = 1 \quad [4]$$

$$v = xz + 2y(z+1). \quad [5]$$

Eqs. **3**, **4**, and **5** have one solution in the range $z \leq v \leq z + 1$:

$$v = z + \{f(f+1)\}^{1/2} - f, \quad [6]$$

in which

$$f = \frac{z(L-z)}{L-2z-1}. \quad [7]$$

Valence of Hyperelectronic Metals. Cu, Ag, and Au have $z = 5$ and $L = 12$. Eqs. **6** and **7** lead to $v = 5.4965$ for these metals. Each atom of Zn, Cd, and Hg forms six short bonds and six long (presumably weaker) bonds. The effective ligancy is between 6 and 12, which with $z = 4$ gives the range $v = 4.5585$–4.4888. For Sn, with $z = 2$ and four short bonds and two long bonds, L between 4 and 6, the range of values of v is 2.5359–2.4949. For all of the hyperelectronic metals, v equals $z + 1/2$ when the ligancy becomes $2z + 1$, corresponding to half bonds.

Because of the approximation of all of these values to $z + 1/2$, it is, we suggest, justified to assume the half-integral values of the valence of hyperelectronic metals, as was done in 1949 on an empirical basis (2).

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The Number of Resonance Structures. In calculating the number of resonance structures per atom, ν_{hyper} for hyperelectronic metals with $v = z + 1/2$, we use the same statistical method as for hypoelectronic metals except that the factor $2^{1/2}$ is introduced to correct for the fact that there are two kinds of atoms forming $z + 1$ bonds, M^+ and M^-, which differ in that M^- has an unshared electron pair and M^+ does not have one. The equation for ν_{hyper} is

$$\nu_{\text{hyper}} = \frac{2^{1/2}\, L!\, v^{(v-1)/2}(L - v)^{(L-v+1)/2}}{L^{L/2}(v - \tfrac{1}{2})!\,(L - v + \tfrac{1}{2})!} \left(1 + \frac{v(L - v + \tfrac{1}{2})}{(v + \tfrac{1}{2})(L - v)}\right). \quad \textbf{[8]}$$

This equation is the hyperelectronic analog of Eq. **1**.

Values of ν_{hyper} are usually a little larger than those of ν_{hypo}; for example, they are 33.45 and 33.26, respectively, for $L = 12$, $v = 4.5$.

Structures with Two Different Bond Lengths. Eq. **8** and the corresponding equation for hypoelectronic metals apply to crystals in which the bonds all have the same length. For a crystal in which each atom forms two kinds of bonds, L_1 bonds with bond number $n_1 = v_1/L_1$ and L_2 bonds with bond number $n_2 = v_2/L_2$, the value of ν_{hypo} is

$$\nu_{\text{hypo}} = C \sum_{n=v-1}^{v+1} \sum_{i=\min(0,n-L_2)}^{\max(n,L_1)} \frac{v_1^i (L_1 - i)^{L_1-i}}{i!(L_1 - i)!} \frac{v_2^{n-i}(L_2 - v_2)^{L_2-n+i}}{(n - i)!\,(L_2 - n + i)!} \quad \textbf{[9a]}$$

with

$$C = L_1!\, L_2!\, [L_1^{L_1} v_1^{v_1}(L_1 - v_1)^{L_1-v_1} L_2^{L_2} v_2^{v_2}(L_2 - v_2)^{L_2-v_2}]^{-1/2}. \quad \textbf{[9b]}$$

For a hyperelectronic metal with two different bond lengths the equation is the same as Eq. **9** except that the sum over n is for only $n = v - 1/2$ and $n = v + 1/2$ and there is an extra factor $2^{1/2}$ in the expression for C.

When $v_1/L_1 = v_2/L_2 = v/L$ Eq. **9a** reduces to Eq. **1** and the hyperelectronic counterpart of Eq. **9a** reduces to Eq. **8**.

The amount of resonance energy for a metal or intermetallic compound is determined by the number of resonance structures. The resonance energy affects the covalent radius, the stability (as evidenced by the resistance of the noble metals to chemical attack), and other properties, in ways that we hope to discuss later.

We thank the Japan Shipbuilding Industry Foundation (Tokyo) for partial support of this research.

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Chapter 4

HYDROGEN BONDING

Contents

Reprinted from *The Nature of the Chemical Bond and the Structure of Molecules and Crystals, 3rd edn.*, by Linus Pauling, Cornell University Press, Ithaca, NY, Section 12–1, pp. 449–454 (1960).

CHAPTER 12

The Hydrogen Bond

12-1. THE NATURE OF THE HYDROGEN BOND

IT was recognized some decades ago that under certain conditions an atom of hydrogen is attracted by rather strong forces to two atoms, instead of only one, so that it may be considered to be acting as a bond between them. This is called the *hydrogen bond.*[1] The bond was for some time thought to result from the formation of two covalent bonds by the hydrogen atom, the hydrogen fluoride ion $[HF_2]^-$ being assigned the structure $[:\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}:H:\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}:]^-$. It is now recognized that the hydrogen atom, with only one stable orbital (the 1*s* orbital), can form only one covalent bond, that the hydrogen bond is largely ionic in character, and that it is formed only between the most electronegative atoms. A detailed discussion of its nature is given in the following sections.

Although the hydrogen bond is not a strong bond (its bond energy, that is, the energy of the reaction $XH + Y \rightarrow XHY$, lying in most cases in the range 2 to 10 kcal/mole), it has great significance in determining the properties of substances. Because of its small bond energy and the small activation energy involved in its formation and rupture, the hydrogen bond is especially suited to play a part in reactions oc-

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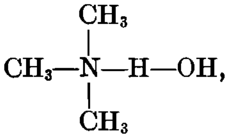
[1] Other names, such as hydrogen bridge, have also been used.

A detailed discussion of the hydrogen bond is given in the book by G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond,* W. H. Freeman Co., San Francisco, 1959. Many excellent review articles have been published; among them are E. N. Lassettre, *Chem. Revs.* **20,** 259 (1937); H. Hoyer, *Z. Elektrochem.* **49,** 97 (1943); J. Donohue, *J. Phys. Chem.* **56,** 502 (1952); A. R. Ubbelohde and K. J. Gallagher, *Acta Cryst.* **8,** 71 (1955); G. M. Badger, *Rev. Pure and App. Chem.* (*Australia*) **7,** 55 (1957); C. A. Coulson, *Research* (London) **10,** 149 (1957); M. Magat, *Nuovo cimento* **10,** 416 (1953); D. Sokolov, *Tagungsber. der chem. Ges. Deutsch. Dem. Rep.* **1955,** 10.

curring at normal temperatures. It has been recognized that hydrogen bonds restrain protein molecules to their native configurations, and I believe that as the methods of structural chemistry are further applied to physiological problems it will be found that the significance of the hydrogen bond for physiology is greater than that of any other single structural feature.

The first mention of the hydrogen bond was made by Moore and Winmill,[2] who assigned to trimethylammonium hydroxide the structure



$$\begin{array}{c} CH_3 \\ | \\ CH_3\text{—}N\text{—}H\text{—}OH, \\ | \\ CH_3 \end{array}$$

accounting in this way for the weakness of this substance as a base as compared with tetramethylammonium hydroxide. Recognition of the importance of the hydrogen bond and of its extensive occurrence was made by Latimer and Rodebush,[3] who used this concept in the discussion of highly associated liquids, such as water and hydrogen fluoride, with their abnormally high dielectric constant values, of the small ionization of ammonium hydroxide, and of the formation of double molecules by acetic acid. The number of molecules recognized as containing hydrogen bonds has been greatly increased by spectroscopic and crystal-structure studies and by analysis of physicochemical information.[4]

With the development of the quantum-mechanical theory of valence it was recognized[5] that a hydrogen atom, with only one stable orbital, cannot form more than one pure covalent bond[6] and that the attraction

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[2] T. S. Moore and T. F. Winmill, *J. Chem. Soc.* **101,** 1635 (1912); see also P. Pfeiffer, *Ann. Chem.* **398,** 137 (1913).

[3] W. M. Latimer and W. H. Rodebush, *J.A.C.S.* **42,** 1419 (1920). G. N. Lewis (*Valence and the Structure of Atoms and Molecules*, Chemical Catalog Co., New York, 1923, p. 109) mentions that the idea was used by Huggins in an unpublished work; see also M. L. Huggins, *Phys. Rev.* **18,** 333 (1921); **19,** 346 (1922).

[4] This method was applied mainly by N. V. Sidgwick (*The Electronic Theory of Valency*, Clarendon Press, Oxford, 1927), who used it in the discussion of compounds such as the enolized β-diketones; see also Lassettre, *loc. cit.* (1).

[5] L. Pauling, *Proc. Nat. Acad. Sci. U.S.* **14,** 359 (1928).

[6] The bond-forming power of the outer orbitals of the hydrogen atom is negligibly small. It has been suggested by several authors that use may be made of an *L* orbital of hydrogen for formation of a second covalent bond. However, in case that a bond A—H with small ionic character is formed the proton is shielded almost completely by its half of the shared electron pair, and it has accordingly no power to attract an *L* electron. Only if the A—H bond were largely ionic would there occur appreciable attraction for an *L* electron, and under this circumstance the proton could use its 1*s* orbital for covalent bond for-

of two atoms observed in hydrogen-bond formation must be due largely to ionic forces. This conception of the hydrogen bond leads at once to the explanation of its important properties.

First, the hydrogen bond is a bond by hydrogen between *two* atoms; the coordination number of hydrogen does not exceed two.[7] The positive hydrogen ion is a bare proton, with no electron shell about it. This vanishingly small cation would attract one anion (which we idealize here as a rigid sphere of finite radius—see Chap. 13) to the equilibrium internuclear distance equal to the anion radius, and could then similarly attract a second anion, as shown in Figure 12-1, to form a stable complex. A third anion, however, would be stopped by anion-anion contacts, which prevent its close approach to the proton. From the ionic point of view the coordination number of hydrogen is thus restricted to the value two, as is observed in general.[8]

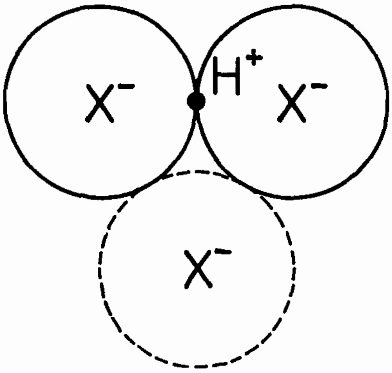

Fig. 12-1.

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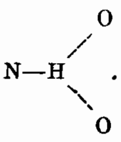
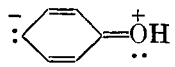
mation with the atom B of the group A—H—B (during the ionic phases of the A—H bond), and so would not need to call on the unstable *L* orbital.

[7] In some circumstances a hydrogen atom with some residual positive charge, as in the ammonium ion, is attracted by the resultant electric field of two or more negative ions. The corresponding weak interactions, although similar in nature to those involved in hydrogen-bond formation, are not conveniently included in this category.

[8] It was shown by G. A. Albrecht and R. B. Corey, *J.A.C.S.* **61**, 1087 (1939), that the crystal structure of glycine is such as to indicate strongly that one of the hydrogen atoms of the $—NH_3^+$ group is attracted about equally by two oxygen atoms, forming a bifurcated hydrogen bond  $N—H\begin{smallmatrix}\diagup O\\ \diagdown O\end{smallmatrix}$. The structure has been refined by R. E. Marsh, *Acta Cryst.* **10**, 814 (1957), and the position of

Second, only the most electronegative atoms should form hydrogen bonds, and the strength of the bond should increase with increase in the electronegativity of the two bonded atoms. Referring to the electronegativity scale, we might expect that fluorine, oxygen, nitrogen, and chlorine would possess this ability, to an extent decreasing in this order. It is found empirically that fluorine forms very strong hydrogen bonds, oxygen weaker ones, and nitrogen still weaker ones. Although it has the same electronegativity as nitrogen, chlorine has only a very small hydrogen-bond-forming power; this may be attributed to its large size (relative to nitrogen), which causes its electrostatic interactions to be weaker than those of nitrogen.

Increasing the electronegativity of an atom increases its power of forming hydrogen bonds. The ammonium ion and its derivatives, such as $[RNH_3]^+$, form stronger hydrogen bonds than ammonia or normal amines. The phenols form stronger hydrogen bonds than aliphatic alcohols because of the increase in electronegativity of the oxygen atom resulting from resonance with structures such as



In almost all hydrogen bonds the hydrogen atom is nearer to one of the two adjacent electronegative atoms than to the other. In ice, for example, the distance between two hydrogen-bonded oxygen atoms is 2.76 Å, and the proton has been shown by neutron diffraction to be 1.00 Å from one oxygen atom and 1.76 Å from the other (Sec. 12-4). Also in diaspore, $AlHO_2$, the oxygen-oxygen distance is 2.650 Å and the oxygen-hydrogen distances, determined by neutron diffraction, are 1.005 Å and 1.68 Å (Sec. 12-7).

The amount of partial ionic character expected for the O—H bond from the electronegativity difference of the atoms is 39 percent. Hence the 1*s* orbital of the hydrogen atom is liberated from use in covalent-bond formation with the adjacent oxygen atom to the extent of 39 percent, and hence available for formation of a fractional covalent bond with the more distant oxygen atom of the hydrogen-bonded group O—H···O; the hydrogen bond in ice can be described as involving resonance among the three structures *A*, *B*, and *C*:

A O—H :O
B O: H^+ :O
C O: H——O

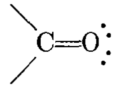
---

the proton has been verified by neutron diffraction by J. H. Burns and H. A. Levy, *Am. Cryst. Ass'n Meeting* June (1958). The bifurcated hydrogen bond seems to be present also in crystals of iodic acid, HIO_3 (M. T. Rogers and L. Helmholz, *J.A.C.S.* **63,** 278 [1941]), and in nitramide, NH_2NO_2 (C. A. Beevers and A. S. Trotman-Dickenson, *Acta Cryst.* **10,** 34 [1957]).

(Here the dashes represent pure covalent bonds.) A rough idea of the amount of covalent bonding to the more distant oxygen atom can be obtained by use of the equation relating interatomic distance to bond number for fractional bonds, Equation 7-7. The long H···O distance in ice is 0.80 Å greater than the single-bond distance, corresponding to bond number 0.05. Hence we conclude that for the hydrogen bonds in ice the three structures *A*, *B*, and *C* contribute about 61 percent, 34 percent, and 5 percent, respectively.[9] The contribution of structure *C* for diaspore is similarly calculated from the distance 1.68 Å to be 6 percent. The shortest reported O—H···O bonds have oxygen-oxygen distance 2.40 Å (Sec. 12-7). This is only 0.06 Å greater than the distance expected for two half-bonds, 2.34 Å, and it is likely that symmetrical hydrogen bonds between oxygen atoms are present in a few substances.

In general the A—H···B hydrogen bond can be taken to be approximately linear; for example, in diaspore the angle between the internuclear lines A—H and A- - -B has been found by neutron diffraction (Sec. 12-7) to be 12.1°. An estimate of the strain energy for deviation of the O—H···O bonds with oxygen-oxygen distance 2.76 Å (as in ice) has been made;[10] it is that the strain energy of bending the hydrogen bond is $0.003\delta^2$ kcal/mole, where δ is the deviation, in degrees, from a straight angle of the O—H and H···O bonds at the hydrogen atom.

The strain energy of extending or compressing the O—H···O bond with length 2.76 Å (as in ice) has been calculated from the compressibility of ice to be $12\,(D - D_0)^2$ kcal/mole, in which $D - D_0$ is the change in length of the bond in Å (Sec. 12-9).

In all molecules and crystals containing hydrogen bonds A—H···B the angles between the bond A—H and other bonds formed by atom A correspond to the principles discussed in Chapter 3; for example, in alcohols (Sec. 12-5) the angle R—O—H··· is close to 105°. Also, in general the angles between the weak H···B bond and the other bonds formed by atom B are those that would be predicted for a covalent H—B bond. There are some exceptions to this rule, however; an example is urea, in which two of the O···H—N bonds formed by the oxygen atom are in the plane of the molecule, as expected for the structure , and the other two are out of the plane. These hydrogen bonds are very weak; the observed O···H—N distance 3.03 Å corresponds (Equation 7-7) to only 1.7 percent contribution of the covalent long-bond structure *C*.

In general a hydrogen bond A—H···B can be considered to involve

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[9] L. Pauling, *J. chim. phys.* **46**, 435 (1949).

[10] L. Pauling and R. B. Corey, *Fortschr. Chem. org. Naturstoffe* **11**, 180 (1954).

an electron pair of atom B. An exception is urea, in which the oxygen atom, with two electron pairs available, forms four hydrogen bonds. Another exception is ammonia; one unshared electron pair of the nitrogen atom is involved in the formation of three hydrogen bonds. It will be seen in the following section that these three N—H···N hydrogen bonds affect the physical properties of the substance to about the same extent that those of hydrogen fluoride are affected by one F—H···F bond.

12-2. THE EFFECT OF THE HYDROGEN BOND ON THE PHYSICAL PROPERTIES OF SUBSTANCES

It is the hydrogen bond that determines in the main the magnitude and nature of the mutual interactions of water molecules and that is consequently responsible for the striking physical properties of this uniquely important substance. In this section we shall discuss the melting point, boiling point, and dielectric constant of water and related substances; other properties of water are treated later (Sec. 12-4).

For the sequence of related substances H_2Te, H_2Se, and H_2S the melting points and boiling points show the decreasing courses expected in view of the decreasing molecular weights and van der Waals forces[11] (Fig. 12-2). The continuation of the sequence in the way indicated by the values for the noble gases would lead to the expectation of values of about −100°C and −80°C, respectively, for the melting point and boiling point of water. The observed values of these quantities are very much higher; this is the result of the formation of hydrogen bonds, which have the extraordinary effect of doubling the boiling point of the substance on the Kelvin scale.

The melting points and boiling points of ammonia and hydrogen fluoride are also considerably higher than the values extrapolated from the sequences of analogous compounds, the effects being, however, somewhat smaller than for water. This decrease for ammonia is due in part to the smaller electronegativity of nitrogen than of oxygen and in part to the presence in the ammonia molecule of only one unshared electron pair, which must serve as the source of attraction for the protons involved in all the hydrogen bonds formed with the N—H groups of other molecules. Hydrogen fluoride can form only one-half as many hydrogen bonds as water, and, although its F—H···F bonds are stronger than the O—H···O bonds in water and ice, the resultant effects are smaller for this substance than for water.

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[11] The van der Waals forces for these substances are due mainly to dispersion forces, which decrease with decrease in atomic number for atoms of similar structure. London's calculations (F. London, *Z. Physik* **63**, 245 (1930) have shown the interaction of permanent dipoles to contribute only a small amount to the van der Waals forces for a substance such as hydrogen chloride.

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The Crystal Structure of Ammonium Hydrogen Fluoride, NH_4HF

By

Linus Pauling

With 6 figures

1933
AKADEMISCHE VERLAGSGESELLSCHAFT M. B. H.
LEIPZIG

Z. Krist. (A)

380

The Crystal Structure of Ammonium Hydrogen Fluoride, NH_4HF_2.

By

Linus Pauling in Pasadena.

(With 6 figures.)

Hassel and Luzanski[1]) have recently published extensive data obtained from rotation and Röntgen-goniometric photographs of the orthorhombic crystal NH_4HF_2, with the statement that they had not been successful in determining the atomic arrangement from these data, and would not have the opportunity to continue the investigation in the near future. Making use of the concept of the hydrogen bond, I have formulated a structure which accounts satisfactorily for their observed intensities of X-ray reflections and which explains the properties of the crystal, in particular the lack of isomorphism with potassium hydrogen fluoride.

Hassel and Luzanski obtained quadratic tabular crystals on evaporation of an aqueous solution containing excess hydrogen fluoride. Laue photographs with the incident beam normal to the basal plane showed rhombic symmetry, with, however, appreciable approximation to ditetragonal symmetry. The unit of structure has the dimensions

$$a = 8.33\ \text{Å}$$
$$b = 8.14\ \text{Å}$$
$$c = 3.68\ \text{Å},$$

containing four NH_4HF_2, and the space group was reported to be V_h^{13}. The authors tabulate visual estimates of intensities from five Röntgen-goniometric photographs.

A Discussion of the Hydrogen Bond and the Formulation of the Structure.

About ten years ago it was pointed out independently by Huggins[2]) and by Latimer and Rodebush[3]) in Berkeley that a number of phe-

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1) O. Hassel and N. Luzanski, Z. Krist. **83**, 448. 1932.

2) M. L. Huggins, quoted by G. N. Lewis, "Valence", 1923.

3) W. M. Latimer and W. H. Rodebush, J. Am. chem. Soc. **42**, 1419. 1920.

nomena, such as, for example, the polymerization of water, hydrogen fluoride, etc., are explained by the assumption that a hydrogen atom can sometimes form a bond with each of two atoms, and hold them together. It was assumed at first that these bonds were Lewis shared-electron-pair bonds, the structure of the acid fluoride ion HF_2' being represented as $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}:H:\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}:'$. In 1928 it was discovered[1]) that according to the quantum mechanics hydrogen is incapable of forming two covalent bonds. However, in a compound having ionic character, with the hydrogen atom ionized to a bare proton, the proton can attract more than one negative ion to it; since the radius of the proton is negligibly small, not more than two negative ions of appreciable size can simultaneously come into contact with the proton, whose coordination number is consequently limited to the value two. This recognition of the ionic character of the hydrogen bond has thrown much light on it, accounting for its most striking properties. Thus only the most electronegative atoms would be expected to form hydrogen bonds, in agreement with observation. The two most electronegative atoms[2]), fluorine and oxygen, form hydrogen bonds with ease, as in $(HF)_x$, $(H_2O)_x$, HF_2', HO_2''' (in diaspore, $AlHO_2$; staurolite, $H_2FeAl_4Si_2O_2$; etc.), $(HCOOH)_2$, etc. Nitrogen shows a smaller though still noticeable tendency to form hydrogen bonds, in NH_3, the amines, acid amides, etc. The stability of the wurtzite-type structure for NH_4F is due to the existence of hydrogen bonds between nitrogen and each of the four fluorine ions surrounding it tetrahedrally, as verified by the energy calculations of Sherman[3]).

In predicting a structure for NH_4HF_2 we make the following assumptions:

1. We expect linear HF_2' groups as in $NaHF_2$ and KHF_2, with the $H—F$ distance equal to 1.2 ± 0.1 Å.

2. We further expect hydrogen bonds between nitrogen and four surrounding fluorine ions. The fluorine ions should be approximately tetrahedrally arranged about the nitrogen ion, at a distance of about 2.63 Å, as in NH_4F.

3. The structure should be related to that of the tetragonal crystal KHF_2. For the Laue photograph on (001) of NH_4HF_2 is described as showing approximate ditetragonal symmetry, and the dimensions of the unit of structure of KHF_2, $2a = 8.60$ Å and $c/2 = 3.53$ Å, bear a simple approximate relation to those for NH_4HF_2.

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[1]) L. Pauling, Pr. Nat. Acad. Washington **14**, 359. 1928.

[2]) L. Pauling, J. Am. chem. Soc. **54**, 3570. 1932.

[3]) J. Sherman, Chem. Rev. **11**, 93. 1932.

On examining the KHF_2 structure we observe that each potassium ion is surrounded by eight fluorine ions at the corners of a twisted cube, no four of them forming an approximately regular tetrahedron. If, however, we make each (001) layer of HF_2' ions like the one above (so that the unit of structure has $c = 3.53$ Å rather than 7.06 Å), the

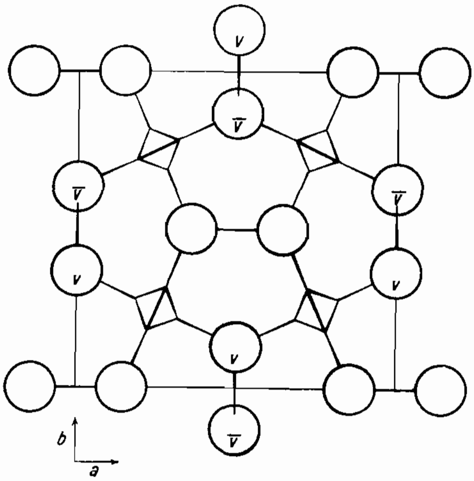

Fig. 1. The structure of NH_4HF_2. Circles represent F, tetrahedra N.

eight fluorine ions lie at the corners of a right square prism; and on replacing the potassium ions by ammonium groups and bringing four of the fluorine ions closer to the nitrogen than the other four, we obtain a structure of the postulated type. This distortion may be made in either of two ways, one of which, however, retains tetragonal symmetry[1]. The other structure, which is the structure of NH_4HF_2, is shown in Fig. 1.

It is seen for this structure that (100) is a reflection plane, (010) a glide plane with translation $a/2$, and (001) a glide plane with translation $a/2 + b/2$. The space group is accordingly V_h^7—*Pman.* The absent reflections required by V_h^7 are $(h0l)$, h odd, and $(hk0)$, $h+k$ odd. Hassel and Luzanski report no reflections of the second class. However, they list (102) in Table V as s.s.schw. This reflection, if real, eliminates this space group and the suggested structure; I believe, however, in view of the reasonableness of the structure and the simple and direct way in which it has been derived, as well as of the fact that although thirty reflections of the type $(h0l)$, h even, were observed, only one apparently

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[1] The tetragonal form of NH_4HF_2 reported by Des Cloizeaux, if it exists, may well have this structure.

very very weak reflection ($h0l$), h odd, is recorded, that this reflection does not exist (the spot on the film being possibly a $CuK\beta$ reflection from some other plane, or having some similar origin). The space group V_h^{13} suggested by Hassel and Luzanski requires only the absences ($hk0$), $h+k$ odd.

The structure is given by the following atomic coordinates (interchanging Wyckoff's b and c axes):

$4\,N$ in $4\,g$: $\frac{1}{4}\,\frac{1}{4}\,z,\ \frac{3}{4}\,\frac{1}{4}\,z,\ \frac{1}{4}\,\frac{3}{4}\,\bar{z},\ \frac{3}{4}\,\frac{3}{4}\,\bar{z};$
$4\,F_1$ in $4\,e$: $w\,0\,0,\ \bar{w}\,0\,0,\ \frac{1}{2}+w\,\frac{1}{2}\,0,\ \frac{1}{2}-w\,\frac{1}{2}\,0;$
$4\,F_2$ in $4\,h$: $\frac{1}{2}\,u\,v,\ \frac{1}{2}\,\bar{u}\,\bar{v},\ 0\,\frac{1}{2}-u\,v,\ 0\,\frac{1}{2}+u\,\bar{v};$

with the approximate parameter values u, $w = 0.13 - 0.14$; $v = 0.14$; $z = 0.57$.

The Evaluation of the Parameters from Intensity Data.

The roughly estimated intensity values for $CuK\alpha$ reflections reported by Hassel and Luzanski are sufficient to permit the evaluation of w and u with a probable error of about ± 0.005 and of v and z to about ± 0.010.

In calculating intensities I have used the formula

$$I = \text{Constant} \cdot \frac{1+\cos^2 2\vartheta}{2\sin 2\vartheta} \cdot F^2,$$

the structure factor F for the four classes of planes having the values

I $F = 4\,f_F \sin 2\pi k u \sin 2\pi l v$ for h odd, k even;

II $F = 4\,f_{NH_4} \cos 2\pi\left(\frac{h+k}{4} + lz\right) - 4\,f_F \sin 2\pi k u \sin 2\pi l v$ for h even, k odd;

III $F = 4\,f_F(\cos 2\pi h w - \cos 2\pi k u \cos 2\pi l v)$ for h odd, k odd;

IV $F = 4\,f_{NH_4} \cos 2\pi\left(\frac{h+k}{4} + lz\right) + 4\,f_F\,(\cos 2\pi h w + \cos 2\pi k u \cos 2\pi l v)$ for h even, k even.

The f-values used for fluorine are those given by Pauling and Sherman[1]) for F'; for nitrogen in ammonium the values given in Table I, obtained by adding to Pauling and Sherman's values for N the difference between O'' and O (to correct roughly for the extra electrons provided by the hydrogen atoms), were used. No temperature factor was introduced; in consequence the calculated intensities for planes with large $\frac{\sin\vartheta}{\lambda}$

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[1]) L. Pauling and J. Sherman, Z. Krist. 81, 1. 1932.

values are somewhat too large. This was taken into account in making intensity comparisons in determining the parameters.

Table I.

f_0-values for ammonium nitrogen.

$\frac{\sin\vartheta}{\lambda}$	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4
f_0	8.11	6.01	3.96	2.65	1.99	1.68	1.55	1.50	1.43	1.36	1.27	1.17	1.09	0.99

The f_0-values of Table I are in rough agreement with the f-values obtained experimentally from NH_4Cl by Wyckoff and Armstrong[1]), which, however, fall off more rapidly with increasing $\frac{\sin\vartheta}{\lambda}$ because of the temperature factor.

The intensities of reflections ($h00$) depend only on the parameter w, and of ($0k0$) on u, so that these parameters can be easily evaluated separately. In Table VI of Hassel and Luzanski the observed intensities are reported to be:

Table II.

$h, k =$	2	4	6	8	10
$h00$	—	st.	m.	st.	s.schw.
$0k0$	s.schw.	st.	m. —	st.	—

From Fig. 2 it is seen that (800) = (400) and (080) = (040) require w and u to lie near 0.125. The observations (200) absent and (020) s.schw. indicate values near 0.135 for w and u; while (600) > (060) and (10.0.0) > (0.10.0) require w to be appreciably greater than u. A lower limit of 0.128 is set for u by the inequality (060) > (020), and an upper limit of 0.147 for w by (10.0.0) > (200). The parameters can accordingly be given the values $w = 0.142 \pm 0.005$ and $u = 0.132 \pm 0.005$ with considerable confidence.

The value of v is verified by the observed intensities from Table V for planes (hkl) with h odd and k even:

121 st.+	141 s.s.schw.	161 schw.	181 abs.
321 m.+	341 s.s.schw.	361 s.schw.	
521 m.+	541 abs.	561 s.schw.	

These reflections all involve the factor sin v, which need not be evaluated in discussing relative intensities in their dependence on u. From Fig. 3

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1) R. W. G. Wyckoff and A. H. Armstrong, Z. Krist. 72, 319. 1930.

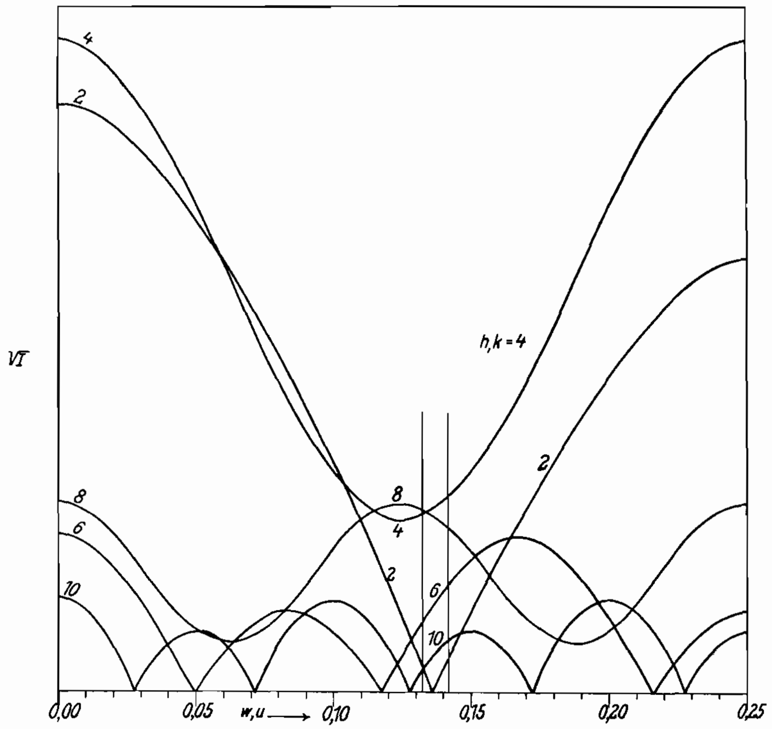

Fig. 2. Curves showing square-root of intensity of reflection for $(h00)$ and $(0k0)$ as functions of the parameters w and u, respectively.

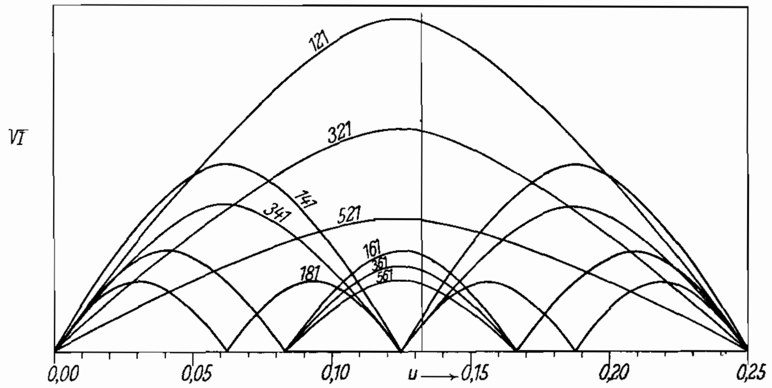

Fig. 3. Some intensities the ratios of which depend on u only.

it is seen that u must lie in the neighborhood of 0.125, the inequality (561) > (141) placing it between 0.111 and 0.139. If it be assumed that the ratio s.schw./s.s.schw. lies between 2 and 25, u is fixed to the region $0.130 \leqq u \leqq 0.135$ (or $0.115 \leqq u \leqq 0.120$), substantiating the previously selected value $u = 0.132 \pm 0.005$.

An approximate value of v can be obtained from the data for planes of type III (h odd, k odd) from Table III:

	330 s.s.schw.
111 m.+	331 s.schw.
112 st, m++.	332 m+, m++.
113 m++.	333 m+.
114 m+.	334 m+, m.

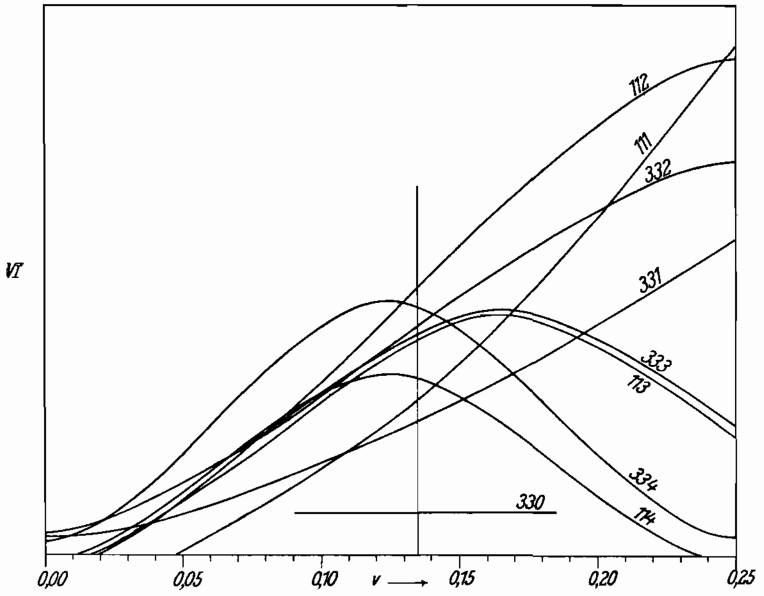

Fig. 4. Intensity curves for the determination of v.

From Fig. 4 it is seen that the observation (114) ≧ (111) requires $v \leqq 0.14$. A lower limit for v cannot be given with certainty, though the relations (332) ≧ (333) ≧ (334) can hardly be accounted for if v falls below 0.125. The value $v = 0.135 \pm 0.010$ may consequently be accepted with considerable confidence.

Knowing the values of w, u, and v, we may use data for planes of Class IV to find z. In Table III there are given the observed intensities

001 s.st.++
002 s.st.++
003 —
004 s.s.schw.

220 s.st.++
221 s.st.++, s.st.+
222 m.
223 m.
224 s.schw.

440 st.+, s.st.
441 s.st.++
442 schw., s.schw.
443 m+, m—, s.schw.

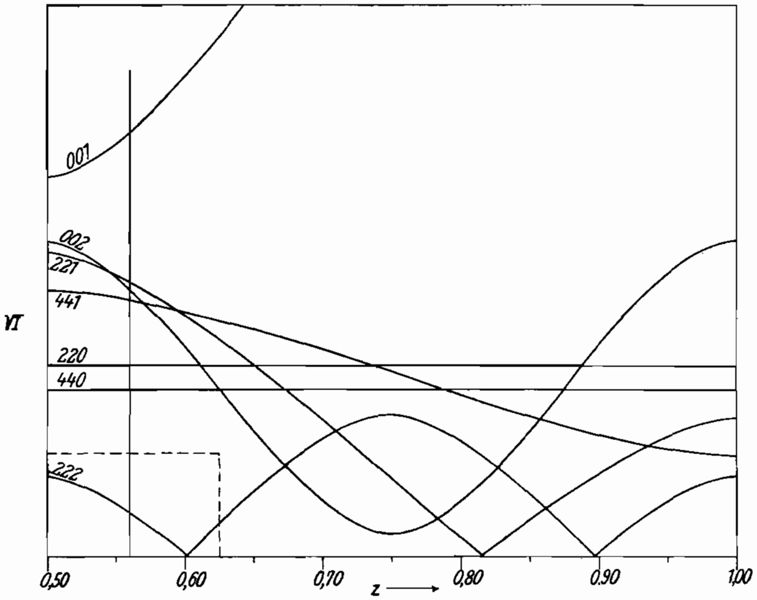

Fig. 5. Intensity curves for the determination of z.

(Note that the intensities as reported are not completely reliable, three different estimates being reported for the form {443}.) From Fig. 5 it is seen that the parameter z must lie in the neighborhood of 0.5, and from Fig. 6, representing on a larger scale the region in the rectangle in the lower left corner of Fig. 5, that z must be equal to about 0.56. This value does not lead to perfect agreement with observation, (003), (004), and (224) having different intensities, rather than the same as calculated. Changing z in either direction from 0.56, however, increases the discrepancies (which are probably due to small errors in the other parameter values), so that we accept the value $z = 0.560 \pm 0.010$.

Calculated and observed intensities for all of the reflections given by Hassel and Luzanski are listed in Tables III to VII, the numbers being the same as for their tables. The forms are listed for each table in order of decreasing calculated intensity. It is seen that the agreement is in general excellent, especially for the stronger reflections. In the case of very weak reflections a very small change in parameter values or in f-values causes a large relative change in calculated intensities, so that for these reasons complete agreement is not expected in this region. Some of the few remaining discrepancies are no doubt to be attributed to errors in the reported observed values; thus in Table III {443} is reported as v.w., m—, and m+, and {334} as m+, m, and v.w.; while {660} is reported as v.w. in Table III and m+ in Table VI.

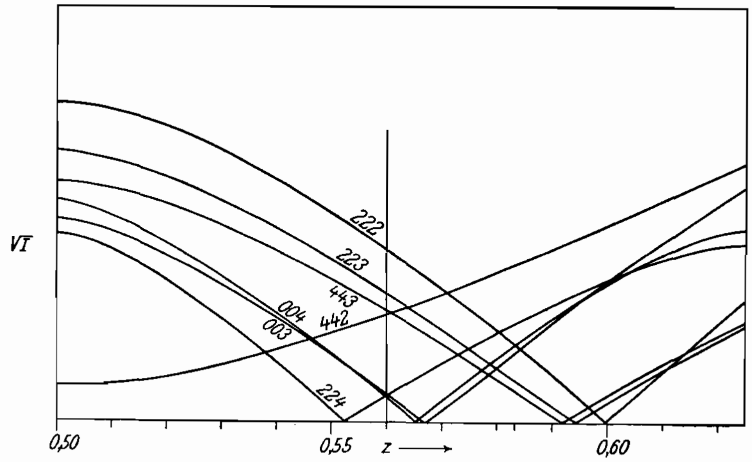

Fig. 6. Intensity curves for the determination of z.

Table III. Equator [110].

hkl	Calculated	Observed	hkl	Calculated	Observed
001	147.1	v.st.++	662	5.90	m++
002	68.2	v.st.++	111	4.54	m+
221	62.5	v.st.++(v.st.+)	331	3.76	w (w—, v.w.)
441	56.5	v.st.++	222	2.56	m
220	31.6	v.st.++	553	2.28	v.v.w.
440	27.9	v.st.(st.+)	223	1.02	m
112	15.0	st.(m++)	443	0.69	v.w (m—, m+)
334	13.6	m+(m, v.w.)	442	.49	v.w. (w)
332	11.1	m++ (m+)	330	.41	v.v.w.
333	10.2	m+	552	.41	v.v.w. (w, v.w.)
660	10.2	v.w.	003	.11	abs.
113	9.99	m++	224	.04	v.w.
114	6.81	m+	004	.03	v.v.w.

Table IV. Equator [100].

hkl	Calculated	Observed	*hkl*	Calculated	Observed
021	295.5	v.st.++	022	6.20	w
001	147.1	v.st.++	063	4.97	w+
002	68.2	v.st.++	024	4.58	v.w.
042	34.5	st.	060	4.08	w
061	31.0	st.	081	3.65	v.w.
080	29.3	m	041	3.17	w
040	26.2	m+	062	1.06	v.v.w.
044	19.3	m—	020	0.81	v.w.
023	12.1	w+	004	.03	v.v.w.
043	9.99	w+			

Table V. Equator [010].

hkl	Calculated	Observed	*hkl*	Calculated	Observed
201	173.7	v.st.++	403	18.1	m
001	147.1	v.st.++	404	16.1	w
002	58.2	v.st.++	600	10.3	m—
601	34.0	m+	204	6.40	w
400	32.4	m+	802	4.97	m
401	26.5	m+	402	3.53	v.w.
800	23.3	m+	801	1.69	w
202	18.8	m	004	0.03	v.v.w.

Table VI. Equator [001].

hkl	Calculated	Observed	*hkl*	Calculated	Observed
310	222.0	st.++	640	7.78	st.—
130	201.9	st.++	390	7.24	m—
240	126.1	st.++	260	5.29	m++
420	101.4	st.++	570	5.24	m++
400	32.2	st.	530	4.12	v.w.
150	31.6	st.+	060	4.08	m—
220	31.6	st.	910	3.03	v.v.w.
080	29.3	st.	680	2.82	v.w.
040	26.2	st.	480	2.46	w
800	23.3	st.	10.0.0	2.37	v.w.
510	19.9	st.	490	2.34	w+
730	15.0	st.	350	1.80	v.w.
370	14.8	st.	930	1.72	m:
620	14.1	st.	020	0.81	v.w.
460	12.1	st.	950	.77	w
600	10.3	m+	710	.64	v.v.w.
660	10.2	m+	330	.41	v.v.w.
750	9.55	st.—	860	.07	v.w.

Table VII. First Layer [001].

hkl	Calculated	Observed	*hkl*	Calculated	Observed
021	295.5	v.st.	361	3.24	v.w.
201	173.7	v.st.	041	3.17	m
311	95.6	v.st.	351	3.17	v.w.
131	70.7	st.+	571	2.86	m
211	65.8	st.+	721	2.59	v.w.
221	62.6	st.+	411	2.50	v.v.w.
441	56.5	st.+	271	2.37	w
121	51.4	st.+	421	2.25	m—
601	34.0	st.	561	2.16	v.w.
061	31.0	st.	251	2.02	v.w.
401	26.5	st.	801	1.69	w
321	22.6	m+	641	1.66	v.v.w.
151	16.0	st.+	711	1.56	v.v.w.
731	9.86	m+	231	1.46	w
371	9.30	m+	241	0.96	v.v.w.
431	9.00	m+	651	0.56	v.v.w.
511	8.07	m ++	141	0.50	v.v.w.
751	7.45	m	341	0.30	v.v.w.
451	5.76	w +	631	0.26	v.w.
281	4.78	m +	471	0.15	v.v.w.
161	4.71	w	621	0.07	v.w.
111	4.54	m	741	0.07	abs.
261	3.50	w			

Description of the Structure.

As discussed in its derivation, the structure found for NH_4HF_2, shown in Fig. 1, is related in a characteristic way to that of KHF_2, the changes being all such as are produced by the introduction of hydrogen bonds. Each nitrogen atom is surrounded by four fluorine ions at tetrahedron corners, two (F_1) at a distance of 2.75 ± 0.06 Å, and two (F_2) at 2.77 ± 0.06 Å, using the values of parameters determined from the X-ray data. This $N—F$ distance of 2.76 Å is 5% larger than that in NH_4F, 2.63 Å, indicating that the hydrogen bond in NH_4HF_2 is not so strong as in NH_4F. Placing the proton midway between the two F' ions in HF_2', the parameter values lead to the distances $H—F_1 = 1.184 \pm 0.04$ Å and $H—F_2 = 1.184 \pm 0.06$ Å; the ranges reported for $NaHF_2$, 1.25 ± 0.10 Å, and KHF_2, 1.12 ± 0.10 Å, include this value, so that we do not know whether (as might be anticipated) the formation of two additional hydrogen bonds with nitrogen by each of the fluorine ions in HF_2' weakens the $F'H^{\cdot}F'$ bonds and correspondingly increases the $H—F$ distance. The $H—F$ distance 1.184 Å in HF_2' is 29% greater than that 0.92 Å in HF, as determined from infrared bands. It would be interesting to know where the proton in the NHF bond is situated on the line between N and F; presumably it is considerably farther from N than in $NH_4^{\bullet}$ (0.94 Å)[1]), though still closer to it than to F. Unfortunately there seems to be no prospect of determining its position experimentally.

The three hydrogen bonds formed by F_1 are coplanar, and those formed by F_2 are nearly so.

It is probable that on heating NH_4HF_2 rotation[2]) of the $NH_4^{\bullet}$ ions is induced, with an accompanying gradual transition to a tetragonal structure with $a = b$, $w = u$, $v = 0$, and $z = \frac{1}{2}$, or a discontinuous transition to the KHF_2 structure (provided that fusion or sublimation does not occur below the transition temperature).

Summary.

The unit of structure of the orthorhombic crystal NH_4HF_2, containing four molecules, has $a = 8.33$ Å, $b = 8.14$ Å, $c = 3.68$ Å, space group V_h^7—*Pman*. The atomic positions are

$4\,N$ in $4\,g$: $\pm(\frac{1}{4}\,\frac{1}{4}\,z,\ \frac{3}{4}\,\frac{1}{4}\,z)$ $z = 0.560 \pm 0.010$;
$4\,F_1$ in $4\,e$: $\pm(w\,0\,0,\ \frac{1}{2}+w\,\frac{1}{2}\,0)$ $w = 0.142 \pm 0.005$;
$4\,F_2$ in $4\,h$: $\pm(\frac{1}{2}\,u\,v,\ 0\,\frac{1}{2}-u\,v)$ $u = 0.132 \pm 0.005$
$v = 0.135 \pm 0.010$.

Each nitrogen is attached to four fluorine ions at a distance of 2.76 Å by hydrogen bonds, and each fluorine ion to two nitrogen and one fluorine ion, the F—H distance in the linear HF_2 groups being 1.184 Å.

I wish to thank Mr. S. Weinbaum for making some of the intensity calculations.

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[1]) R. Pohlman, Z. Physik 79, 394. 1932.

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THE STRUCTURE OF CHLORINE HYDRATE

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In 1811 Humphry Davy[1] showed that water is a component of the phase that had earlier been thought to be solidified chlorine, and twelve years later Michael Faraday[2] reported an analysis that corresponds to the formula $Cl_2 \cdot 10H_2O$. He surmised that his determination of the chlorine content was low, and later studies have indicated the composition to be close to $Cl_2 \cdot 8H_2O$. Since Faraday's time similar crystalline hydrates of many gases with small molecular volume, including the noble gases and simple hydrocarbons, have been reported. The determination of the structure of ice and the development of an understanding of the nature of the hydrogen bond have strongly suggested that these substances are clathrate compounds, with a tetrahedral hydrogen-bonded framework of water molecules (with $O—H \cdots O = 2.76$ A, as in ice) defining cavities large enough to contain the other molecules.

Only recently have serious steps been taken toward determining the structure of these hydrates. About ten years ago von Stackelberg and his collaborators[3,4] made x-ray studies of some of these compounds, including the hydrates of xenon, chlorine, bromine, sulfur dioxide, hydrogen sulfide, methyl bromide, methyl iodide, ethyl chloride and chloroform. They reported that most of the crystals have a cubic unit cell with a_0 equal to about 12.0 A. From single-crystal x-ray photographs of the hydrate of sulfur dioxide they decided on the space group O_h^3, and postulated a structure consisting of a framework of 48 oxygen atoms in a set of general positions x, y, z in the unit cell. With this structure each oxygen atom has neighboring oxygen atoms at a distance of about 2.4 A, and the framework has eight cavities in which the gas molecules could lie. The ideal formula would thus be $M \cdot 6H_2O$. This structure is not acceptable because of the very short $O—H \cdots O$ distance of 2.4 A; in addition, the hydrogen bonds lie at angles between 60° and 145°, which differ greatly from the expected tetrahedral angle.

Claussen[5] then proposed a structure based on a larger cubic unit cell, about 17 A on edge, containing 136 water molecules. The oxygen atoms would be arranged to form 16 pentagonal dodecahedra and 8 hexakaidecahedra. This structure leads to the empirical formula $M \cdot 5^2/_3H_2O$ for smaller molecules which occupy all of the polyhedra, and $M \cdot 17H_2O$ for larger molecules which occupy only the hexakaidecahedra. The obvious advantage of such a structure is the presence of hydrogen bond angles of about 108° in the dodecahedra and in the twelve pentagonal faces of the hexakaidecahedra; the other hydrogen bond angles, in the four hexagonal faces of the hexakaidecahedra, are about 120°. Von Stackelberg and Müller[6] have recently reported evidence for the existence of this structure derived from analysis of x-ray diffraction photographs of alkyl halide hydrates.

We have been studying the structures of intermetallic compounds that involve icosohedral and pentagonal dodecahedral arrangements of atoms, and in the course of this work a structure was found which seemed to be ideally suited to the hydrates of smaller gas molecules. This structure is based on the cubic group O_h^3, and has a_0 equal to 11.88 A for the O—H $\cdots$ O distance 2.76 A, in close agreement with the first results reported by von Stackelberg. The unit cell contains 46 water molecules, with the oxygen atoms arranged so as to form two pentagonal dodecahedra and six tetrakaidecahedra; the empirical formula is hence $\mathrm{M}\cdot 7^2/_3\mathrm{H_2O}$ for molecules M occupying only the tetrakaidecahedra, and $\mathrm{M}\cdot 5^3/_4\mathrm{H_2O}$ for smaller molecules which occupy all of the polyhedra.[7] In order to test the predicted structure we have prepared and interpreted x-ray diffraction photographs of chlorine hydrate.

Experimental Methods and Results.—A length of 6-mm. Pyrex tubing was drawn to a capillary at one end and connected to a tank of commercial chlorine. After thorough flushing, the capillary was sealed off and the end was immersed in a dry-ice–acetone bath. When some chlorine had condensed in the capillary a drop of water was admitted into the large end of the glass tube, which was then sealed off. Alternate warming and cooling of the capillary permitted thorough mixing of the water and chlorine. Small pale-yellow crystals soon formed in the capillary, and remained as the temperature was brought up to 0°C. A small amount of liquid chlorine also remained, showing the chlorine to be in excess and indicating a pressure of about 4 atmospheres.

The Pyrex tube was suspended, with capillary down, in a small-holed rubber stopper which, in turn, was fastened to a goniometer head by a length of stout copper wire. The solid material within the capillary was photographed in a cold room (4°C.) using copper x-radiation, a camera with radius 5 cm., and oscillation range 30°. The effective camera radius was established by superimposing a powder spectrum of NaCl during an exposure of the sample; the lattice constant for NaCl at 4°C. was taken to be 5.634 A.

The diffraction pattern of the sample of chlorine hydrate consisted of powder lines on which were superimposed a large number of more intense single-crystal reflections; for some planes only the latter were visible. The intensities of the lines were estimated by comparison with a previously calibrated powder photograph, and were averaged for several films prepared from different parts of the capillary (and which, accordingly, varied as to the intensities of the single-crystal reflections). Despite this precaution, it was expected that the intensity estimations would be subject to considerably larger errors than would a properly ground powder sample. The averaged intensities were corrected for Lorentz and polarization factors and were adjusted by an empirical scale factor to give values of G^2_{obs}.

All of the observed reflections could be indexed on the basis of a cubic unit cell with $a_0 = 11.82$ A; the estimated probable error is 0.01 A. The only systematic absences were *hhl* with *l* odd; this is characteristic of the space group O_h^3-*Pm3n*, which also was reported by von Stackelberg from his single-crystal work on sulfur dioxide hydrate. For 46 H_2O and 6 Cl_2 in the unit cell the calculated density is 1.26; densities reported by various observers range from 1.23 to 1.29.

In order for all of the O—H · · · O distances within the unit cell to be the same the oxygen atoms must lie in the following positions:

$$6\ O_{\text{I}} \text{ in } 6(c)\frac{1}{4}\ 0\ \frac{1}{2} \dots;$$
$$16\ O_{\text{II}} \text{ in } 16(i)\ xxx, \dots, x = 0.183;$$
$$24\ O_{\text{III}} \text{ in } 24(k)\ 0yz, \dots, y = 0.310, z = 0.116.$$

For comparison with G^2_{obs}. values, calculated values were determined as follows: $G^2_{\text{calc.}} = \sum_i m_i F_i^2$ where F_i is the structure factor and m_i the multiplicity of each set of planes i contained in the powder line. For preliminary calculations only the contributions of the oxygen atoms were included in the structure factor; nevertheless, there was rough agreement with the observed G^2 values.

The oxygen atoms placed in the above positions form, in each unit cell, a framework consisting of two pentagonal dodecahedra, centered at (000) and $\left(\frac{111}{222}\right)$, and six tetrakaidecahedra, centered at $\left(\frac{1}{4}\frac{1}{2}0\right)$, $\left(\frac{3}{4}\frac{1}{2}0\right)$, $\left(\frac{1}{2}0\frac{1}{4}\right)$, $\left(\frac{1}{2}0\frac{3}{4}\right)$, $\left(0\frac{1}{4}\frac{1}{2}\right)$, and $\left(0\frac{3}{4}\frac{1}{2}\right)$. It soon became apparent that the agreement between calculated and observed values of G^2 was markedly improved if the chlorine molecules were placed within the six tetrakaidecahedra only, leaving the dodecahedra empty. These tetrakaidecahedra have two nearly regular hexagonal faces at opposite ends, separated by twelve nearly regular pentagons, as shown in figure 1. A cross-section taken parallel to the hexagonal faces is nearly circular, and the equatorial diameter is considerably larger than the polar diameter (between hexagons). The figure thus is a close approximation to an oblate spheroid. If the twelve chlorine atoms are to lie in fixed positions within the tetrakaidecahedra conforming to the crystal symmetry, a pair must lie along the short polar axis. This arrangement is sterically unfavorable, and calculations based on it gave rather poor intensity agreement. Since the tetrakaidecahedra containing the chlorine molecules so nearly approximate spheroids, it was decided to treat the chlorine molecules as freely rotating about their centers or else as being statistically distributed over a large number of orientations within the polyhedra. In either case, a sufficiently close

TABLE 1

Calculated and Observed G^2 Values for Chlorine Hydrate

	$mF^2_{calc.}$				
hkl	(I) UNIFORM SHELL	(II) EQUAT. CIRCLE	(III) WEIGHTED SHELL	(IV) V. STACKELBERG	$G^2_{obs.}$
110	555	488	527	34	207
200	10	18	0	722	<48
210	865	986	916	278	636
211	8	4	1	221	<74
220	412	809	562	3204	582
310	981	602	808	23	694
222	4390	4283	4390	1656	2732
320	4195	3120	3741	2307	3394
321	6416	6037	6304	723	9216
400	970	1083	972	207	679
410	1579	4494	2528	60	1817
330	522	844	653	83	1074
411	274	1142	525	292	
420	94	389	167	2679	139
421	246	16	117	3	323
332	429	666	509	357	318
422	4	528	107	1144	141
430	346	0	110	2323	206
431	37	299	128	1354	229
510	330	80	194	128	
432	1129	1260	1109	701	2411
520	180	5	42	2949	
521	161	493	272	46	196
440	0	4	0	631	<183
433	2401	2599	2578	1144	10080
530	5040	3863	4437	1234	
531	2611	2611	2611	10	1374
442	484	955	730	1080	1020
600	1568	274	957	234	
610	1152	2	459	750	304
532	5685	4264	5069	10	5236
611	392	2035	764	99	
620	960	2964	1562	359	1320
540	620	1008	890	5317	1654
621	296	3192	973	1290	
541	49	85	37	491	<378
622	166	95	164	689	<400

approximation to the electron density is given by considering the centers of the chlorine atoms to lie on spherical shells concentric with the tetrakaidecahedra; the diameter of these shells is the Cl—Cl bonded distance, taken as 1.98 A. Since the tetrakaidecahedra are oblate, it would be expected that the chlorine atoms would be concentrated toward the equator. Calculations of structure factors were made on the basis of three different configurations for the chlorine atoms within each tetrakaidecahedron: (I) a spherical shell of uniform density; (II) the limiting case in which all of the chlorine atoms were assumed to lie on the equator; that is, on a circle parallel to and midway between the hexagonal faces; (III) a spherical shell with density weighted according to the function $\cos^2 \alpha$, where α is the angle of latitude. For arrangement I the calculated structure factor for the center of the sphere, including the form factor for two chlorine atoms, was multiplied by the factor $\frac{\sin P}{P}$, where $P = \frac{2\pi r}{d_{hkl}}$, d_{hkl} is the spacing of the diffracting plane, and r (= 0.99 A) is the radius of the sphere. For the circle in arrangement II the factor is $J_0\ (P \sin \psi)$, where J_0 is the zero-order Bessel coefficient and ψ is the angle between the axis of the circle and the normal to the diffracting plane *hkl*. Arrangement III was approximated by summing up the appropriately weighted contributions of circles with radius $r \cos \alpha$, taken at each 15° of latitude; the calculated structure factor for the center of each circle was multiplied by the correction factor $J_0\ (P \cos \alpha \sin \psi)$. As a check that 15° was a sufficiently small interval, another calculation was made in which the latitudinal circles were weighted so as to give an approximation to a uniform spherical shell; the results were essentially identical with those of arrangement I throughout the observed range of diffraction angle.

In table 1 there are listed the values of G^2 calculated on the basis of these three arrangements, together with the observed values; it is seen that arrangement III—the spherical shell of non-uniform density—gives the best agreement, especially for the reflections 430, 610, and 540 + 621. Indeed, the agreement with the observed values is quite satisfactory in view of the relatively large uncertainty in observed intensities. Contributions of the hydrogen atoms were not included in the calculations, and no temperature factor was applied. The reliability factor $R^2 = \frac{\sum|G^2_{\text{obs.}} - G^2_{\text{calc.}}|}{\sum G^2_{\text{obs.}}}$ has a value of 0.32, which corresponds to a value of 0.16 if F values were used.

In column IV there are listed the G^2 values calculated from the parameters proposed by von Stackelberg. As an approximation to the configuration of the chlorine molecules spherical shells of uniform density were placed at the centers of the eight cavities formed by the oxygen atoms. It is seen that the calculated values are not compatible with the observed ones, and it seems extremely unlikely that any change in the positions of the chlorine atoms would make the agreement between calculated and observed intensities satisfactory.

Discussion of the Structure.—Figures 1 and 2 show two different representations of the framework of oxygen atoms. The structure may be derived, as shown in figure 2, by placing dodecahedra at the corners and body center of the unit cube and adding six additional atoms per unit cell (three of these are indicated by circles) to form the tetrakaidecahedra. Each dodecahedron shares its faces with twelve surrounding tetrakaidecahedra, and each tetrakaidecahedron shares its two hexagonal faces and eight pentagonal faces with neighboring tetrakaidecahedra, the remaining four pentagonal faces being shared with dodecahedra. With the oxygen parameters given above, which result in O—H··· O distances of 2.75 A throughout, the pentagons deviate slightly from planarity, while the hexagons are planar but not equi-angular. The O-O-O angles on the pentagonal faces range from 106.1° to 114.8°, while each hexagon has two angles of 109.6° and four of 125.2°.

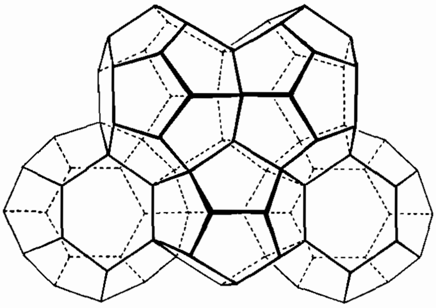

FIGURE 1

Dodecahedron of oxygen atoms surrounded by four out of a total of twelve tetrakaidecahedra.

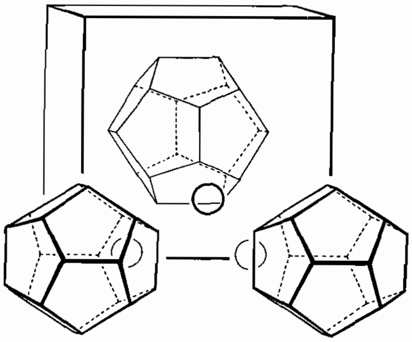

FIGURE 2

Dodecahedra of oxygen atoms at two corners and body center of unit cell, with three additional oxygen atoms (circles) needed to complete the structure.

The average radius of the tetrakaidecahedra at the equator is 4.46 A, while the average distance from the center to the six vertices of the hexagonal faces is 4.03 A; the average radius of the dodecahedra is 3.85 A. Using a single-bond radius for chlorine of 0.99 A and van der Waals radii for chlorine and oxygen of 1.80 and 1.40 A, respectively, we would expect a minimum radius of 4.19 A for accommodation of a chlorine molecule. Even if the presence of hydrogen-chlorine contacts would decrease somewhat the effective van der Waals radius of chlorine, it is doubtful that the over-all minimum radius could drop to 3.85 A; hence one would predict that the dodecahedra are too small to accommodate the chlorine molecules. Moreover, the tetrakaidecahedra are barely long enough to hold the chlorine molecules along the polar axis; the $\cos^2 \alpha$ weighting of the density of the spherical shells representing the centers of the chlorine atoms thus appears to be justified.

On the basis of this structure for chlorine hydrate, the empirical formula is $6Cl_2 \cdot 46H_2O$, or $Cl_2 \cdot 7^2/_3H_2O$. This is in fair agreement with the generally accepted formula $Cl_2 \cdot 8H_2O$, for which Harris[7] has recently provided further support. For molecules slightly smaller than chlorine, which could occupy the dodecahedra also, the predicted formula is $M \cdot 5^3/_4H_2O$.

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[*] Contribution No. 1652.

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[5] Claussen, W. F., *J. Chem. Phys.*, **19**, 259, 662 (1951).

[6] v. Stackelberg, M., and Müller, H. R., *Ibid.*, **19**, 1319 (1951).

[7] In June, 1951, a brief description of the present structure was communicated by letter to Prof. W. H. Rodebush and Dr. W. F. Claussen. The structure was then independently constructed by Dr. Claussen, who has published a note on it (*J. Chem. Phys.*, **19**, 1425 (1951)). Dr. Claussen has kindly informed us that the structure has also been discovered by H. R. Müller and M. v. Stackelberg,

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THE STRUCTURE OF WATER

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Abstract—There is little doubt that liquid water consists of water molecules joined together to a considerable extent by hydrogen bonds. The assumption that the principal aggregates of water molecules in liquid water have a structure similar to that of ice or have an analogous quartz-like structure is not compatible with some of the properties of water and with theoretical arguments. A structure for water has now been proposed that seems to be acceptable as a first approximation. This structure may be described as involving complexes of 21 water molecules, with icosahedral symmetry, or still larger complexes, perhaps with 41 molecules. The complexes are not stable and rigid, but are labile.

THIRTY-FIVE years ago LATIMER and RODEBUSH [1] showed the great usefulness of the concept of the hydrogen bond in explaining many physical properties of substances containing hydrogen atoms attached to electronegative atoms. Since that time more and more applications of the hydrogen bond have been made, and more and more has been learned about the nature of the hydrogen bond. During recent years we have seen the formulation of precise configurations of polypeptide chains, held together by hydrogen bonds, and have also seen the formulation of the extraordinarily stimulating proposal by Watson and Crick of a structure for deoxyribosenucleic acid in which pairs of nitrogen bases, one pair adenine and thymine, the other guanine and cytosine, are held together specifically by the formation of two or three hydrogen bonds. It seems likely that the hydrogen bond will continue to play an important role in the field of molecular biology.

Water is a substance of great importance in both the physical world and the biological world. It has a number of unusual properties, such as its increase in volume on freezing. Its properties are determined by its structure, which has for long been recognized as strongly influenced by hydrogen-bond formation. During the last year Peter Pauling and I have been working on the problem of the structure of water, and we have discovered a structure (or, rather, a complex of structures, as is appropriate for a fluid) that seems in many ways to be more satisfactory than any of those that have been described previously.

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*Contribution No. 2299.

Ordinary ice is known to have a structure similar to that of the hexagonal form of silica called tridymite. The oxygen atoms lie at the positions in the hexagonal crystal that are occupied by silicon atoms in tridymite. Each oxygen atom is surrounded tetrahedrally at the distance 2·76 Å by four other oxygen atoms, with which it forms hydrogen bonds. The experimental values of the residual entropy of ice and of deuterium oxide at low temperatures have been shown to require that the hydrogen atoms lie closer to one oxygen atom than to the other in the hydrogen bond, each oxygen atom having two hydrogen atoms near it, about 0·99 Å away, and two at a larger distance, about 1·77 Å. This unsymmetric structure of the hydrogen bond in ice has been verified by neutron diffraction. Cubic ice, formed by condensation of water vapour at temperatures around that of liquid air, is closely similar in structure, its structure being analogous to that of the cubic form of silica, cristobalite.

The structure for water that has so far received most serious consideration is that of BERNAL and FOWLER [2]. Bernal and Fowler suggested that water remains in part a hydrogen-bonded structure similar to that of ice. They pointed out that as more and more hydrogen bonds are broken the water molecules may arrange themselves in a manner approximating more and more closely to closest packing of spheres, which would result in a significant increase in density. They suggested also the possibility that the increase in density on melting might result in considerable part from the existence in water of hydrogen-bonded aggregates with a structure resembling that of quartz, which is denser than tridymite, although the interatomic distances are the same.

The suggestion that water contains significant numbers of aggregates with a quartz-like structure must be rejected on the basis of theoretical arguments. There is no way in which a complex with a quartz-like structure can be stabilized relative to one with a tridymite-like structure or a cristobalite-like structure. The hydrogen-bond energies stabilizing these structures are approximately equal to those stabilizing the quartz-like structure, except that in the quartz-like structure the hydrogen bonds would be strained, because the O—H···O angle would be about 135°, instead of the normal 180°. There is no entropy factor or other factor to give a compensating stabilization.

A large number of molecular substances form crystalline hydrates in which there are many more molecules of water than of the substance with which it is associated in the crystal: compositions approximating $Cl_2 \cdot 8H_2O$, $Kr \cdot 6H_2O$, $CH_4 \cdot 6H_2O$, $CHCl_3 \cdot 18H_2O$ are representative. The substances were subjected to x-ray investigation by VON STACKELBERG and collaborators [3, 4], who reported that many of them, such as chloroform hydrate, form cubic crystals with edge of the unit cell about

17 Å, and that others, such as methane hydrate and chlorine hydrate, form cubic crystals with edge of the unit cell about 12 Å. A structure involving tetrahedral hydrogen-bonding of water molecules was proposed for the 17-Å crystals by Claussen [5]. This structure is based upon pentagonal dodecahedra of water molecules condensed together into a three-dimensional framework by the sharing of pentagonal faces, with each of the dodecahedra sharing six faces with six surrounding dodecahedra. The framework comprises 16 dodecahedra, formed by 136 molecules. A somewhat similar structure was then formulated for the 12-Å hydrates by Pauling and Marsh [6], who, using x-ray diffraction photographs of chlorine hydrate, made a complete structure determination. The structure is shown in Fig. 1.

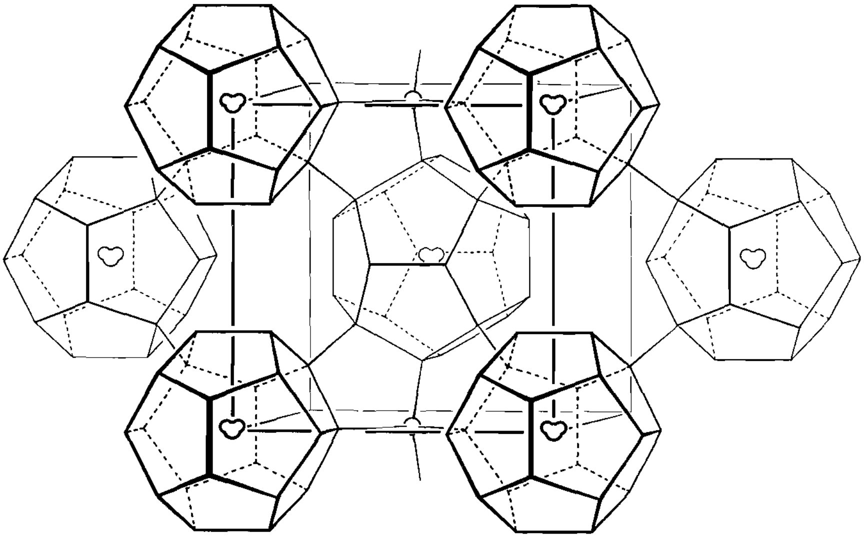

Fig. 1. The structure of gas hydrates containing a hydrogen-bonded framework of 46 water molecules. Twenty molecules, arranged at the corners of a pentagonal dodecahedron, form a hydrogen-bonded complex about the corners of the unit cube, and another 20 form a similar complex, differently oriented, about the centre of the cube. In addition there are six hydrogen-bonded water molecules, one of which is shown in the bottom face of the cube. In the proposed structure for water additional water molecules, not forming hydrogen bonds, occupy the centres of the dodecahedra, and also other positions

It consists of discrete pentagonal dodecahedra each of which forms eight hydrogen bonds with eight surrounding dodecahedra. In addition, there are six water molecules in positions $\frac{1}{2}$ $\frac{1}{4}$ 0, etc., each of which forms four hydrogen bonds with molecules of the four surrounding dodecahedra in such a way that a complete tetrahedrally-bonded framework of 46 water molecules per unit cube is achieved. In this structure there are cavities of two kinds: there are two positions, at the centres of the dodecahedra, in which molecules with van der Waals diameter not over 5 Å may be placed, and there are six positions, at the centres of the six tetrakaidecahedra that are also formed by the framework, that can be occupied by molecules with van der Waals diameter about 6 Å (Fig. 2). In methane hydrate all eight of these positions are occupied by methane molecules.

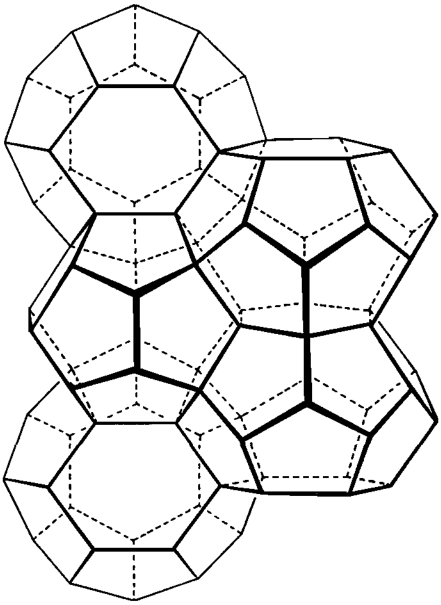

Fig. 2. In the centre of this drawing there is shown a dodecahedral complex. The polyhedra that surround it are tetrakaidecahedra, each having two hexagonal faces and 12 pentagonal faces

The structure of these hydrates suggests that water may have a structure based largely upon a complex of 21 water molecules, 20 of which lie at the corners of a pentagonal dodecahedron, each of them forming three hydrogen bonds with the adjacent neighbours in the dodecahedron, and the 21st forming no hydrogen bonds and occupying the central position in the dodecahedron. In addition, other water molecules may be present, either forming hydrogen bonds or not forming hydrogen bonds. A possible structure is that identical with methane hydrate, with a completely hydrogen-bonded framework of 46 water molecules per cubic unit cell (unit edge 11·82 Å), and 8 additional water molecules, forming no hydrogen bonds, in the centres of the polyhedra, giving a total of 54 H_2O per unit cube. The density calculated for this structure is 0·98 g/cm^3, only slightly different from that of water.

It is not necessary that the dodecahedra retain the orientations found for the chlorine hydrate structure; equally satisfactory structures are obtained by having all of the dodecahedra in the same orientation, giving a true body-centred structure, or by grouping the dodecahedra in other combinations of the two orientations compatible with cubic symmetry. In addition the dodecahedra can be arranged in other ways, such as cubic closest packing or hexagonal closest packing, giving closely-packed arrangements of dodecahedra corresponding closely to the density 1·00 g/cm^3 of water, and with about 85% of the maximum number of hydrogen bonds.

The advantage that the dodecahedral complex has over an ice-like aggregate of similar size is in its stability, as represented by the number of hydrogen bonds that are formed, and its mobility while keeping hydrogen bonds formed with surrounding complexes. The dodecahedral complex of 21 water molecules contains 30 hydrogen bonds, along the 30 edges of the dodecahedron; this is 71·5 per cent of the maximum number possible. On the other hand, there is no complex of approximately 21 atoms that can be cut out of the ice structure in which the number of hydrogen bonds is as much as 60 per cent of the maximum possible.

We have found that the proposed structure of water, based upon the centred pentagonal dodecahedron, accounts in a reasonably satisfactory way for several properties of water, including the dispersion of dielectric constant and the radial distribution curve as determined by x-ray diffraction. A detailed description of this work will be published later.

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1 LATIMER W. M. & RODEBUSH W. H. *J. Amer. Chem. Soc.* 1920 **42** 1419.
2 BERNAL J. D. & FOWLER R. H. *J. Chem. Phys.* 1933 **1** 515.
3 VON STACKELBERG M., GOTZEN O., PIETUCHOVSKY J., WITSCHER O., FRUHBUSS H. & MEINHOLD W. *Fortschr. Mineral.* 1947 **26** 122.
4 VON STACKELBERG M. & MÜLLER H. R. *J. Chem. Phys.* 1951 **19** 1319.
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6 PAULING L. & MARSH R. E. *Proc. Nat. Acad. Sci. U.S.* 1952 **38** 112.

DISCUSSION

J. A. Pople (Cambridge): Professor Pauling has proposed a structural model for water based principally on a particular configuration for 21 molecules. The criterion by which the validity of this model should be judged is the following. How many other ways are there of joining together groups of molecules of the size in which the same percentage of possible hydrogen bonds are formed? If there are N such ways, they will all appear with equal weight in the total partition function describing the liquid and Professor Pauling's structure would only represent (1/N)th of the real situation. I should like to ask for an estimate of such a number, which will, I feel, be quite large.

L. Pauling (Pasadena): I have attacked the problem of finding structures of a finite number of water molecules with hydrogen bonds at tetrahedral angles (± 10°) which have the maximum number of hydrogen bonds. So far as I have been able to discover, the $(H_2O)_{21}$ structure and the condensed complexes $(H_2O)_{37}$ etc., obtained by sharing faces between centred pentagonal dodecahedra give a curve of number of hydrogen bonds vs. number of water molecules that lies above the curves for complexes of all other types, such as those taken from a tridymite-like or cristobalite-like structure. Hence I conclude, in answer to Dr. Pople's question, that there are no other ways.

J. D. Bernal (London): My only criticism of this extremely elegant and ingenious theory of water structure is that from its very nature it would not be the structure of a liquid at ordinary temperatures, certainly not a liquid as fluid as water. It may well, however, be the structure of vitreous water at low temperatures. My reason for this view is that the degree of order postulated is far too high. Pauling realizes this when he admits that the 21 H_2O molecule unit cannot be considered as a permanent in the liquid. Insofar as these entities are continually transforming into each other, they represent only an actually unrealized ideal configuration, the real one at any instant being much more irregular. Such criticisms obviously apply with greater force to the types of idealized tridymite-like and quartz-like structures that Fowler and I put forward twenty-four years ago. They were never intended as models for more than a distance of three or four molecular neighbourhoods, and consequently it does not make much sense to liken them to specific extended crystal structures. We only wanted then to give a rough picture of the breakdown of the tending to tetrahedral coordination in liquid water from — 20° to 4° as evidenced by the diminution of volume.

Another objection to Pauling's model is that it would include hydrogen bonds of different kinds which should show up in the infrared spectrum but for which there is so far no evidence.

Note added later, June 1958. Panthaleon van Eck* in his studies of HDO water claims from spectral evidence that the hydrogen bonds in water are approximately of uniform character, but all weaker than in ice, and consequently longer, 2·85 as against 2·76 Å. If we accept this it should be possible energetically to attribute two hydrogen bonds of the weaker type to each H_2O molecule in water as in ice. The extra length of the bond, however, would give a structure such as proposed by Pauling in the density of 0·9 instead of 1·0.

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* Paper read at Royal Society meeting on "Physics of Water and Ice", November 1957.

Photos for Parts I and II

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Photo 1 Linus Pauling in 1923, the year after his arrival at Caltech for graduate work.

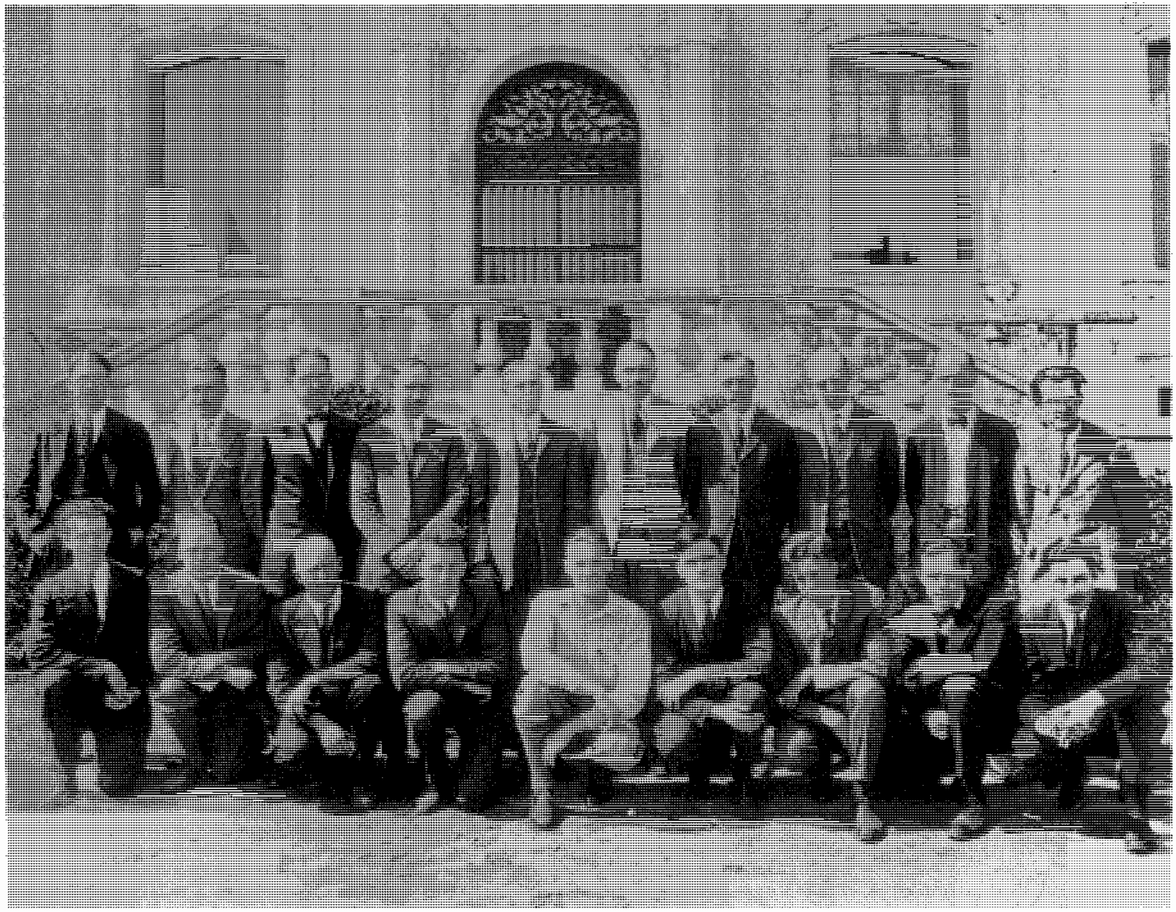


Photo 2 Caltech department of chemistry in 1923. Standing are the faculty; in the center, Prof. Arthur Amos Noyes (founder of the chemistry department) and Prof. Richard Chase Tolman (renowned chemical physicist). In the front row are the graduate students, with Linus Pauling at far left. Behind is the main entrance of the Gates Laboratory of Chemistry, built in 1917, the second building on the Caltech campus. Faculty, from left to right: Charles Prescott, Richard Badger, James Bell, Howard Lucas, Noyes (Director of the Laboratory), Tolman, William Lacey, Stuart Bates, Ernest Swift, and Roscoe Dickinson. Graduate students, from left to right: Pauling, Ernest White, Reinhardt Schumann, William Holton, Joseph Mayer, Paul Emmett, Vincent Manchee, Oliver Wulf, and L. Merle Kirkpatrick. Enlargements of parts of this picture are in Photos 1, 3, and 4.

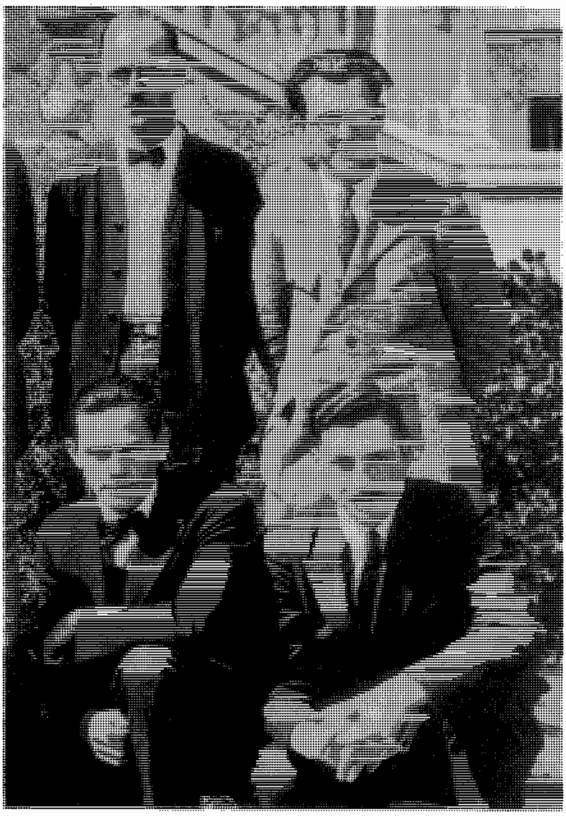


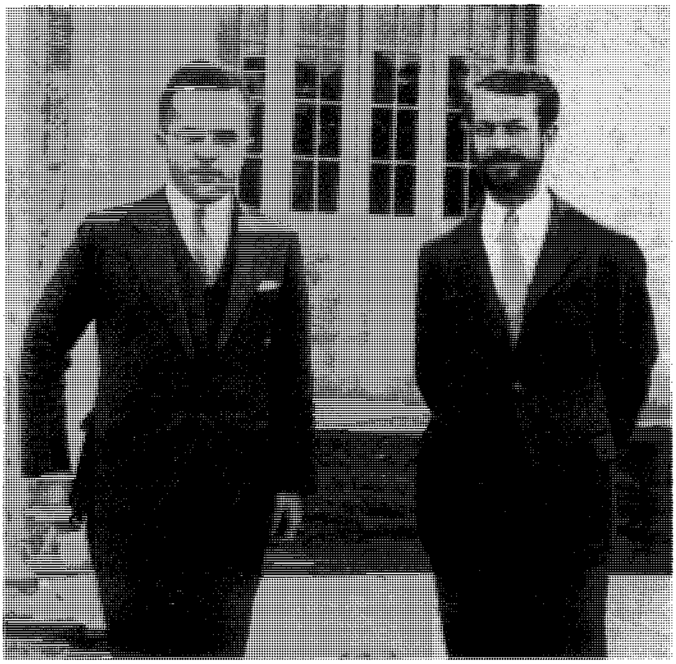
Photo 3 (left) At upper right is Pauling's Ph.D. thesis supervisor, Prof. Roscoe G. Dickinson, from whom he learned x-ray crystallography. At lower right is L. Merle Kirkpatrick, co-author of SP 41 (in German, reflecting Pauling's residence in Munich in 1926–1927). At lower left is graduate student Oliver Wulf, whose spectroscopic work on intramolecular hydrogen bonds figures prominently in Pauling's treatment of the nature of the hydrogen bond in SP 35, Section 12-7 (not reproduced here). At upper left is Ernest Swift, Caltech professor of analytical chemistry who much later (1958) succeeded Pauling as Chairman of Caltech's Division of Chemistry and Chemical Engineering, a position to which Pauling was appointed in 1937. This picture is an enlargement of the right-hand part of Photo 2, taken in 1923.

Photo 4 (right) At top center is the well-known chemical physicist Richard Chase Tolman, who co-authored a paper with Pauling on statistical mechanics (SP 71). At lower right is Paul H. Emmett—good friend and co-author of SP 40. Paul Emmett and Sterling Hendricks (SP 39, Photo 29) were the first students to co-author papers with Pauling. At upper left is Prof. Arthur Amos Noyes, who as head of chemistry at Caltech was quick to recognize Pauling's talents and to provide the support to keep him at Caltech. At lower left is Joseph E. Mayer, a graduate student who went on to become a prominent physical chemist and made notable contributions in the subject area of Chapter 2. At upper right is William Lacey, professor of chemical engineering and later dean of the graduate school. This picture is an enlargement of the center part of Photo 2, taken in 1923.

Photo 5 (left) Linus Pauling with Arnold Sommerfeld (on left). Sommerfeld, well-known professor of theoretical physics in the University of Munich, Germany, was an expert on an early form of quantum mechanics, the Bohr-Sommerfeld atomic model. The picture was taken on the occasion of Sommerfeld's visit to Caltech in 1928. Pauling studied quantum mechanics with Sommerfeld in 1926–1927, which is where Pauling got his start in the application of quantum mechanics to chemical bonding (Chapter 1) and to the calculation of molecular properties (Chapter 8).

Photo 6 (right) Linus Pauling and his wife, Ava Helen, in Munich, 1927, with German physicists Walter Heitler (left) and Fritz London (right). Heitler and London had just published their quantum-mechanical analysis of the hydrogen molecule, which Pauling called "the greatest single contribution to the clarification of the chemist's conception of valence" (SP 15, p. 340), and which in Pauling's hands became the widely used valence-bond method of molecular quantum mechanics.

Photo 7 Linus Pauling with Jack Sherman at Caltech, 1933. Sherman, along with G. W. Wheland, were two of Pauling's closest collaborators in developing and applying his concepts of the nature of the chemical bond (SP 8, SP 9, SP 10, SP 13, SP 16) and in using quantum mechanics to analyze molecular properties (SP 66).



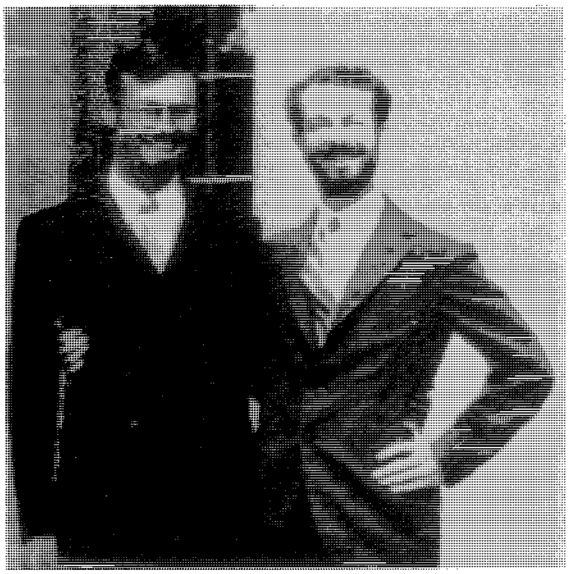


Photo 8 Linus Pauling with Charles D. Coryell (left), who collaborated in the study of the magnetic properties of hemoglobin (SP 83, SP 84). Picture taken about 1933.

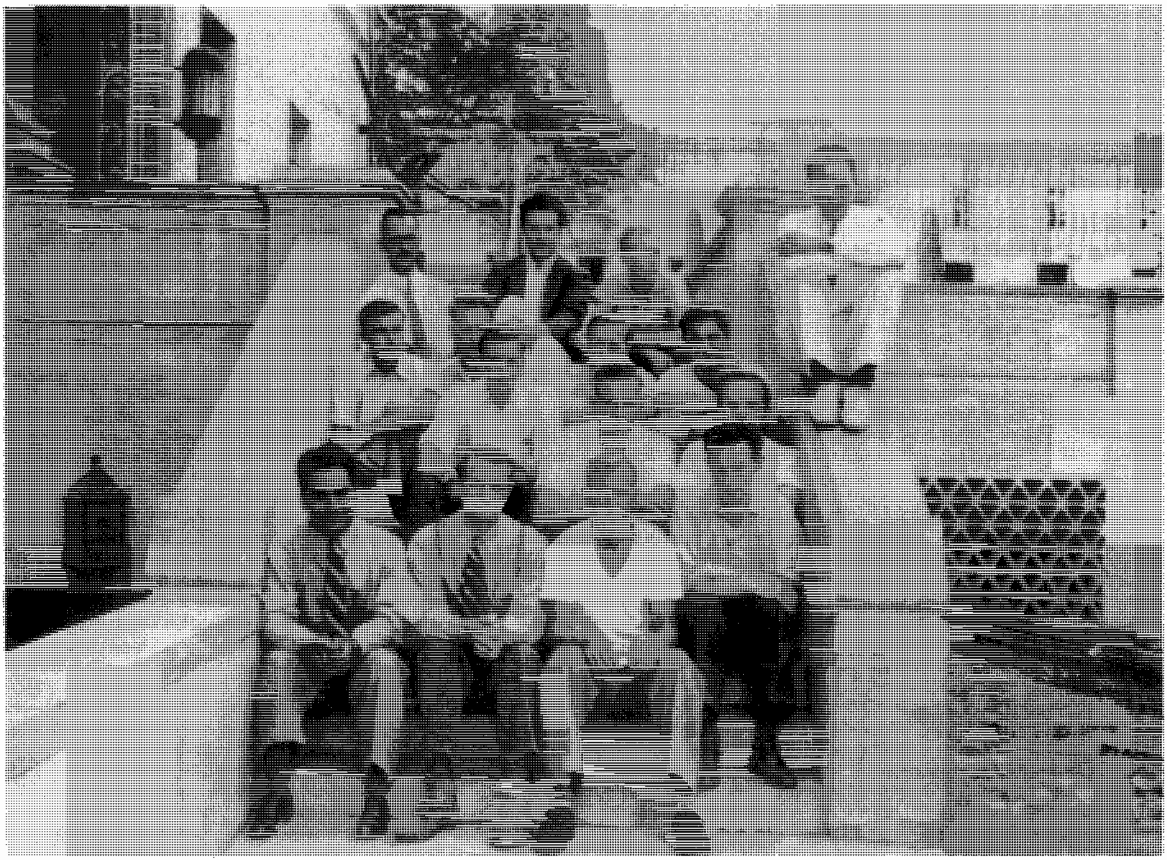


Photo 9 Linus Pauling with his research group, in 1937. Front row, left to right: Henri Levy, Pauling, Norman Elliot, Sidney Weinbaum. Second row: Kenneth Palmer, Hicks, Jack Sherman (partly hidden). Third row: Verner Schomaker, Yearnian, James Holmes Sturdivant (partly hidden), Stosick. Top row: Robert B. Corey, Gustav Albrecht, Herbert Sergent. On right-hand bannister: Lindsay Helmholz. The group is assembled on the stairs in front of Robinson Laboratory of Astrophysics, which they occupied before moving to the new Crellin Laboratory of Chemistry late in 1937. In the background, under construction, is the Kerckhoff Laboratory of Biology (east wing).

Photo 10 Linus Pauling delivering the Richards Medal Address at Cambridge, Massachusetts, in 1947. At the left is Prof. E. Bright Wilson, Jr., who in the 1930's collaborated with Pauling in writing *Introduction to Quantum Mechanics* (see SP 15), a book that is still used in teaching quantum mechanics to chemists.

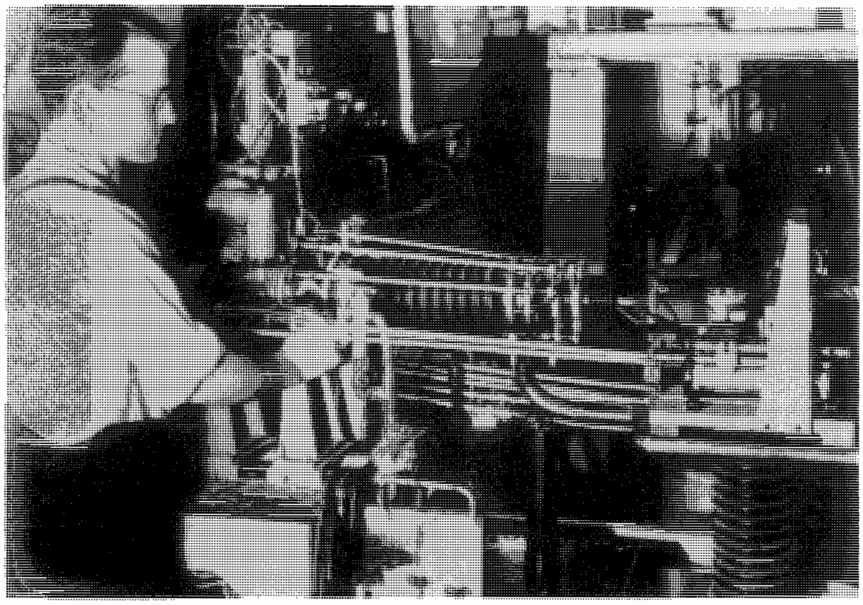


Photo 11 Graduate student Lawrence D. Brockway (SP 59, SP 60, SP 61) operating electron-diffraction apparatus in the mid 1930's.

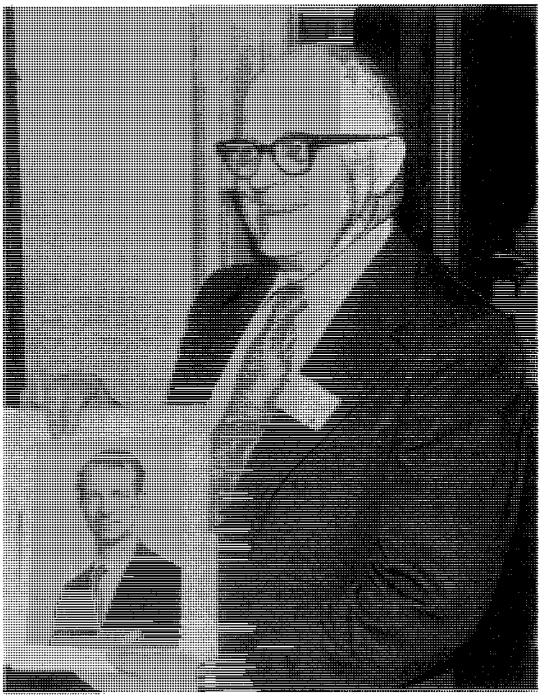


Photo 12 Dr. Lawrence O. Brockway in later life, holding a photograph of Linus Pauling.

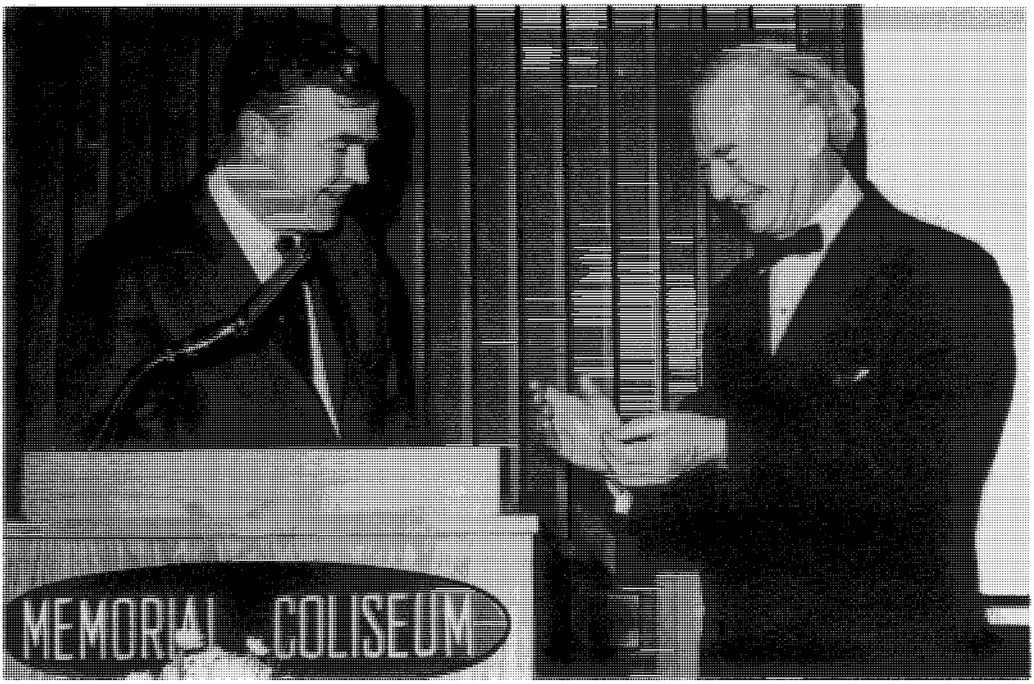


Photo 13 Linus Pauling (right) with Prof. Verner Schomaker (SP 61), about 1960.

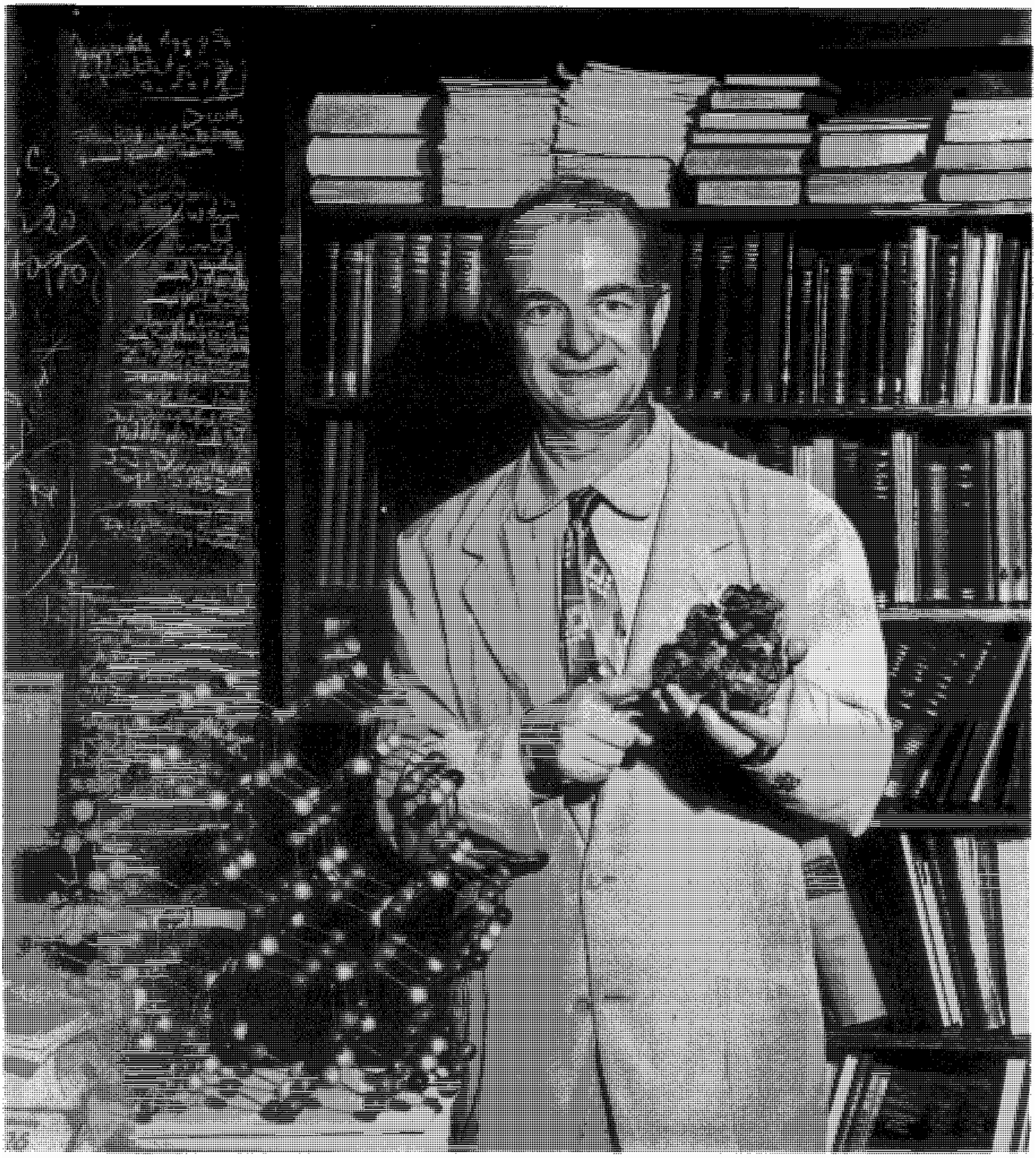


Photo 14 Linus Pauling in 1950, showing his still evident enthusiasm for the structures of complex minerals (Chapters 5, 6), in this case possibly beryl. In a typical pose, he holds a specimen of the mineral and stands beside an atomic model. The enthusiasm for minerals continued even though Pauling had by this time largely moved on to studies of biological macromolecules (Part III).

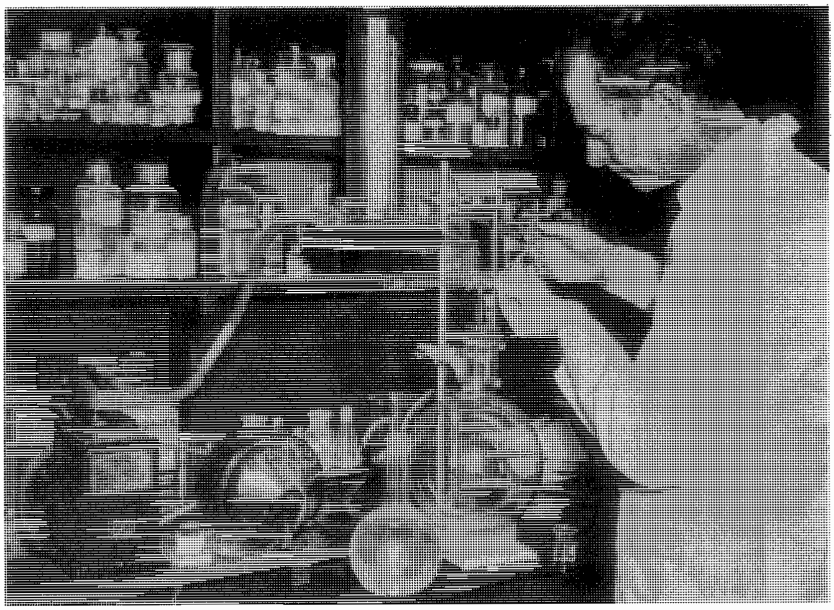


Photo 15 Linus Pauling trying out an experiment to be used in one of his freshman chemistry lectures at Caltech, in 1942.

Photo 16 Linus Pauling in the late 1940's with William H. Freeman (left), whose publishing company published Pauling's *General Chemistry*, a textbook that had great influence in the teaching of chemistry via the chemical-bonding approach. It was published in 1947 and went through many editions, including many in foreign languages.

PART II

CRYSTAL AND MOLECULAR STRUCTURE AND PROPERTIES

INTRODUCTION TO PART II

CRYSTAL AND MOLECULAR STRUCTURE AND PROPERTIES

Part II groups together papers on partly related and partly unrelated subject areas of Linus Pauling's research in physical science going beyond the nature of the chemical bond, though often related to it, and mostly preceding his major move to the bio-organic subjects in Parts III and IV. Chapters 5, 6, and 7 contain a selection of papers on observational structural chemistry—the determination of crystal and molecular structures that provided factual data used by Pauling in developing and testing his concepts of directed valence and his rules for the structure of ionic crystals. Chapters 5 and 6 contain his earliest scientific papers (SP 48, SP 49, SP 39, SP 40, SP 41), preceding by a couple of years the first of his papers on the nature of the chemical bond.

The crystal structures in Chapters 5 and 6 were determined by x-ray diffraction, and the papers illustrate Pauling's approach to this experimental technique, including his most notable methodological contributions—the *coordination method* (SP 42) and the *stochastic method* (SP 47). In its day, SP 47 was a tour de force in the determination of a complex crystal structure. SP 46 contains Pauling's famous discovery of two quite different crystal structures giving the same x-ray diffraction pattern, which violated the then-current conventional wisdom in x-ray crystallography.

The inclusion of both covalent and intermetallic crystals in Chapter 6 is predicated on the close relation between the covalent and metallic bonds, as discussed in Chapter 3. SP 54 and SP 55 are beautiful examples of the complexity of the atomic packing and bonding arrangements in alloy structures, which fascinated Pauling.

The covalent crystals in Chapter 6 are mostly sulfide minerals (SP 48, SP 50, SP 51, SP 57). They call attention to Pauling's interest in finding general rules for sulfide crystal structures analogous to his rules for ionic crystals (SP 24). This interest remained unrealized in part for reasons of research funding: he once recounted how in the late thirties the Geological Society of America declined his requests for support of structural work on the sulfide minerals, whereas the Rockefeller Foundation offered generous support for structural studies of biologically relevant molecules. An example of an early study of this type is SP 52; a much later one is SP 117 (in Chapter 14). Summaries of much of this x-ray work on molecular crystals are in SP 105 and SP 106, and additionally in papers [39-5] and [48-16], which are listed in Appendix III, Group 6c.

Chapter 7 contains studies of molecular structure by the then-new technique of electron diffraction (SP 58). Applied to molecules in the gas phase, it yielded accurate bond angles and bond lengths that helped to establish Pauling's concepts of directed valence and the *dependence of bond length on bond character* or *bond number*, especially for carbon-carbon bonds (SP 60, SP 61). The adjacent-charge rule developed in SP 59 is related to, and a forerunner of, the electroneutrality principle in SP 18. Pauling with his students and colleagues carried out numerous electron-diffraction studies and published many more papers on the subject than can be reproduced here, but a good impression of their style and content is given by SP 58, SP 59, SP 60, and SP 61. For a listing of all of these papers see Appendix III, Group 7.

SP 62, on the invention of the *Pauling oxygen meter*, represents a practical culmination of Pauling's strong interest in the magnetic properties of chemical substances in relation to the formation of chemical bonds (Chapter 1, SP 5; Part III, Chapter 11). It is placed here because it is based on a molecular property (paramagnetism of oxygen) measured in the gas phase (air). The oxygen meter was developed commercially by Arnold Beckman (Caltech Ph.D. in chemistry, 1928) and his company, Beckman Instruments.

In Chapter 8 we return to quantum mechanics, this time not applied to the chemical bond but to elucidating the physical properties of substances. Pauling's first ventures into quantum mechanics (SP 63, SP 64) were in this realm of physical-property analysis rather than in covalent bonding theory, which developed a couple of years later (Chapter 1, SP 3, SP 5). SP 63 made use of the Old Quantum Theory (based on Bohr orbits) and was superseded by SP 64 based on the New Quantum Theory (Schrödinger's wave mechanics). The calculation of *atomic scattering factors for x-rays* (SP 65) was important to people doing x-ray diffraction, and the *van der Waals interaction* (SP 66) is important in the forces between large molecules (Part III, Chapter 14, SP 114). The most notable paper, however, is SP 69, which puts forward a theory of the ferromagnetism of iron and the other transition metals. It is based not directly on quantum mechanical calculations but instead on Pauling's theory of the metallic bond, which is in turn based on quantum mechanical principles as described in Part I, Chapter 3, especially SP 28.

Chapter 9, on entropy and molecular rotation in crystals and liquids, is concerned mostly with statistical mechanics rather than quantum mechanics, but the two appear together in SP 74. Chapter 9 contains one of Pauling's most celebrated papers, SP 73, in which he explains the experimentally measured *zero-point entropy* of ice as due to *water-molecule orientation disorder* in the tetrahedrally H-bonded ice structure with *asymmetric hydrogen bonds* (in which the bonding proton is not at the center of the bond). This concept has proven fully valid, and the disorder phenomenon is now known to affect greatly the physical properties of ice via the rotations of the water molecules among the six different H-bonded orientations allowed to each molecule in the disordered structure. Since the disorder at absolute zero and the related zero-point entropy are a violation of the third law of thermodynamics, it is curious that SP 74, on the third law, makes no mention of SP 73. Also, SP 71, on the same general subject, does not anticipate SP 73. It might seem at first sight that SP 70, in Chapter 8, belongs in Chapter 9, but in fact the rotation treated in SP 70 is internal rotation of one part of a molecule with respect to another part, whereas SP 72 and SP 73 in Chapter 9 are concerned with the "external" rotation of a molecule with respect to its crystalline surroundings. These two types of molecular rotation are physically quite distinct.

Chapter 10 contains papers on three unrelated subjects that, together with orthomolecular medicine, occupied much of Pauling's research time in the later years of his life. His effort to model the atomic nucleus as a close-packed cluster of spherons (α particles, etc.) and to account for nuclear properties with this model, which was a natural approach for a structural chemist (SP 75, SP 76, SP 77), was ignored by physicists, as was his model of superconductivity (SP 78, SP 79), based on the resonating valence bond theory of metals (SP 31). In the controversy over quasicrystals (SP 80, SP 81), Pauling took on ironically the role of the conservative, defending classic crystallographic thinking against the radical ideas of the quasicrystal advocates, who ultimately carried the day. Undaunted by the setbacks, Pauling enjoyed his work on these subjects, and much of his time in the later years was spent happily carrying out the calculations that provided the basis for papers of the types reproduced in Chapter 10 (see Photo 43).

Chapter 5

IONIC CRYSTALS AND X-RAY DIFFRACTION

Contents

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Vol. XLVII, No. 3. March, 1925.]

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 56]

THE CRYSTAL STRUCTURES OF HEMATITE AND CORUNDUM

BY LINUS PAULING AND STERLING B. HENDRICKS

RECEIVED JANUARY 12, 1925 PUBLISHED MARCH 5, 1925

Introduction

Hematite, Fe_2O_3, and corundum, Al_2O_3, form crystals which have been assigned,[1] on the basis of observed face development, to the holohedral class of the rhombohedral system, with the rhombohedral angle α equal to 85° 42′ and 85° $42\frac{2}{3}'$, respectively. Spectrometric measurements have been made[2] of the reflection of X-rays from three faces of ruby, Al_2O_3, and two of hematite. Utilizing the hypothesis that in ruby each aluminum atom is equidistant from six oxygen atoms, and each oxygen atom equidistant from four aluminum atoms, a possible structure has been devised[3] which is not incompatible with these spectrometric observations. This structure has been used in a theoretical consideration of the influence of atomic arrangement on birefringence,[4] and in the explanation of the observed variation with temperature of the intensity of reflection of X-rays from faces of crystals of ruby and sapphire.[5] An exact knowledge of the arrangement of the constituent atoms in ruby would make the arguments of these papers much more convincing.

Powder photographic data from aluminum and ferric oxides prepared

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[1] Groth, "Chemische Krystallographie," Engelmann, Leipzig, **1908**, Vol. 1, p. 105.

[2] W. H. and W. L. Bragg, "X-Rays and Crystal Structure," G. Bell and Sons, London, **1915**, p. 171.

[3] W. H. and W. L. Bragg, "X-Rays and Crystal Structure," 4th edition, G. Bell and Sons, London, **1924**, p. 183.

[4] W. L. Bragg, *Proc. Roy. Soc.*, **106**, 346 (1924).

[5] I. Backhurst, *ibid.*, **102**, 340 (1922).

under different conditions have been published;[6] but no attempt has been made to deduce their structures from them. The dimensions of units of structure of aluminum, ferric, and chromic oxides which are said to agree with unpublished powder photographic data have been reported.[7]

We have, therefore, made a thorough X-ray study of crystals of hematite and of corundum, utilizing the results of the theory of space groups to interpret the data obtained from Laue and spectral photographs and considering all possible structures. Well-formed natural crystals of hematite, transparent faintly blue crystals of Ceylon corundum,[8] and sections cleaved from massive corundum were used. The X-ray data were obtained by the usual photographic methods described by Wyckoff.[9] The investigation was aided financially by a grant made to Professor A. A. Noyes by the Carnegie Institution of Washington.

The Structure of Hematite

Photographic Data.—The data obtained from spectral and Laue photographs are presented in the usual way in Tables I and II, respectively.

The Unit of Structure.—A spectral photograph of the K-radiation of molybdenum reflected from the face (100)′ of hematite (planes denoted by primes refer to the axes used by Groth) gave, as shown in Table I, the value 3.682 ± 0.010 Å. for d/n. If n is one, this corresponds to a unit of structure with a = 3.70 Å., and α = 85° 42′. With one Fe_2O_3 in this unit, the density calculated from the X-ray data is 5.25, in good agreement with the observed values,[1] which range from 5.15 to 5.30.

Table I

Spectral Photographic Data from (110) of Hematite

Line[a]	Order	Angle of reflection	$\frac{d_{110}}{n}$	Intensity of reflection[b]
β	n	4° 54′	3.693 Å.	w
α	n	5 31	3.700	m
γ	$2n$	9 41	3.683	vw
β	$2n$	9 52	3.678	m
α_1	$2n$	11 5	3.686	s
α_2	$2n$	11 9	3.681	ms

[a] In Tables I and III, γ indicates MoKγ, λ = 0.6197 Å.; β, MoKβ, λ = 0.6311; α_1, MoKα_1, λ = 0.7078; α_2, MoKα_2, λ = 0.7121; α, mean of α_1 and α_2, λ = 0.710.

[b] The abbreviations signify: s, strong; ms, medium strong; m, medium; mw, medium weak; w, weak; vw, very weak; vvw, very very weak.

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[6] Hedvall, *Z. anorg. Chem.*, **120,** 327 (1922).

[7] Davey and Hoffman, *Phys. Rev.*, **15,** 333 (1920). Davey, *ibid.*, **21,** 716 (1923).

[8] We wish to thank Professor Charles Palache of Harvard University for the Ceylon corundum.

[9] Wyckoff, "The Structure of Crystals," The Chemical Catalog Co., New York, **1924,** pp. 109–116 and 161–164.

TABLE II

LAUE PHOTOGRAPHIC DATA FROM HEMATITE

Incident beam normal to (110). Structure factors calculated for $u = 0.292$, $w = 0.1050$.

hkl	d_{hkl} Å.	$n\lambda$ Å.	Estimated intensity	S_1	S_2	S_3
032	1.415	0.34	1	1.16	1.16	1.16
$\bar{1}31$	1.215	.32	2	1.88	1.88	1.88
$\overline{315}$	0.971	.44	2.5	1.88	1.88	1.88
$\bar{3}2\bar{2}$	.932	.28	0.4	1.59	1.59	1.59
053	.927	.32	1.3	1.36	1.98	2.60
154	.909	.30	6	5.33	6.42	7.51
$\overline{326}$	.870	.38	0.03	0.61	0.61	0.61
456	.862	.42	.06	2.44	2.44	2.44
405	.808	.30	.2	1.84	1.84	1.84
567	.732	.43	2.5	2.17	3.06	3.95
275	.717	.43	8	5.63	6.76	7.89
174	.678	.41	0.05	1.16	1.09	1.02
578	.636	.30	.6	3.32	4.25	5.18
678	.623	.40	.1	2.44	2.44	2.44
$\bar{1}72$	.586	.33	.2	1.73	2.35	2.97
497	.567	.42	.6	2.61	3.54	4.47
$\bar{4}3\bar{5}$	.560	.40	1.3	2.94	3.73	4.52
789	.559	.39	1.6	5.94	7.08	8.22
$\bar{4}1\bar{7}$	.552	.43	1.5	3.64	4.73	5.82
$\bar{1}81$	.534	.42	0.3	1.87	2.49	3.11
194	.527	.39	1.5	5.26	6.39	7.52
3.10.7	.504	.34	0.4	5.89	6.82	7.75
$\bar{5}2\bar{7}$	.497	.35	.3	3.78	4.87	5.96
$\bar{5}3\bar{6}$	.495	.32	.05	1.02	1.64	2.26
$\bar{3}6\bar{2}$	.493	.35	.04	2.54	2.54	2.54
9.9.10	.489	.42	.4	4.76	5.83	6.90
$\bar{5}0\bar{9}$	.488	.35	.6	5.70	6.83	7.96
$\bar{5}.\bar{1}.\overline{10}$	.469	.33	.04	3.14	3.63	4.12
$\bar{4}.\bar{3}.\overline{11}$	.461	.33	.1	3.76	4.65	5.54
$\bar{6}1\bar{9}$	.439	.28	.04	1.96	3.09	4.22

Upon assigning indices to the spots on a Laue photograph and calculating values of $n\lambda$ on the basis of this unit, a number of forms, including $\{5\bar{3}1\}'$, $\{\bar{7}31\}'$ and $\{91\bar{1}\}'$, were found to have $n\lambda$ less than 0.24 Å., the lower wave-length limit of X-rays present in the incident radiation. This unit is accordingly eliminated.

The corresponding hexagonal unit, as well as any hexagonal unit with the same value of $d_{00\cdot1}$, is also eliminated by these data. However, the hexagonal unit with twice this value for $d_{00\cdot1}$ does account for the Laue data. Similarly the rhombohedral unit containing two Fe_2O_3 obtained by taking new axes along the diagonals of the faces (100)′, (010)′ and (001)′, accounts for all the Laue data, and is the smallest rhombohedral unit that does this. The hexagonal unit is improbable, for all planes of the large class for which $2H + I + L$, $-H + I + L$, and $-H-2I + L$ are not all divisible by three are found to give only third-order reflections, and it is difficult to explain the absence of first- and second-order reflections. Accordingly, the rhombohedral unit with $\alpha = 55° 17'$ and $a = 5.42 \pm 0.01$ Å., containing two Fe_2O_3, is taken to be correct. Indices (*hkl*) used in this paper refer to the axes of this unit.

The Space Group.—Laue photographs show the symmetry of point group D_{3d}; the structure is, accordingly, isomorphous with one of the point groups C_{3v}, D_3 and D_{3d}. The only space groups fulfilling this requirement and based on a rhombohedral lattice are C_{3v}^6, C_{3v}^5, D_3^7, D_{3d}^6 and D_{3d}^5. Each of these space groups provides one or more arrangements of two Fe_2O_3 in the unit of structure.[10] Those afforded by C_{3v}^6, D_3^7 and D_{3d}^5 are improbable because they do not account for the observed absence of all planes of the type (*hhl*) with *l* odd, many of which were in positions favorable to reflection. Of the two remaining space groups C_{3v}^5 and D_{3d}^6 the latter is taken as correct, for the crystallographic data strongly indicate the structure to be isomorphous with point group D_{3d}.

The Atomic Arrangement.—The possible arrangements allowed by D_{3d}^6 are

Fe at (a) 000, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ and (b) $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, $\frac{3}{4}\frac{3}{4}\frac{3}{4}$,
or at (c) www, $\overline{www}$, $\frac{1}{2}-w$ $\frac{1}{2}-w$ $\frac{1}{2}-w$, $w+\frac{1}{2}$ $w+\frac{1}{2}$ $w+\frac{1}{2}$,
with O at (d) $\frac{1}{4}\frac{3}{4}\frac{3}{4}$, $\frac{3}{4}\frac{3}{4}\frac{1}{4}$, $\frac{3}{4}\frac{1}{4}\frac{3}{4}$, $\frac{1}{4}\frac{3}{4}\frac{1}{4}$, $\frac{3}{4}\frac{1}{4}\frac{1}{4}$, $\frac{1}{4}\frac{1}{4}\frac{3}{4}$,
or at (e) $u\bar{u}0$, $\bar{u}0u$, $0u\bar{u}$, $\frac{1}{2}-u$ $u+\frac{1}{2}$ $\frac{1}{2}$, $u+\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}-u$, $\frac{1}{2}$ $\frac{1}{2}-u$ $u+\frac{1}{2}$.

Any arrangement with oxygen atoms at (d) requires that there be no first-order reflections from planes with $h + k + l$ odd. The presence of such reflection on Laue photographs eliminates such arrangements.

For oxygen atoms at (e) and iron atoms at (a) and (b), first-order reflections from planes with $h + k + l$ odd are due entirely to oxygen atoms, and the range of possible values of the oxygen parameter u can be limited by a consideration of their intensities. This consideration does not involve any assumption regarding the relative reflecting powers of different atoms. The structure factor S for these planes is given by the equation $S = 2\bar{O}[\sin 2\pi(h-k)u + \sin 2\pi(k-l)u + \sin 2\pi(l-h)u]$. The value of S for a plane reflecting in the first order more strongly than another plane with the same or larger interplanar distance must be greater than that for the second plane. Reference to Fig. 1 shows that the intensity relations $(\bar{1}31) > (032)$ and $(456) > (\overline{326})$ observed on Laue photographs (Table II) are effective in limiting u to the region between 0.286 and 0.40.

Within this region the comparison $(\bar{3}6\bar{2}) > (\overline{326})$ is also effective, requiring that u be less than 0.360. For this range of values of u, from 0.286 to 0.364, S for (154) is less than S for (0.53) if iron atoms are at

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[10] Wyckoff, "The Analytical Expression of the Results of the Theory of Space-Groups," *Carnegie Inst. Pub.*, No. **318**, pp. 153–157 (1922).

(a) and (b); the observation that (154) reflects much more strongly than (053) accordingly eliminates this arrangement.

For planes with $h + k + l$ even,

$$S = 4\overline{\text{Fe}} \cos 2\pi(h + k + l)\text{w} + 2\overline{\text{O}}\ [\cos 2\pi(h - k)\text{u} + \cos 2\pi(k - l)\text{u} + \cos 2\pi(l - h)\text{u}]$$

In calculating values of S we have taken the relative reflecting powers of iron and oxygen atoms approximately proportional to 23 and 10, the

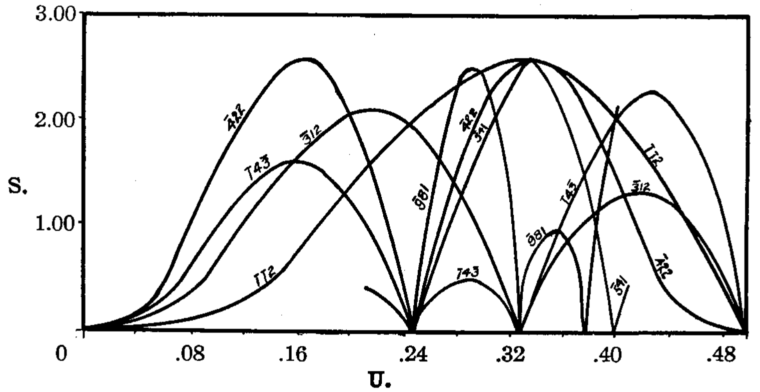

Fig. 1.—Curves showing values of the structure factor S for planes with $h + k + l$ odd; the numbers on each curve signify values of $h-k$, $k-l$ and $l - h$; for example, $\bar{4}22$ gives values of S for all planes with $h + k + l$ odd and with $h - k = -4$, $k - l = 2$, and $l - h = 2$.

electron-numbers of the ionized atoms. The second-order reflection from (110) (Table I) is stronger than the first-order reflection; w is

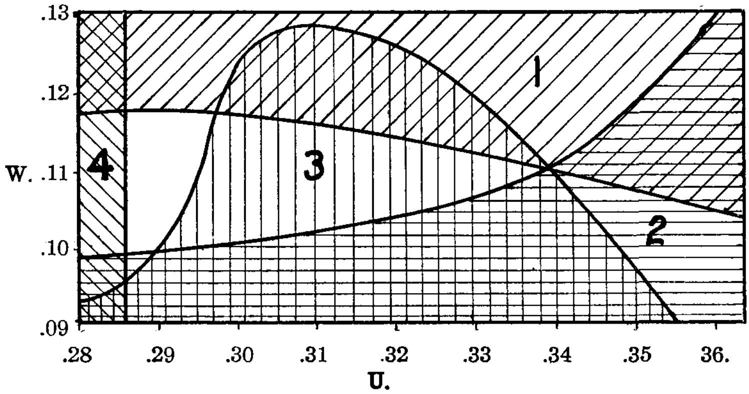

Fig. 2.—The shaded areas represent values of the parameters u and w for hematite excluded by the following comparisons: 1, (154) > (053); 2, (194) > $(\bar{4}3\bar{5})$; 3, $(\bar{4}1\bar{7})$ > $(\bar{4}3\bar{5})$; 4, comparisons from planes with $h+k+l$ odd.

accordingly restricted to the range between 0.07 and 0.17. With the range of values of u previously obtained, the following intensity inequalities observed on Laue photographs restrict w to the region between 0.095 and 0.120: (275) > (567); (154) > (053); (789) > $(\bar{4}3\bar{5})$; $(\bar{4}3\bar{5})$ > (174); $(\bar{5}0\bar{9})$ > $(\bar{5}2\bar{7})$; $(\bar{4}1\bar{7})$ > $(\bar{4}3\bar{5})$; (9.9.10) > $(\bar{1}81)$; and (194) > $(\bar{4}3\bar{5})$. Moreover, as shown in Fig. 2, these data further limit u to the region between 0.287 and 0.297, and w to between 0.098 and 0.115. By means of the intensity relations (4.3.11) > (5.1.10), (578) > $(\bar{4}05)$, $(\bar{4}3\bar{5})$ > (497), and (497) > (678), w is still further restricted to between 0.1040 and 0.107.

It is probable that the reflecting power of an atom compared with that of another atom with a smaller electron number is somewhat greater than the value calculated assuming proportionality with the first power of the electron number. We have considered the effect on the calculated values of S of increasing the relative reflecting power of iron, and have found that the assumption that an iron atom reflects as much as 50% more strongly than indicated by its electron number does not invalidate the above limitation of the parameters u and w. For Table II the structure factor S_1 is calculated on the assumption of direct proportionality between reflecting power and electron number, S_2 involves an increase of 25% in the reflecting power of iron, and S_3 an increase of 50%. The observed data are not well explained on the assumption of direct proportionality, and the consequent increase in the reflecting power of iron, in conjunction with the comparisons used above, requires a decrease of the upper limit of w to about 0.106.

TABLE III

SPECTRAL PHOTOGRAPHIC DATA FOR CORUNDUM

Line	Order of reflection	Angle of reflection	$\frac{d_{111}}{n}$	Estimated intensity
		DATA FROM (111), CEYLON CORUNDUM		
			Å.	
γ	n	8° 13′	2.170	vvw
β	n	8 22	2.170	w
α_1	n	9 22.7	2.172	m
α_2	n	9 25.7	2.175	mw
γ	$2n$	16 38	2.165	vw
β	$2n$	16 56	2.168	m
		DATA FROM (110), MASSIVE CORUNDUM		
			$\frac{d_{110}}{n}$	
γ	n	5° 8.6′	3.454	vw
β	n	5 13.3	3.468	mw
α_1	n	5 51	3.480	ms
α_2	n	5 53	3.475	m
γ	$2n$	10 17.3	3.473	w
β	$2n$	10 28.3	3.474	m
α_1	$2n$	11 45.2	3.479	s
α_2	$2n$	11 49.7	3.478	ms

We accordingly adopt for the oxygen parameter u the value 0.292 ± 0.007, and for the iron parameter w the value 0.1050 ± 0.0010.

The Structure of Corundum

Photographic Data.—The observations obtained by the spectrographic and the Laue methods are presented in Tables III and IV, respectively.

TABLE IV

LAUE PHOTOGRAPHIC DATA FROM CEYLON CORUNDUM

Incident beam at small angles with the normal to (111). Structure factors calculated for u = 0.303, w = 0.1050.

hkl	d_{hkl} Å.	$n\lambda$ Å.	Estimated intensity	S_1	S_2	S_3
$02\bar{1}$[a]	1.582	0.39	0.4	0.87	0.87	0.87
$\bar{1}31$[a]	1.173	.35	.6	2.21	2.21	2.21
...	..	..	...	..	..	..
$\bar{1}34$	0.848	.38	1.0	2.46	2.80	3.14
$\bar{1}54$	.687	.37	0.1	0.16	0.43	0.70
$16\bar{1}$	.642	.38	1.0	2.43	2.77	3.11
$34\bar{3}$	.631	.36	0.5	0.94	1.38	1.82
037	.614	.37	1.6	3.70	4.18	4.66
071	.599	.36	0.4	1.88	2.15	2.42
$5\bar{2}4$	.599	.42	.05	0.65	0.65	0.65
$6\bar{1}\bar{1}$	.591	.37	.04	.70	0.26	0.18
$6\bar{2}1$	.586	.38	.05	1.10	1.10	1.10
$53\bar{3}$	.572	.40	.1	1.99	1.99	1.99
$3\bar{1}7$	.562	.35	.1	1.48	1.48	1.48
$45\bar{3}$	.541	.35	.4	1.85	2.19	2.53
239	.532	.45	.2	1.15	1.64	2.13
$\bar{1}47$	.532	.28	.04	0.87	1.35	1.83
$6\bar{2}5$	.523	.39	.04	1.17	1.17	1.17
$7\bar{2}2$	.518	.38	.08	1.86	1.86	1.86
$3\bar{1}8$	.499	.30	.06	1.00	1.48	1.96
169	.486	.42	.3	1.88	2.09	2.30
$5\bar{1}8$	.479	.37	.08	0.98	0.95	0.92
$7\bar{3}2$	.475	.29	.06	2.38	2.72	3.06
1.3.10	.452	.30	.07	2.16	2.65	3.14
1.5.10	.450	.35	.06	1.75	1.96	2.17

[a] These two planes are from Photograph No. 1; the remainder from No. 2.

The Atomic Arrangement.—The same transformation of axes as for hematite is found necessary in order to account for the Laue data for corundum; from the spectral data the smallest rhombohedral unit is found to have a = 5.12 ± 0.01 Å., and α = 55° 17′, and to contain two Al_2O_3. The density from these data is 3.96; the directly determined value is 3.99.

The Laue data for corundum (Table IV) are similar to those for hematite. By the arguments previously given the correct space group is seen to be D_{3d}^6, and the possible arrangements are accordingly those listed above. First-order reflections were observed from planes with $h + k + l$ odd, eliminating any arrangement with oxygen atoms at (d). The observation that $(\bar{1}31)$ reflected more strongly than $(02\bar{1})$ limits the oxygen parameter u in (e) to the region 0 to 0.20, or that of 0.28 to 0.40. We have found that the Laue data in Table IV eliminate the 0 to 0.20 region. The following comparisons from planes with $h + k + l$ odd, due to oxygen atoms alone, definitely limit u to between 0.296 and 0.310: $(53\bar{3}) > (5\bar{2}4)$, $\therefore 0.28 < u < 0.33$; $(7\bar{2}2) > (6\bar{2}5)$, $\therefore 0.28 < u < 0.310$; and $(3\bar{1}7) > (6\bar{2}1)$, $\therefore 0.296 < u$.

For this range of values of u the structure factor for $(\bar{1}54)$ is much greater than that for (037), if aluminum atoms are at (a) and (b); the observation that the latter plane reflects much more strongly than the former despite its smaller interplanar distance accordingly eliminates this arrangement.

As shown in Table III, the second-order reflection from (110) is much stronger than the first-order reflection; this requires that the value of the aluminum parameter in (c) lie between about 0.075 and 0.20. The following comparisons restrict w to between 0.095 and 0.108: $(45\bar{3}) > (6\bar{1}\bar{1})$, $(34\bar{3}) > (\bar{1}54)$, and $(169) > (239)$. Moreover, a further limitation of the range of possible values of u and w can be made; the intensity relations $(3\bar{1}8) > (\bar{1}47)$, $(1.3.10) > (7\bar{3}2)$, and $(169) > (7\bar{2}2)$ require that u lie between 0.300 and 0.306, and that w lie between 0.1040 and 0.1060.

In calculating the values of S_1 given in Table IV, the relative reflecting powers of aluminum and oxygen atoms have been taken as proportional to the electron numbers of the ions, namely, 10 and 10; S_2 and S_3 have been calculated on the basis of an increase of 25% and 50%, respectively, in the reflecting power of aluminum. The comparisons used above in limiting u to 0.303 ± 0.003 and w to 0.1050 ± 0.0010 are not invalidated by assuming that the reflecting power of aluminum is as much as 50% greater than that of oxygen.

Discussion of the Structures

The arrangement of atoms in the units of structure of hematite and corundum is shown in Fig. 3. The values derived for the oxygen parameter u give for the smallest oxygen-oxygen distance the values 2.545 ± 0.060 Å. and 2.495 ± 0.025 Å., respectively. These relatively large distances show the effect of the mutual repulsion of similarly charged ions. It is noteworthy that these distances are larger than the oxygen-oxygen distances in calcite[11] (2.16 Å.) and in sodium nitrate[12] (2.19 Å.), in which the three oxygen atoms are grouped about an atom of carbon or nitrogen (at O).

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[11] Wyckoff, *Am. J. Sci.*, **50,** 317 (1920).

[12] Wyckoff, *Phys. Rev.*, **16,** 149 (1920).

The distance between the oxygen atom A and the point O is 1.470 ± 0.035 Å. for hematite, and 1.385 ± 0.020 Å. for corundum. From these the oxygen-iron distances are found to be 2.060 ± 0.035 Å. (A to B or C) and 1.985 ± 0.025 Å. (A to D or E); and the oxygen-aluminum distances to be 1.990 ± 0.020 Å. and 1.845 ± 0.015 Å.

Each metal atom is surrounded by six oxygen atoms, which are not at the corners of a regular octahedron. Three of these oxygen atoms are a few per cent. nearer the metal atom than the other three, indicating that the location of the electrons in the outer shells of an ion causes it to have different effective radii in different directions. The difference between the two oxygen-metal distances is 0.075 ± 0.060 Å. for hematite, and 0.145 ± 0.035 Å. for corundum; this is in agreement with the conception that an iron ion, with 23 electrons within a volume only slightly greater than that of an aluminum ion with 10 electrons, would approximate a sphere much more closely than the aluminum ion.

Each oxygen atom is surrounded by four metal atoms, two of which are nearer than the other two. These atoms are not at the corners of a regular tetrahedron; the angle between the line connecting atoms B and C and that connecting D and E is about 60°, instead of 90° as in a regular tetrahedron.

The structures determined for hematite and corundum show that these crystals consist of a compact arrangement of approximately, but not exactly, spherical ions of oxygen and of iron or aluminum, held together by inter-ionic forces which are probably electrostatic in nature. No evidence of molecular grouping is observed.

The value 2.73 Å. for the distance between aluminum atoms B and C in ruby deduced[3] with the aid of empirical quantitative laws from the spectrometrically measured relative intensities of different orders of reflection from (111) is in agreement with the value 2.74 ± 0.03 Å. determined by us. However, we have found that the hypothesis of a constant aluminum-oxygen distance is incorrect, and the value 1.33 Å. for the A to O distance

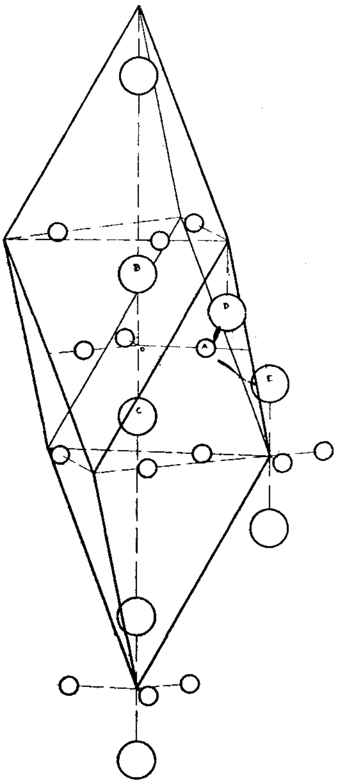

Fig. 3.—The arrangement of atoms in the units of structure of hematite and corundum; small circles represent atoms of oxygen, large circles atoms of iron or aluminum.

(Fig. 3) obtained[8] through the use of this hypothesis is also wrong. The distance 1.440 ± 0.015 Å. determined by us is not completely outside of the range 1.45 to 1.58 Å. for A to O, which has been calculated to be necessary in order to account for the observed birefringence of ruby.[4]

Summary

The crystal structures of hematite and corundum have been determined through the use of Laue and spectral photographs, interpreted with the aid of the theory of space groups. The unit of structure is a rhombohedron with $\alpha = 55° 17'$ and $a = 5.420 \pm 0.010$ Å. for hematite, and with $\alpha = 55° 17'$ and $a = 5.120 \pm 0.010$ Å. for corundum. The space group underlying the atomic arrangement is D_{3d}^6.

The data require that atoms of iron or aluminum be located at www, $\bar{w}\bar{w}\bar{w}$, $\frac{1}{2}-w\,\frac{1}{2}-w\,\frac{1}{2}-w$, $w+\frac{1}{2}\,w+\frac{1}{2}\,w+\frac{1}{2}$, and atoms of oxygen at $u\bar{u}0$, $\bar{u}0u$, $0u\bar{u}$, $\frac{1}{2}-u\;u+\frac{1}{2}\;\frac{1}{2}$, $u+\frac{1}{2}\;\frac{1}{2}\;\frac{1}{2}-u$, $\frac{1}{2}\;\frac{1}{2}-u\;u+\frac{1}{2}$, with $u = 0.292 \pm 0.007$ and $w = 0.1050 \pm 0.0010$ for hematite and $u = 0.303 \pm 0.003$ and $w = 0.1050 \pm 0.0010$ for corundum. These structures show that crystals of hematite and corundum consist of a compact arrangement of approximately but not exactly spherical ions, as shown in Fig. 3. The derived inter-atomic distances in Ångström units are as follows.

	Hematite	Corundum
Smallest oxygen-oxygen distance............	2.545±0.060	2.495±0.025
Metal-oxygen distance (B or C to A)........	2.060± .035	1.990± .020
Metal-oxygen distance (D or E to A)........	1.985± .025	1.845± .015

PASADENA, CALIFORNIA

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[Contribution from the Gates Chemical Laboratory, California Institute of Technology, No. 57]

THE CRYSTAL STRUCTURE OF BARITE

By Linus Pauling and Paul H. Emmett

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Introduction

Barite, $BaSO_4$, a member of a large class of isomorphous crystals, is described by Groth[1] as orthorhombic bipyramidal, with axial ratios $a{:}b{:}c$ = 0.8152:1:1.3136. This crystal has been recently investigated by Allison[2] by means of X-rays. The axial ratios were redetermined by goniometric measurements, using X-rays instead of visible light, and the values 0.8148:1:1.3131 were obtained. Spectrometric measurements were made from thirteen planes, using a tungsten tube operated at 90,000 volts; and values of d/n were then calculated from the angles of reflection of the tungsten lines and the barium K absorption edge. The conclusions drawn from the data as to the structure of the crystal seem, however, to be clearly erroneous. For the author bases the determination of the unit of structure upon the assumption that the unit must have the crystallographic axial ratios, which in fact result from an arbitrary choice of a parametral plane from among the many permitted by the crystallographic data. Moreover, his derived unit of structure is inconsistent with his data, in that he gives in Table IV for plane (102) $d_{\text{calcd.}} = 2.792$ and $d_{\text{obs.}} = 5.562$; yet his observation shows that $d/n = 5.562$; and this obviously requires that $d = 5.562\,n$, where n is an integer, and hence does not permit that $d = {}^1/_2 \times 5.562$ as calculated (approximately) from his unit of structure.[3] The

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[1] Groth, "Chemische Krystallographie," Engelmann, Leipzig, **1908**, Vol. II, p. 388.

[2] S. K. Allison, *Am. J. Sci.*, [5] **8**, 261 (1924).

[3] The author is aware that there is a difficulty here, for he states that this result from (102) may be due to some "accidental" arrangement of atoms; however, it is not possible with any arrangement of atoms in his unit to explain the observed reflection. The analogy suggested to (100) of succinic acid and (010) of succinic anhydride [Yardley, *Proc. Roy. Soc.*, **105A,** 451 (1924)] is not pertinent, for in these cases $d_{\text{calcd.}}$ is twice $d/n_{\text{obs.}}$, not one-half of it.

author's conclusion as to the space group involved is also invalidated, since it is based on his unit of structure.

It has seemed to us desirable, therefore, to investigate anew the crystal structure of this substance, utilizing data obtained from Laue as well as from spectral photographs. This research was made with the help of a grant made to Professor A. A. Noyes by the Carnegie Institution of Washington, for which we wish to express our appreciation.

The Experimental Method

Spectral photographs were taken of the K-radiation of molybdenum reflected from the faces (100), (010) and (001) of a natural crystal. These faces were previously roughened by grinding with fine carborundum and oil; the face (100), which was not developed, was ground normal to the other two pinacoids. Reflections from (100) of calcite were taken at the same time for calibration. The data are given in Table I. The lines have the following wave lengths in Ångström units: molybdenum $K\alpha_1$, 0.7078; α_2, 0.7121; β, 0.6311; γ 0.6197.

TABLE I

SPECTRAL PHOTOGRAPHIC DATA FROM BARITE

(*hkl*)	Order of reflection	Line	Angle of reflection	d/n Å.	Estimated intensity
(100)	*n*	γ	4° 1.0′	4.429	vw
	n	β	4 6.0	4.411	m
	n	α_1	4 35.4	4.425	s
	n	α_2	4 37.0	4.422	ms
	2*n*	γ	8 3.5	4.420	vvw
	2*n*	β	8 12.7	4.419	vw
	2*n*	α_1	9 12.5	4.425	mw
	2*n*	α_2	9 16.4	4.420	w
	3*n*	β	12 22.4	4.414	vvw
	3*n*	α_1	13 52.5	4.429	mw
	3*n*	α_2	13 58.7	4.426	w
(010)	*n*	β	6 41	2.715	vvw
	n	α_1	7 30.1	2.712	s
	n	α_2	7 31.7	2.718	ms
	2*n*	β	13 27.4	2.712	mw
	2*n*	α_1	15 6.5	2.717	s
	2*n*	α_2	15 12.5	2.715	ms
(001)	*n*	γ	4 59.8	3.557	vvw
	n	β	5 5.0	3.562	mw
	n	α_1	5 42.0	3.564	s
	n	α_2	5 44.2	3.561	s
	2*n*	γ	10 2.3	3.555	vvw
	2*n*	β	10 12.3	3.562	w
	2*n*	α_1	11 27.9	3.560	m
	2*n*	α_2	11 32.1	3.551	w

[a] The abbreviations signify: s, strong; ms, medium strong; m, medium; mw, medium weak; w, weak; vw, very weak; vvw, very very weak.

Laue photographs[4] were made with the incident beam at small angles with the normal to (001), the crystal slips used being cleaved along (001) from the large specimen. The radiation had a minimum wave length of 0.24 Å., for the tungsten tube used was operated at a peak voltage of about 52,000 volts. Gnomonic projections were used in interpreting the photographs. Laue data are given in Tables II and III.

TABLE II

LAUE PHOTOGRAPHIC DATA FROM BARITE: PHOTOGRAPH 1

hkl	d_{hkl} Å.	$n\lambda$ Å.	Estimated intensity[a]	*hkl*	d_{hkl} Å.	$n\lambda$ Å.	Estimated intensity
$1\bar{4}1$	1.407	0.42	a	$\bar{9}11$	0.960	0.40	0.4
$6\bar{1}1$	1.400	.34	5	$\bar{9}\bar{1}1$	.960	.38	.4
$3\bar{4}1$	1.285	.29	0.02	$\bar{1}\bar{6}2$	.931	.42	1.3
341	1.285	.42	1.6	$\bar{4}61$	.881	.30	0.01
$\bar{4}\bar{4}1$	1.199	.42	1.6	$5\bar{6}3$	.802	.42	1.0
$\bar{2}51$	1.114	.42	3	$\bar{9}\bar{4}2$	.793	.41	0.6
251	1.114	.33	0.1	$\overline{10}.\bar{3}.2$	.785	.42	.1
$\bar{2}\bar{5}1$	1.114	.30	.05	943	.770	.42	.05
$\bar{7}31$	1.048	.39	.2	$\bar{9}52$	.735	.40	.1
$\bar{6}41$	1.025	.42	.3	$\overline{11}.3.2$	.728	.41	.8
$7\bar{3}2$	1.016	.41	1.6	$\overline{13}.1.2$	.664	.34	.05

[a] a signifies absent.

The Unit of Structure

Spectral data in Table I give for d/n for (100), (010) and (001), values of 4.423, 2.715 and 3.55 Å. On assigning indices on the basis of the unit obtained by putting $n = 1$ in each case and calculating values of $n\lambda$, a number of planes such as $(\bar{7}\bar{3}1)$, $(\bar{9}\bar{1}1)$, $(\bar{4}61)$, $(\overline{13}.1.2)$, etc., gave values less than 0.24 Å., eliminating this unit, and all units in which $n = 1$ for one or two of the pinacoids. The smallest unit which accounts for these observed reflections is obtained by taking $n = 2$ for each of the pinacoids; this unit has $d_{100} = 8.846$, $d_{010} = 5.430$, and $d_{001} = 7.10$ Å. This unit accounts completely for all Laue data obtained, and may accordingly be accepted as the correct one. The amount of data accounted for is shown by the fact that on one Laue photograph over 200 planes, belonging to 90 different forms, gave first-order reflections. Representative data are given in Table II, in which indices refer to the axes of this unit. It is to be noted that these indices may be obtained from those based on the usual crystallographic axes by doubling *h*.

The number of molecules in this unit is four, corresponding to the density 4.51, which is in good agreement with the directly determined values[1] 4.48 to 4.50. The density calculated from the values of d/n obtained

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[4] A reproduction of a Laue photograph through (001) of barite has been published by Wyckoff, "The Structure of Crystals," The Chemical Catalog Co., New York, **1924**, p. 110.

spectrometrically by Allison[2] is 4.43. We have estimated the probable error in our spectrographic observations to be less than 0.1%; the agreement in calculated density and the directly determined values (which in general tend to be low) verifies this estimate.[5]

The Space Lattice and the Space Group

Observed first-order reflections from planes with one or two indices even, with the sum of all three indices even, and with the sum of any two indices even (Table II) require[6] that the lattice underlying the structure be the simple orthorhombic lattice Γ_0. The types of prism planes giving first-order reflections (Table III) are such as to eliminate definitely all of the holohedral space groups[7] V_h^1 to V_h^{16} (2Di−1 to 2Di−16) based on this lattice except V_h^1, V_h^5, V_h^{13} and V_h^{16}.

TABLE III

LAUE PHOTOGRAPHIC DATA FROM BARITE. PRISM PLANES

Photograph 1				Photograph 2			
hkl	d_{hkl} Å.	$n\lambda$ Å.	Estimated intensity	hkl	d_{hkl} Å.	$n\lambda$ Å.	Estimated intensity
$\bar{3}10$	2.630	0.38	a	$\bar{2}10$	3.520	0.34	6.0
$\bar{4}10$	2.070	.32	2.5	120	2.770	.36	a
$0\bar{4}1$	1.430	.45	a	130	1.896	.38	a
051	1.150	.40	0.4	140	1.439	.29	a
902	0.994	.39	1.0	701	1.245	.38	0.05
10.0.3	.829	.46	0.02	052	1.110	.44	a
072	.811	.38	a	801	1.094	.39	0.2
11.0.2	.784	.46	a	061	0.962	.43	a
11.0.3	.733	.37	1.0	$0\bar{7}4$	.753	.46	a
				11.0.3	.733	.43	1.5

The observed data show that all types of planes with $k = 0$ give first-order reflections, those with $h = 0$ do so only if $k + l$ is even, and those with $l = 0$ only if h is even. These data render space groups V_h^1, V_h^5 and V_h^{13} improbable, for these space groups require the absence of first-order reflections from certain planes in no prism zone, or in only one, and accordingly do not account for all the observed absences. Space group V_h^{16} permits first-order reflections from all types of planes with $h = 0$, from those with $k = 0$ only if $h + l$ is even, and from those with $l = 0$ only if k is even. This space group, which completely explains the experimental observations, is accepted as correct. It is to be noted that to change from indices (***hkl***) used in this paper to those $(hkl)_{SG}$ based on the assignment

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[5] The agreement between $d_{\text{calcd.}}$ and $d_{\text{obs.}}$ given in Table IV of the previous research is such as to indicate a probable error somewhat greater than 0.1% in the spectrometric observations reported.

[6] Pauling and Dickinson, THIS JOURNAL, **46**, 1615 (1924).

[7] R. W. G. Wyckoff, "The Analytical Expression of the Results of the Theory of Space-Groups," *Carnegie Inst. Pub.*, No. 318, **1922**.

of axes to V_h^{16} in the course of the development of the theory of space groups, the transformation $h = k_{SG}$, $k = h_{SG}$, $l = l_{SG}$ is required.

A complete determination of the atomic arrangement is impracticable at this time, because of the number of parameters involved. An attempt was made to determine the location of barium atoms alone, using the statistical treatment of intensities successfully applied to uranyl nitrate hexahydrate.[6] This treatment should be applicable, since the structure factors for barite are made up mainly of the barium term, on account of the large relative reflecting power of this heavy atom. The possible arrangements of the four barium atoms in the unit are[7]

(a) $\frac{1}{4}\,\frac{1}{4}\,0,\ \frac{3}{4}\,\frac{1}{4}\,0,\ \frac{3}{4}\,\frac{3}{4}\,\frac{1}{2},\ \frac{1}{4}\,\frac{3}{4}\,\frac{1}{2};$
(b) $\frac{1}{4}\,\frac{1}{4}\,\frac{1}{2},\ \frac{3}{4}\,\frac{1}{4}\,\frac{1}{2},\ \frac{3}{4}\,\frac{3}{4}\,0,\ \frac{1}{4}\,\frac{3}{4}\,0;$
(c) $0\,u\,v,\ \frac{1}{2}\,\frac{1}{2}-u\,\bar{v},\ 0\,u+\frac{1}{2}\,\frac{1}{2}-v,\ \frac{1}{2}\,\bar{u}\,v+\frac{1}{2}.$

For arrangements (a) and (b) the structure factor in the first order is $4\overline{\mathrm{Ba}}$ for planes with h_{SG} even and $k_{SG} + l_{SG}$ even, and 0 for all other planes. These arrangements are definitely eliminated by the experimental data; for example, $(\bar{4}11)_{SG}$ is absent, and $(5\bar{2}1)_{SG}$, with smaller interplanar distance, reflects very strongly at the same wave length. Such wide discrepancies cannot be explained as due to the effect of sulfur and oxygen atoms. The barium atoms are, therefore, located as in (c). Because of the presence of other atoms no attempt was made to determine the two parameters involved.

Summary

It is shown by Laue and spectral photographs, interpreted with the aid of the theory of space-groups, that the unit of structure of the orthorhombic crystal barite ($BaSO_4$) has $d_{100} = 8.846$, $d_{010} = 5.430$ and $d_{001} = 7.10$ Å., and contains $4BaSO_4$. These conclusions are not in accord with those previously drawn by Allison. The data further require that the structure be based on the simple orthorhombic lattice Γ_0. A consideration of prism reflections led to the assignment of this crystal to space group V_h^{16}. The general arrangement of the four barium atoms was determined, but the two parameters defining their exact locations were not evaluated.

PASADENA, CALIFORNIA

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Über die Kristallstruktur der kubischen Tellursäure.

Von

L. Merle Kirkpatrick und **Linus Pauling**[1]) in Pasadena.

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[1]) National Research Fellow, U. S. A.

Einleitung.

Die Tellursäure, $Te(OH)_6$, bildet sowohl kubische als auch monokline Kristalle[2]. Wir haben die Struktur der kubischen Kristalle unter Benützung von spektralen und Laueschen Aufnahmen studiert und sind dann mittels der Theorie der Raumgruppen zu gewissen Schlußfolgerungen gelangt.

Das TeO_3 wurde aus Tellur durch Behandlung mit Salpetersäure und Chromsäureanhydrid erhalten. Bei langsamer Abkühlung einer heißen Lösung von TeO_3 in Salpetersäure (spez. Gew. 1,32) kristallisierten kleine Oktaeder von $Te(OH)_6$ auf den Wänden der Flasche aus. Sie waren optisch isotrop. Wir arbeiteten mit Kristallen, deren längste Kante kleiner als 0,3 mm ist. Es ist bemerkenswert, daß so kleine Kristalle sehr gute Aufnahmen geben.

Die Röntgenmethoden, welche wir benutzten, sind von R. W. G. Wyckoff[3] beschrieben worden. Die Spektren zeigten die K-Strahlung von Molybdän, reflektiert an Ebenen der rotierenden Kristalle.

Die Laueschen Aufnahmen wurden mit der Röntgenstrahlung einer Wolfram-Antikathode erhalten. Der Kristall bedeckte vollständig die hintere der beiden das Strahlenbündel begrenzenden Spalten. Die Zugehörigkeit der Indizes zu den verschiedenen spiegelnden Ebenen wurde mit Hilfe von gnomonischer Projektion gefunden.

Die Durchführung dieser Arbeit wurde ermöglicht durch die Freundlichkeit des Herrn Prof. A. A. Noyes, der uns mit den, ihm von der Carnegie Institution of Washington zur Verfügung gestellten Geldmitteln unterstützte.

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[2] Groth, »Chemische Kristallographie«, Engelmann, Leipzig. **1**, 123 (1906)

[3] R. W. G. Wyckoff, »The Structure of Crystals«, The Chemical Catalog Co., New York, 109—177 (1924).

Der Elementarbereich.

Die in Tabelle 1 angegebenen spektralen Daten betr. (110) liefern für $\frac{d_{100}}{n}$ den Wert 3,87 Å.

Tabelle 1.

	Linie von *Mo*	Abbeugungswinkel	d_{110}/n	Geschätzte Intensität
n	$K_\beta = 0{,}6311$ Å	6° 33,5′	2,762 Å	2,5
n	$K_\alpha = 0{,}710$	7 22,5	2,769	6
$2n$	$K_\beta = 0{,}6311$	13 14,2	2,755	1
$2n$	$K_{\alpha_1} = 0{,}7018$	14 53,2	2,755	2,5
$2n$	$K_{\alpha_2} = 0{,}7121$	14 57,6	2,756	2

Die Zahlen in Tabelle 2 sind einer Laueaufnahme entnommen. Da die maximale Röhrenspannung 40 k. v. betrug, war die kurzwellige Grenze des einfallenden Bündels gleich 0,31 Å. Um die Lage der Flecken dieser Aufnahme zu erklären, müssen wir n gleich 4 setzen. Die Würfelzelle, die man erhält, hat eine Kantenlänge $d_{100} = 15{,}48$ Å. Da keine Anzeichen, die auf einen größeren Bereich hindeuten, entdeckt werden konnten, werden wir den genannten Würfel als den wahren Elementarbereich betrachten. Auf dieser Basis sind die Werte in Tabelle 2 berechnet.

Tabelle 2.

hkl	n	d_{hkl}/n	λ	Geschätzte Intensität
$5\bar{3}\bar{1}$	1	2,62 Å	0,41 Å	4
$\bar{5}33$	1	2,36	,43	ab.
$\bar{5}51$	1	2,17	,44	ab.
$0\bar{2}3$	2	2,15	,52	ab.
$\bar{3}7\bar{3}$	1	1,89	,40	ab.
$4\bar{2}\bar{1}$	2	1,69	,31	ab.
$4\bar{1}\bar{2}$	2	1,69	,41	0,05
$5\bar{7}5$	1	1,56	,40	ab.
$\bar{3}40$	2	1,55	,44	ab.
$7\bar{7}3$	1	1,50	,46	ab.
$\bar{5}\bar{1}9$	1	1,50	,43	ab.
$5\bar{7}7$	1	1,40	,61	ab.
$91\bar{7}$	1	1,35	,43	0,3
$3\bar{4}3$	2	1,33	,42	0,8
$\bar{4}33$	2	1,33	,53	0,4
$0\bar{3}5$	2	1,33	,42	0,1
$11.\bar{5}.\bar{1}$	1	1,28	,55	0,1
$57\bar{9}$	1	1,24	,41	ab.
$\bar{5}.11.\bar{3}$	1	1,24	,43	0,125
$51\bar{4}$	2	1,19	,42	ab.
$\bar{1}.11.7$	1	1,18	,40	ab.
$43\bar{5}$	2	1,10	,40	0,05
$25\bar{5}$	2	1,06	,40	ab.
$4\bar{5}4$	2	1,03	,39	0,15
$\bar{2}\bar{2}7$	2	1,03	,40	0,1

Die Dichte der Metalle wurde nach der Methode von Retgers zu 3,12 g/cm³ bestimmt. Dieser Wert ist etwas größer als ein früher (3,053 g/cm³) gegebener. Nimmt man 32 $Te(OH)_6$ im gefundenen Elementarbereich an, so ergibt sich die Dichte zu 3,26 g/cm, was in genügender Übereinstimmung mit der gefundenen Größe steht.

Das Gitter und die Raumgruppe.

Keine der Laueaufnahmen zeigte Reflexionen erster Ordnung mit Ausnahme von Ebenen, deren Indizes alle ungerade sind. Es ist also äußerst wahrscheinlich, daß die Struktur sich durch ein kubisches flächenzentriertes Gitter Γ_c' beschreiben läßt. Eine weitere Laueaufnahme, bei welcher das einfallende Bündel um wenige Grade gegen [111] geneigt war, ließ auf eine Symmetrieebene schließen, welche die dreizählige Achse enthält. Die Struktur ist daher isomorph mit der Punktgruppe T_d, O oder O_h.

Die möglichen Raumgruppen, vereinbar mit diesen Begrenzungen, sind T_d^2, T_d^5, O^3, O^4, O_h^5, O_h^6, O_h^7 und O_h^8. Man kann zwischen diesen mit Hilfe von Raumgruppenkriterien¹) entscheiden. Keine Reflexe erster Ordnung von Ebenen, deren Indizes alle ungerade sind, wobei zugleich $h = \pm k$ ist, wurden beobachtet, obgleich Ebenen der Formen {533}, {551}, {733}, {755}, {11.3.3}, {775} und {955} in der Lage waren, zu reflektieren. Die einzigen Raumgruppen, welche diese Abwesenheit erklären, sind T_d^5, O_h^6 und O_h^8. Überdies wurden keine Reflexe zweiter Ordnung von Ebenen der Form $\{0kl\}$ mit geradem k und ungeradem l beobachtet, obwohl Ebenen der Form {023}, {043} und {047} solche hätten erzeugen können. Die Raumgruppen T_d^5 und O_h^6 erklären diesen zweiten Ausfall nicht, O_h^8 andererseits verlangt sie; danach zeigen die Röntgenergebnisse, daß man die Kristalle der Raumgruppe O_h^8 zuteilen muß.

Die Atomanordnung.

Der Elementarbereich wird von 32 *Te*-, 192 *O*- und 192 *H*-Atomen aufgebaut. Eine Tabelle der Ergebnisse der Theorie der Raumgruppen²) zeigt, daß die Raumgruppe O_h^8 alle möglichen Stellen für diese Atome enthält. Nimmt man an, daß alle Atome derselben Art kristallographisch äquivalent sind, dann bestehen zwei Möglichkeiten, die *Te*-Atome zu ordnen:

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1) Verw. **2**, 219.

2) R. W. G. Wyckoff, »The Analytical Representation of the Results of the Theory of Space Groups« Publications Carnegie Institution No. 318 (1922).

32d. $\frac{1}{8}\,\frac{1}{8}\,\frac{1}{8};\ \frac{1}{8}\,\frac{7}{8}\,\frac{7}{8};\ \frac{7}{8}\,\frac{1}{8}\,\frac{7}{8};\ \frac{7}{8}\,\frac{7}{8}\,\frac{1}{8};$
$\frac{3}{8}\,\frac{1}{8}\,\frac{3}{8};\ \frac{1}{8}\,\frac{3}{8}\,\frac{3}{8};\ \frac{3}{8}\,\frac{3}{8}\,\frac{1}{8};\ \frac{5}{8}\,\frac{5}{8}\,\frac{5}{8};$
$\frac{5}{8}\,\frac{7}{8}\,\frac{7}{8};\ \frac{7}{8}\,\frac{5}{8}\,\frac{7}{8};\ \frac{7}{8}\,\frac{7}{8}\,\frac{5}{8};\ \frac{3}{8}\,\frac{5}{8}\,\frac{3}{8};$
$\frac{5}{8}\,\frac{3}{8}\,\frac{3}{8};\ \frac{3}{8}\,\frac{3}{8}\,\frac{5}{8};\ \frac{5}{8}\,\frac{5}{8}\,\frac{1}{8};\ \frac{5}{8}\,\frac{3}{8}\,\frac{1}{8};$
$\frac{3}{8}\,\frac{5}{8}\,\frac{7}{8};\ \frac{7}{8}\,\frac{5}{8}\,\frac{3}{8};\ \frac{5}{8}\,\frac{7}{8}\,\frac{3}{8};\ \frac{1}{8}\,\frac{1}{8}\,\frac{5}{8};$
$\frac{1}{8}\,\frac{3}{8}\,\frac{7}{8};\ \frac{3}{8}\,\frac{1}{8}\,\frac{7}{8};\ \frac{7}{8}\,\frac{1}{8}\,\frac{3}{8};\ \frac{1}{8}\,\frac{7}{8}\,\frac{3}{8};$
$\frac{5}{8}\,\frac{1}{8}\,\frac{5}{8};\ \frac{3}{8}\,\frac{7}{8}\,\frac{5}{8};\ \frac{7}{8}\,\frac{3}{8}\,\frac{5}{8};\ \frac{1}{8}\,\frac{5}{8}\,\frac{1}{8};$
$\frac{3}{8}\,\frac{7}{8}\,\frac{1}{8};\ \frac{7}{8}\,\frac{3}{8}\,\frac{1}{8};\ \frac{1}{8}\,\frac{5}{8}\,\frac{5}{8};\ \frac{5}{8}\,\frac{1}{8}\,\frac{1}{8};$

32e. $\frac{3}{8}\,\frac{3}{8}\,\frac{3}{8};\ \frac{7}{8}\,\frac{7}{8}\,\frac{7}{8};\ \frac{7}{8}\,\frac{7}{8}\,\frac{3}{8};\ \frac{3}{8}\,\frac{3}{8}\,\frac{7}{8};$
$\frac{7}{8}\,\frac{3}{8}\,\frac{7}{8};\ \frac{3}{8}\,\frac{7}{8}\,\frac{3}{8};\ \frac{3}{8}\,\frac{7}{8}\,\frac{7}{8};\ \frac{7}{8}\,\frac{3}{8}\,\frac{3}{8};$
$\frac{3}{8}\,\frac{5}{8}\,\frac{5}{8};\ \frac{5}{8}\,\frac{7}{8}\,\frac{5}{8};\ \frac{3}{8}\,\frac{1}{8}\,\frac{1}{8};\ \frac{1}{8}\,\frac{7}{8}\,\frac{1}{8};$
$\frac{7}{8}\,\frac{1}{8}\,\frac{5}{8};\ \frac{1}{8}\,\frac{3}{8}\,\frac{5}{8};\ \frac{7}{8}\,\frac{5}{8}\,\frac{1}{8};\ \frac{5}{8}\,\frac{3}{8}\,\frac{1}{8};$
$\frac{5}{8}\,\frac{3}{8}\,\frac{5}{8};\ \frac{7}{8}\,\frac{5}{8}\,\frac{5}{8};\ \frac{1}{8}\,\frac{3}{8}\,\frac{1}{8};\ \frac{7}{8}\,\frac{1}{8}\,\frac{1}{8};$
$\frac{1}{8}\,\frac{7}{8}\,\frac{5}{8};\ \frac{3}{8}\,\frac{1}{8}\,\frac{5}{8};\ \frac{5}{8}\,\frac{7}{8}\,\frac{1}{8};\ \frac{3}{8}\,\frac{5}{8}\,\frac{1}{8};$
$\frac{5}{8}\,\frac{5}{8}\,\frac{3}{8};\ \frac{5}{8}\,\frac{5}{8}\,\frac{7}{8};\ \frac{1}{8}\,\frac{1}{8}\,\frac{3}{8};\ \frac{1}{8}\,\frac{1}{8}\,\frac{7}{8};$
$\frac{1}{8}\,\frac{5}{8}\,\frac{7}{8};\ \frac{1}{8}\,\frac{5}{8}\,\frac{3}{8};\ \frac{5}{8}\,\frac{1}{8}\,\frac{7}{8};\ \frac{5}{8}\,\frac{1}{8}\,\frac{3}{8};$

die *O*- und die *H*-Atome werden den allgemeinen Stellungen zugeteilt.

Man bemerkt, daß 32d sich von 32e nur durch eine Translation der ganzen Anordnung unterscheidet. In beiden Fällen kann man sagen, daß der größere Würfel aufgebaut wird von acht kleineren Würfeln, deren jeder vier *Te*-Atome in einer flächenzentrierten Anordnung enthält. Der Kristall erscheint daher zusammengesetzt aus annähernd kugelförmigen $Te(OH)_6$-Molekülen in dichtester Packung.

Weder in 32d noch in 32e tragen die *Te*-Atome zur Reflexion in erster Ordnung von Ebenen bei, deren Indizes alle ungerade sind, ebensowenig haben sie Anteil an der Reflexion zweiter Ordnung von anderen Ebenen. In diesem Falle sind nämlich die Glieder, welche das *Te* enthalten, durch Verschwinden des Strukturfaktors $S = \sqrt{A^2 + B^2}$ ausgeschaltet. Es bedeutet $A = \sum^i R_i \cos 2\pi n\,(hx_i + ky_i + lx_i)$ und $B = \sum^i R_i \sin 2\pi n\,(hx_i + ky_i + lx_i)$, wo R_i das Streuungsvermögen des Atoms mit den Koordinaten $x_i y_i x_i$ ist. Die Summe ist über alle Atome im Elementarbereich zu erstrecken. Da die *H*-Atome äußerst kleine Reflexionsvermögen besitzen, sollte es möglich sein, die Stellungen der *O*-Atome mit Hilfe von Intensitäten der Reflexion an diesen Ebenen zu bestimmen. Obgleich wir ausgedehnte Rechnungen vornahmen, konnten wir die drei Parameter, welche diese Stellungen charakterisieren, nicht finden.

Mit den *Te*-Atomen in 32d oder 32e ist die Punktgruppensymmetrie des Moleküls C_{3i} bzw. D_3[1] verbunden. Dies ist eher in Einklang mit der Formel $Te(OH)_6$ als mit $H_2TeO_4 \cdot 2H_2O$. Die erstere wird auch durch andere Tatsachen gestützt[2]. Es erscheint vernünftig, die sechs *O*-Atome symmetrisch (Oktaeder) um das *Te*-Atom anzuordnen.

Es ist indessen zu bemerken, daß, mangels einer wirklich vollständigen Bestimmung der Atomanordnung, über die Gestalt des Moleküles nichts genaueres ausgesagt werden kann.

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[1] Niggli, »Geometrische Kristallographie des Diskontinuums.« Leipzig, Bornträger. 411 (1919).

[2] Baker u. Aldam, Journ. Chem. Soc. **99**, 507 (1911).

Zusammenfassung.

Wir studierten die Kristallstruktur der kubischen Tellursäure mit Hilfe von Röntgenaufnahmen (Laueschen sowie spektralen) und interpretierten diese auf Grund der Theorie der Raumgruppen. Die Struktur wird als ein kubisches flächenzentriertes Gitter Γ'_c beschrieben, dessen Elementarwürfel (enthaltend 32 $Te(OH)_6$) eine Kantenlänge $d_{100} = 15{,}48$ Å aufweist. Die Isomorphie mit T_d, O und O_h wird gezeigt. Die Interpretation der Laueaufnahme ergibt, daß die Struktur der Raumgruppe O_h^8 zugeordnet werden muß. Zum Schluß wird noch kurz die gegenseitige Anordnung der Atome diskutiert.

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The crystal structure of brookite.

By

Linus Pauling and **J. H. Sturdivant** in Pasadena.

(With 6 figures.)

I. Introduction.

In the study of the structure of a crystal with X-rays the effort has been made by many workers, especially **Wyckoff** and **Dickinson** in America, to eliminate rigorously all but one of the possible atomic arrangements consistent with the smallest unit of structure permitted by the experimental data, without reference to whether or not the arrangements were chemically reasonable or were in accord with assumed interatomic distances. The importance of this procedure arises from the certainty with which its results can be accepted. For although structure determinations by less rigorous methods have been found to be false, no important error has yet been detected in any investigation which interpreted photographic data solely with space-group theory aided by merely qualitative assumptions regarding the factors affecting the intensity of X-ray reflection. It would accordingly be desirable to conduct all structure determinations by this method; but unfortunately the labor involved in its application to complex crystals, involving more than a very few parameters, makes this impossible. Furthermore, if several different atoms are present in the structure, it is often necessary to make quantitative assumptions regarding their relative reflecting powers, so that for this reason too the rigorous method cannot be used.

But complex crystals are of great interest, and it is desirable that structure determinations be carried out for them even at the sacrifice of rigor. The method which has been applied in these cases is this: one atomic arrangement among all of the possible ones is chosen, and its agreement with the experimental data is then examined. If the agreement is complete or extensive, it is assumed that the structure is the correct one. Striking regularities in the intensities of reflection from simple planes may suggest an approximate structure. This occurred in

Dickinson's study of tin tetraiodide¹); he then considered values of the five parameters involved which differed only slightly from those suggested by the intensities of simple reflections, and found a set giving complete agreement with the Laue photographic data. On account of the large amount of experimental information accounted for by it, this structure can be confidently accepted as correct. In other cases it is necessary to make use quantitatively of relative reflecting powers or F-curves, and often agreement is found between the assumed structure and data from rotation photographs or ionization chamber measurements only; then the structure can usually be accepted as approximately correct, the uncertainty depending upon the paucity of the experimental data or the lack of agreement with them.

As a result of the recent increase in knowledge of the effective radii of various ions in crystals, Professor W. L. Bragg has suggested and applied²) a simple and useful theory leading to the selection of possible structures. His fundamental hypothesis is this: if a crystal is composed of large ions and small ions, its structure will approximate a close-packed arrangement of the large ions alone, with the small ions tucked away in the interstices. In case all of the close-packed positions are not occupied by large ions an open structure results. To apply this theory one determines the unit of structure in the usual way, and finds by trial some close-packed arrangement of the large ions of known radius (usually oxygen ions with a crystal radius of about 1,35 Å) compatible with this unit. The other ions are then introduced into the possible positions in such a way as to give agreement with the observed intensities, and if necessary the large ions are shifted somewhat from the close-packed positions. With the aid of this close-packing method Bragg and his co-workers have made a promising attack on the important problem of the structure of the silicate minerals.

During the investigation of the structure of brookite, the orthorhombic form of titanium dioxide, another method of predicting a possible structure for ionic compounds was developed. This method, which is described in detail in Section III of this paper, depends on the assumption of a coordination structure. It leads to a number of possible simple structures, for each of which the size of the unit of structure, the space-group symmetry, and the positions of all ions are fixed. In some cases, but not all, these structures correspond to close-packing of the large ions; when they do, the method further indicates

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1) R. G. Dickinson, J. Am. Chem. Soc. **45**, 958. 1923.

2) W. L. Bragg and G. B. Brown, Pr. Roy. Soc., A, **110**, 34. 1926; W. L. Bragg and J. West, ibid., A, **114**, 450. 1927.

the amount and nature of the distortion from the close-packed arrangement.

The general method of investigation which we used is the following. Spectral photographs from the three pinacoids provided accurate dimensions of the possible units of structure. Data from Laue photographs then led to the determination of the smallest allowable unit, and the presence and absence of reflections on Laue photographs served as criteria in finding the space-group symmetry. (Laue photographs rather than rotation photographs were used because the chance of error in assigning indices to Laue spots is very small[1].) On applying the coordination theory we found that one of the predicted structures had the same space-group symmetry and unit of structure as the crystal itself. The predicted parameter values agreed reasonably well with the intensities of reflections on rotation photographs, and better agreement was obtained by changing one of the nine parameters slightly. On account of lack of knowledge of F-curves the intensities of Laue spots were not accounted for.

II. The unit of structure and space-group.

Three forms of titanium dioxide, TiO_2, are known. Of these the crystal structures of the two tetragonal forms, rutile and anatase, have been thoroughly investigated[2]; in each case only one parameter is involved, and the atomic arrangement has been accurately determined. The third form, brookite, is orthorhombic, with axial ratios

$$0{,}8416 : 1 : 0{,}9444.$$

Data obtained from photographs of the K-radiation of molybdenum reflected from the ground pinacoids of a brookite crystal (variety arkansite from Magnet Cove, Ark.)[3] are given in Table I. These lead to a unit with $d_{100}/n_1 = 2{,}291$ Å, $d_{010}/n_2 = 2{,}718$ Å, and $d_{001}/n_3 = 1{,}284$ Å, in which n_1, n_2, and n_3 are the orders of reflection of the first lines on the photographs. Laue photographs were taken with the incident beam of X-rays at various small angles with the normal to (100) of a thin plate of brookite tabular on {100} (from Riedertobel, Uri Canton,

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[1] As an example of an incorrect space-group determination resulting from error in assigning indices to reflections on rotation photographs mention may be made of the assignment of olivine to V_h^5 by Rinne, Leonhardt, and Hentschel (Z. Krist. **59**, 548. 1924). Bragg and Brown (Z. Krist. **63**, 538. 1926) determined the space-group of olivine to be V_h^{16} and pointed out the source of the previous error.

[2] L. Vegard, Phil. Mag. **1**, 1151. 1926; G. Greenwood, ibid. **48**, 654. 1924; M. L. Huggins, Phys. Rev. **27**, 638. 1926.

[3] We are indebted to Mr. René Engel for the crystals used in this research.

Table I.

Spectral data.

(hkl)	Order of Reflection	Line (MoK)	Angle of Reflection	d/n
(100)	$2n_1$	β	7°54,5′	4,586 Å
	$2n_1$	α	8 53,5	4,592
	$3n_1$	α_1	13 24	4,580
	$3n_1$	α_2	13 29	4,581
	$4n_1$	γ	15 41	4,585
	$4n_1$	β	15 59	4,583
	$4n_1$	α_1	17 59	4,584
	$4n_1$	α_2	18 6	4,582
(010)	n_2	β	6 40	2,718
	n_2	α	7 30,5	2,716
	$2n_2$	γ	13 11	2,718
	$2n_2$	β	13 25	2,720
	$2n_2$	α_1	15 5	2,721
	$2n_2$	α_2	15 11	2,718
(001)	n_3	γ	13 58	1,2835
	n_3	β	14 14	1,2833
	n_3	α_1	16 0	1,2841
	n_3	α_2	16 6	1,2840

Switzerland). The short wave-length limit of X-radiation present in the incident beam was 0,24 Å; values of $n\lambda$ calculated for Laue spots on the basis of the unit obtained by putting $n_1 = n_2 = n_3 = 1$ were found often to be much smaller than 0,24 Å, so that this unit cannot be the correct one. The smallest unit which will account for the Laue data is that with $n_1 = 4$, $n_2 = 2$, $n_3 = 4$; i. e., with[1])

$$d_{100} = 9{,}166\ \text{Å},\quad d_{010} = 5{,}436\ \text{Å},\quad d_{001} = 5{,}135\ \text{Å}.$$

The presence of all observed Laue spots, produced by planes belonging to over two hundred different forms, is accounted for by this unit. (Representative Laue data are recorded in Table II.) No evidence was found for the existence of a larger unit; hence this unit may be accepted as the true one. All indices used in this paper (including Table II) are referred to the axes of this unit of structure. The unit contains $8\,TiO_2$; the density calculated from the X-ray data is 4,12, within the range 4,03—4,22 of the experimental determinations reported in Groth,

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[1] During the preparation of this manuscript, a note has appeared (A. Schröder, Z. Krist. **66**, 493. 1928) giving the dimensions of the unit of structure for brookite as $a = 9{,}136 \pm 0{,}02$, $b = 5{,}439 \pm 0{,}01$, $c = 5{,}153 \pm 0{,}03$ Å. No space-group determination or discussion of the atomic arrangement was reported.

Table II.

Laue data for $n\lambda$ between 0,35 and 0,45 Å.

(hkl)	d_{hkl}	$n\lambda$	Estimated intensity
2 $\bar{4}$ 1	1,25 Å	0,42 Å	0,02
2 1 $\bar{4}$	1,20	,36	,5
1 4 $\bar{2}$	1,18	,44	,8
1 $\bar{2}$ 4	1,15	,44	,1
3 $\bar{4}$ $\bar{2}$	1,11	,37	,5
2 $\bar{4}$ 3	1,03	,40	a
2 3 $\bar{4}$	1,02	,37	1
3 $\bar{5}$ 1	1,00	,41	0,3
1 $\bar{1}$ 5	1,00	,44	,01
1 5 $\bar{2}$	0,99	,36	,1
4 $\bar{4}$ $\bar{3}$	,96	,42	,2
3 1 $\bar{5}$	,95	,36	,2
1 $\bar{2}$ 5	,95	,35	,1
2 5 $\bar{3}$	,89	,42	,4
4 $\bar{2}$ $\bar{5}$	,88	,35	,8
3 $\bar{5}$ 3	,87	,40	,5
2 $\bar{3}$ 5	,87	,41	,05
3 3 $\bar{5}$	,85	,38	,05
1 $\bar{1}$ 6	,84	,35	,15
1 1 6	,84	,43	,2
4 $\bar{6}$ 1	,83	,39	,15
5 $\bar{5}$ $\bar{3}$	,82	,41	,2
5 $\bar{6}$ $\bar{1}$	,80	,43	,1
3 $\bar{5}$ 4	,80	,37	,02
3 5 $\bar{4}$	,80	,43	,03
1 6 3	,79	,45	,2
5 $\bar{6}$ $\bar{2}$	,77	,36	,15
1 3 6	,77	,42	,2
2 7 $\bar{1}$	,75	,43	,05
1 5 5	,74	,42	,02
1 7 2	,74	,39	,2
1 4 6	,72	,40	,2
5 3 $\bar{6}$	,71	,45	,05
1 2 7	,70	,36	,1
2 $\bar{2}$ 7	,70	,35	,01
2 2 7	,70	,45	,05
3 $\bar{2}$ 7	,69	,44	,15
3 7 $\bar{3}$	,68	,40	,05
5 $\bar{7}$ 2	,68	,37	,05
7 $\bar{3}$ $\bar{6}$	,66	,43	,1
7 $\bar{7}$ $\bar{1}$	,66	,45	a
2 7 4	,65	,44	0,2
3 8 $\bar{1}$	,65	,44	,05

Table II (cont.).

(hkl)	d_{hkl}	$n\lambda$	Estimated intensity
$4\ 6\ \bar{5}$	0,65 Å	0,38 Å	0,1
$7\ \bar{7}\ \bar{2}$	,64	,41	,15
$7\ \bar{1}\ \bar{7}$	,63	,41	,1
$7\ \bar{2}\ \bar{7}$	,62	,37	,03
$6\ \bar{7}\ 4$	,61	,41	,1
$5\ \bar{4}\ 7$	,61	,45	,05
$4\ 8\ \bar{3}$	,60	,41	,03
$2\ 3\ 8$	,60	,37	,1
$5\ 6\ \bar{6}$	,59	,36	,02
$7\ \bar{8}\ 3$	,57	,39	,04
$3\ 7\ 6$	,56	,43	,05
$7\ 5\ \bar{7}$	,55	,41	,05
$9\ \bar{4}\ \bar{7}$	,54	,38	,02
$4\ 2\ 9$	,54	,43	,03
$4\ 4\ 9$	,51	,41	,03
$5 \cdot 10 \cdot 2$	,51	,45	,02
$5 \cdot 10 \cdot \bar{2}$	,51	,39	,02
$10 \cdot \bar{1} \cdot \bar{9}$	,47	,36	,02
$10 \cdot 1 \cdot \bar{9}$	,47	,38	,03

and in good agreement with the experimental value 4,125 obtained by Schröder.

The presence of first-order reflections from all types of pyramidal planes (Table II) eliminates from consideration all space-groups based on any but the simple orthorhombic lattice Γ_0. Of these the following are further definitely eliminated[1]) by the occurrence of first-order reflections from the prism planes given in Table III:

$$C_{2v}^3,\ C_{2v}^6,\ C_{2v}^7,\ C_{2v}^8,\ C_{2v}^9,\ C_{2v}^{10},$$
$$V_h^2,\ V_h^4,\ V_h^6,\ V_h^7,\ V_h^8,\ V_h^9,\ V_h^{10},\ V_h^{12},\ V_h^{13},\ V_h^{14},\ V_h^{16}.$$

If the structure is based on one of the space-groups

$$C_{2v}^1,\ C_{2v}^2,\ C_{2v}^4,\ C_{2v}^5,\ V^1,\ V^2,\ V^3,\ V^4,\ V_h^1,\ V_h^3,\ V_h^5, \text{ or } V_h^{11},$$

it is very difficult to account for the fact that no first-order reflections were observed from planes with $h = 0$ and k odd, $k = 0$ and l odd, or $l = 0$ and h odd; these space-groups may accordingly be removed from consideration. But just these absences are required for any arrangement derived from V_h^{15}, which may hence be accepted as the correct space-group.

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[1]) Space-group criteria are given by Bozorth and Pauling, J. Am. Chem. Soc. **47**, 1568. 1925. Cf. also references in ootnote 13, ibid.

Table III.

Prism reflections.

a) Incident beam normal to (100).

(*hkl*)	d_{hkl}	$n\lambda$	Estimated intensity
1 4 0	1,33 Å	0,43 Å	a
1 0 4	1,26	,33	0,15
1 0 $\bar{4}$	1,26	,37	,20
2 0 5	1,00	,43	a
2 0 $\bar{5}$	1,00	,45	a
2 7 0	0,76	,28	0,03
4 7 0	,73	,49	a
4 $\bar{7}$ 0	,73	,44	a
4 0 $\bar{7}$	,70	,42	a
5 0 $\bar{8}$	,60	,41	0,02
b) Crystal tipped 14°			
0 3 1	1,70	0,47	a
0 3 2	1,47	,44	a
0 2 3	1,44	,42	3,5
0 4 1	1,31	,35	1,2
1 5 0	1,07	,48	a
0 4 3	1,06	,32	1,8
0 3 4	1,04	,31	a
1 0 5	1,01	,43	a
1 0 6	,85	,33	0,3
0 5 4	,82	,24	a
0 4 5	,81	,24	a
2 7 0	,76	,41	0,6
6 $\bar{7}$ 0	,69	,48	,2
3 0 8	,63	,38	,1
c) Crystal tipped 20°.			
0 2 $\bar{1}$	2,39	0,29	2
0 4 1	1,31	,47	1,9
0 4 $\bar{1}$	1,31	,27	0,5
0 1 4	1,24	,44	a
0 4 3	1,06	,44	0,3
0 5 1	1,06	,36	a
0 5 $\bar{1}$	1,06	,24	a
0 3 4	1,04	,43	a
3 $\bar{5}$ 0	1,02	,39	a
0 1 5	1,00	,34	a
3 0 $\bar{5}$	,97	,34	a
0 2 5	,96	,36	0,2
4 0 $\bar{5}$	,93	,49	a
1 0 6	,85	,40	0,5
0 5 4	,82	,34	a
0 4 5	,82	,33	0,1

Table III (cont.).

c) Crystal tipped 20° (cont.).

(hkl)	d_{hkl}	$n\lambda$	Estimated intensity
$5\ \bar{6}\ 0$	0,81 Å	0,47 Å	a
$5\ 0\ \bar{6}$	,77	,42	0,2
2 7 0	,76	,47	,6
1 0 7	,73	,32	a
2 0 7	,72	,43	a
$6\ \bar{7}\ 0$	,69	,42	0,17
3 0 8	,63	,43	,1
$7\ \bar{8}\ 0$	,60	,39	a
2 9 0	,59	,32	0,02
3 8 0	,50	,35	a

The coordinate positions for equivalent atoms provided by V_h^{15} are[1])

4a: $0\ 0\ 0;\ \frac{1}{2}\,\frac{1}{2}\,0;\ 0\,\frac{1}{2}\,\frac{1}{2};\ \frac{1}{2}\,0\,\frac{1}{2};$

4b: $\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2};\ 0\ 0\,\frac{1}{2};\ \frac{1}{2}\,0\ 0;\ 0\,\frac{1}{2}\,0;$

8c: $x, y, z;\ \bar{x}, \bar{y}, \bar{z};\ \frac{1}{2}+x, \frac{1}{2}-y, \bar{z};\ \frac{1}{2}-x, \frac{1}{2}+y, z;$
$\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z;\ x, \frac{1}{2}-y, \frac{1}{2}+z;\ \frac{1}{2}-x, \bar{y}, \frac{1}{2}+z;$
$\frac{1}{2}+x, y, \frac{1}{2}-z.$

Six parameters must be evaluated to determine the positions of 8 *Ti* and 16 *O* in the unit in case that both the no-parameter positions 4a and 4b are occupied, and nine parameters in case that all atoms are in positions 8c. A structure dependent on such a large number of parameters can not be determined by rigorous methods.

III. The prediction of a structure with the coordination theory.

The structures of rutile and anatase, represented in Figs. 1 and 2, seem at first sight to have very little in common beyond the fact that each is a coordination structure, with six oxygen atoms about each titanium atom and three titanium atoms about each oxygen. On closer examination, however, it is found that from a certain point of view the structures are closely similar. Let us consider as the basis of the structures an octahedron with a titanium atom at its center and an oxygen atom at each corner. The rutile and anatase structures are both made of such octahedra sharing edges and corners with each other; in rutile two edges of each octahedron are shared and in anatase four. In both crystals the titanium-oxygen distance is a constant, with

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1) R. W. G. **Wyckoff**, "The Analytical Presentation of the Results of the Theory of Space-Groups", Publ. Carnegie Institution No. 318, 1922.

the value 1,95—1,96 Å. The basic octahedra are only approximately regular; they are in both rutile and anatase deformed in such a way as to cause each shared edge to be shortened from 2,76 Å (the value for regular octahedra) to 2,50 Å, other edges being correspondingly lengthened. (The distorted octahedra occurring in rutile and in anatase are indicated in Figs. 1 and 2.) Just such a distortion is to be expected, for the Coulomb repulsion of the two quadrivalent metal ions brought near each other when an edge is shared will cause the titanium-titanium distance to increase until the repulsion of the two oxygen ions defining the shared edge becomes large enough to counteract the effect. The theoretical discussion[1] of the rutile and anatase structures with the help of the known properties of ions has led to results which are in each case in quantitative agreement with the observed contraction of shared edges.

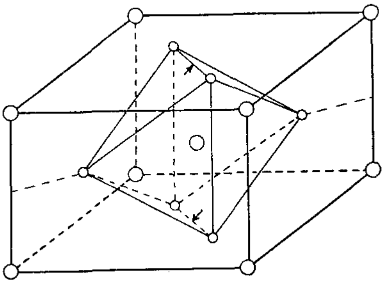

Fig. 1.

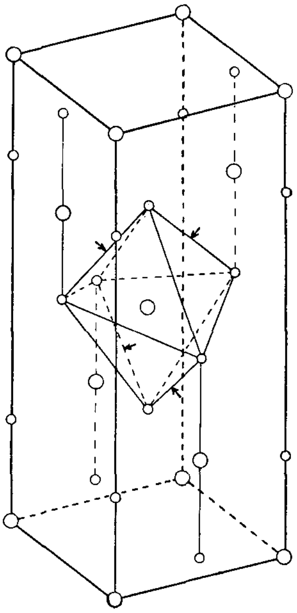

Fig. 2.

Fig. 1. The structure of rutile. Large circles represent the centers of titanium atoms, small circles those of oxygen atoms. One octahedron with oxygen atoms at its cornex and a titanium atom at its center is shown; two of its edges, those indicated by arrows, are shared with adjoining octahedra.

Fig. 2. The structure of anatase. Four edges of the octahedron shown, indicated by arrows, are shared with adjoining octahedra.

As a result of these considerations the following assumptions were made:

1. Brookite is composed of octahedra, each with a titanium atom at its center and oxygen atoms at its corners.

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[1] Linus Pauling, Z. Krist. 68, 377. 1928.

2. The octahedra share edges and corners with each other to such an extent as to give the crystal the correct chemical composition.

3. The titanium-oxygen distance throughout is about 1,95 Å. The octahedra are not regular, but are distorted in such a way as to maintain the titanium-oxygen distances constant and to shorten each shared edge to the length 2,50 Å.

An infinite number of structures satisfy these conditions. The number of simple structures, that is, structures referable to a small unit, which do so is small. We made no attempt to consider exhaustively the possible simple structures, but instead investigated the two which presented themselves first. The second of these we have found to be the structure of brookite.

In rutile there occur strings of octahedra in parallel orientation connected by shared edges; these strings, which extend in the direction of the *c*-axis, then are connected by sharing corners to form the complete crystal. This suggested that staggered strings such as are represented in Fig. 3, with two edges of each octahedron shared, might combine to form a reasonable structure. If the combination is effected by the sharing of corners alone the simple structure represented in Fig. 4 results. This structure, Structure *A*, has orthorhombic symmetry, and in fact the space-group symmetry V_h^{14}. Its unit of structure contains four octahedra ($4\,TiO_2$), and, if distortion is neglected, has the dimensions 4,79 Å, 4,51 Å, and 5,52 Å. It is not the structure of brookite.

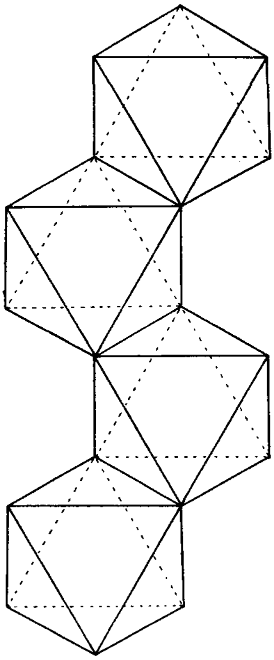

Fig. 3. A staggered string of octahedra with shared edges.

The next simplest structure built from these staggered strings results if each octahedron shares one edge with an octahedron of an adjoining string. This structure is shown in Fig. 5. It is orthorhombic, and has the space-group symmetry V_h^{15}. The unit of structure contains eight octahedra ($8\,TiO_2$). Its dimensions, if the octahedra are assumed regular with edges 2,76 Å long, are $d_{100} = 9{,}02$ Å, $d_{010} = 5{,}52$ Å, and $d_{001} =$ 4,79 Å. The space-group permits cyclical but not non-cyclical permutations of these dimensions.

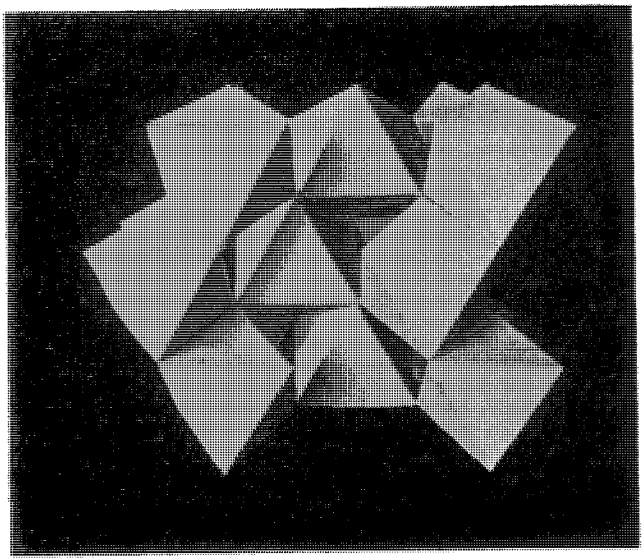

Fig. 4. A model representing a possible structure for TiO_2 (Structure *A*), composed of staggered strings of octahedra (Fig. 3) combined by sharing octahedron corners only.

Fig. 5. A photograph of the model representing the structure of brookite.

The fact that brookite also was found experimentally to have the symmetry of V_h^{15} and to have $8\,TiO_2$ in the unit suggests strongly that our second structure is to be attributed to this crystal. There is also approximate agreement (within 7%) in the dimensions of the unit. It is worthy of mention that the choice of axes for comparison is not completely arbitrary: assuming that 9,02 Å (model) is to be compared with 9,166 Å (crystal), then the space-group requires that 5,52 Å be compared with 5,436 Å and 4,79 Å with 5,135 Å.

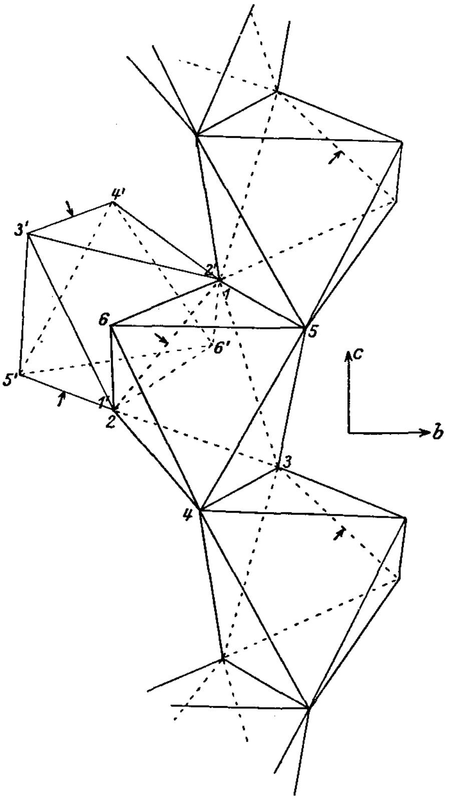

Fig. 6. A portion of the brookite structure, showing the three edges of each octahedron which are shared with adjoining octahedra, and the resulting deformation.

Since the analytical consideration of the effect of deformation appearedto be too complicated to permit its execution, the following method based upon the construction and measurement of a model was used. The basic distorted octahedron employed is shown in Fig. 6; in it all titanium-oxygen distances are equal to 1,95 Å; the three shared edges are 2,50 Å long; and the other edges are chosen so as to be distorted as little as possible from their original lengths. Such octahedra were constructed to scale (2,54 cm. = 1 Å) from heavy paper, and were then glued together to represent a section of the crystal including one unit of structure (Fig. 5). The carefully measured dimensions of the unit were found to be 23,65 cm., 14,0 cm., and 13,2 cm.; if these are reduced in the ratio 2,57 cm. = 1 Å (the increase in scale being due to incomplete coincidence of edges and corners of the octahedra) they give the values shown in Table IV, which agree within the limit of error of the measurement with the experimental values for brookite.

The suggested structure places eight titanium atoms and two groups of eight oxygen atoms each in the positions 8c, with three sets of

Table IV.

Dimensions of the unit of structure.

	d_{100}	d_{010}	d_{001}
From model, with undistorted octahedra	9,02 Å	5,52 A	4,79 A
From model, with distorted octahedra	9,20	5,45	5,13
Experimental, for brookite	9,166	5,436	5,135

parameter values. In order to predict values of these parameters the coordinates of the oxygen atoms were measured on the model, and positions were assigned the titanium atoms in the octahedra such as to make the titanium-oxygen distances nearly constant. Representing by x, y, z; ξ, η, ζ; and X, Y, Z the parameters for oxygen of the first kind, oxygen of the second kind, and titanium, respectively, the values that were predicted are

$$\begin{array}{lll} O_1 & O_2 & Ti \\ x = 0{,}010 & \xi = 0{,}230 & X = 0{,}131 \\ y = 0{,}155 & \eta = 0{,}105 & Y = 0{,}113 \\ z = 0{,}180 & \zeta = -0{,}465 & Z = -0{,}127. \end{array}$$

These may be compared with those corresponding to undistorted octahedra, namely,

$$\begin{array}{lll} O_1 & O_2 & Ti \\ x = 0{,}000 & \xi = 0{,}250 & Y = 0{,}125 \\ y = 0{,}124 & \eta = 0{,}125 & Y = 0{,}125 \\ z = 0{,}250 & \zeta = -0{,}417 & Z = -0{,}083. \end{array}$$

It is seen that the parameter changes due to distortion are considerable, being equivalent to translations of atoms as large as 0,35 Å.

IV. Testing the structure with the intensities of X-ray reflections.

A number of rotation photographs were made with molybdenum K-radiation filtered through a zirconium oxide filter to isolate the $K\alpha$ line. The positions of useful reflections, the indices of the planes producing them, and their visually estimated intensities are given in Table V. The factor placed beside the estimated intensity is a correction for the varying time of reflection, namely $\sqrt{1-(u\lambda/d\sin 2\theta)^2}$, where λ is the wave-length, and u and d represent respectively the index of the axis of rotation and the unit translation along it[1]. (A number of reflections

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[1] Ott, Z. Phys. **22**, 201. 1924.

not included in the tables occurred on each photograph; namely, those produced by planes whose traces in the developed or ground face of the crystal [the faces (100), (010), and (001) for Table V] were not perpendicular to the axis of rotation of the crystal. These reflections were not considered because of the probability that their intensities would be largely affected by absorption in the crystal.)

Table V.

Spectral reflections[1]).

a) Planes of form $(0kl)$.

1. Beam incident on (0 1 0).

$k=$	2	4	6
$l=0$	w 1	s 17	w 4

2. Beam incident on (0 0 1).

$l=$	2	4	6
$k=0$	a 0,8	mw 9	vw 5

b) Planes of form $(h0l)$.

1. Beam incident on (1 0 0)

$h=$	2	4	5	6	7	8	9	10	12	14
$l=0$	vvw 0,2	ms 3,5		w 1,7		vs 17		a 0,5	mw 8	w 5,5
$l=2$			s 0,8 12	w 0,8 3,5	mw 0,9 4	vvw 0,9 3	mw 0,9 12	a 3,5		

2. Beam incident on (0 0 1)

$l=$	2	4	6
$h=1$	m 6,5	vw 3,5	w 12
$h=2$	mw 0,9 6	a 0,6	a 2,5
$h=3$	mw 0,8 7	a 3	
$h=4$		mw 0,9 12	

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[1]) The estimated intensities of the various reflections are indicated by the abbreviations vs, very strong; s, strong; ms, medium strong; m, medium; mw, medium weak; w, weak; vw, very weak; vvw, very very weak; a, absent. The number placed below the estimated intensity for each plane gives the computed structure-factor.

c) Planes of form $\{hk0\}$.

1. Beam incident on (1 0 0)

$h =$	2	4	6	8	10
$k = 1$	s 0,7 8	vw 0,9 2	m 4	a 3	m 10
$k = 2$		w 0,8 2	a 1,5	vw 0,9 0,7	a 2,5

2. Beam incident on (0 1 0)

$k =$	1	2	3	4	5	6	7
$h = 2$	s 0,7 8	vw 0,9 2,5	s 0,9 10	a 0,8	a 5	a 6,5	a 11
$h = 4$		w 0,6 2,5	a 0,2	vw 0,9 4	a 0,4	mw 0,9 6	

Structure factors were calculated with the use of the predicted parameter values and with the assumption that the relative reflecting powers of titanium and oxygen atoms are proportional to their atomic numbers. These structure factors reproduced the salient features of the observed intensities for fifty forms; this general agreement is strong evidence that the predicted structure closely approximates the actual one. There was, however, disagreement in a few cases, when one reflection was observed to be stronger than another from a plane with larger interplanar distance despite the fact that its calculated structure factor was the smaller of the two. Accordingly, the parameter values were varied slightly, and a change of $-0{,}004$ in X was found sufficient to remove most of the points of discrepancy. Structure factors calculated for the new parameter values with the assumption of relative reflecting powers proportional to atomic numbers are included in Table V. It will be seen that when qualitative consideration is taken of the effect of other factors causing a decrease in intensity with decrease in interplanar distance, the agreement for all fifty forms is good. The changed parameter values given in Table VI may accordingly be accepted as correct.

Table VI.

Final parameter values for brookite.

O_1	O_2	Ti
$x = 0{,}010$	$\xi = 0{,}230$	$X = 0{,}127$
$y = 0{,}155$	$\eta = 0{,}105$	$Y = 0{,}113$
$z = 0{,}180$	$\zeta = -0{,}465$	$Z = -0{,}127$

The few remaining discrepancies are probably due to error in the assumed relative reflecting powers. To test this, we made use of an *F*-curve for $O^{=}$ obtained by linear extrapolation from Na^{+} and Cl^{-}, and one for Ti^{4+} from Cl^{-} and K^{+}. These *F*-curves (which are not reproduced here because of uncertainty in their derivation) lead to structure factors which are, for the same final parameter values, also in good but not complete agreement with the observed intensities. Possibly somewhat different *F*-curves (corresponding to non-linear extrapolation) would give better agreement, but because of the arbitrariness of this procedure no attempt was made to utilize it.

It is worthy of mention that the rotation photographs yield information substantiating the choice of V_h^{15} as the correct space-group. Thus no reflections occurred from {100}, {300}, {500}, {700}, {900}, {11·0·0}, {13·0·0}, {301}, {501}, {701}, {901}, {11·0·1}, {401}, {601}, {801}, {10·0·1}, {12·0·1}, etc. on one photograph recorded in Table V, although planes of all these forms were in positions favorable to reflection. Similar failures to reflect were observed on the other photographs.

On account of the lack of definite knowledge of the *F*-curves no attempt was made to account for the intensities of Laue spots.

V. Discussion of the structure and the coordination method.

The structure found for brookite is that shown in Fig. 5. Each titanium atom is surrounded by six oxygen atoms and each oxygen by three titanium atoms. The various interatomic distances, given in Table VII, are similar to those in rutile and anatase; for example, the average titanium-oxygen distance is 1,95 Å. The oxygen-oxygen distances and the distortion of the basic octahedra have been discussed in the previous sections in the course of derivation of the structure.

Table VII.

Interatomic distances in brookite.

$Ti—O_1$	1,919 Å	$O_1—O_3$	2,767 A
$Ti—O_2$	1,942	$O_2—O_3$	2,818
$Ti—O_3$	1,929	$O_2—O_4$	2,997
$Ti—O_4$	1,976	$O_2—O_6$	2,817
$Ti—O_5$	1,983	$O_3—O_5$	2,731
$Ti—O_6$	1,953	$O_3—O_4$	2,514
		$O_4—O_5$	3,012
$O_1—O_2$	2,508	$O_4—O_6$	2,833
$O_1—O_6$	2,869	$O_5—O_6$	2,743
$O_1—O_5$	2,514		

We believe that our conclusions can be accepted with considerable certainty, for the agreement between the predicted structure and the experimental results in regard to space-group symmetry, size of the unit of structure, and intensities of reflections on rotation photographs is so striking as to remove nearly completely from consideration the possibility of its being accidental.

The arrangement of the oxygen atoms approximates double hexagonal close-packing[1]. It is evident, then, that **Bragg**'s close-packing method of deriving a possible structure might have been used. But both hexagonal and double hexagonal close-packing of oxygen ions are roughly compatible with the observed unit (compare Rows 1 and 3 of Table IV). To decide between these possibilities intensity comparisons would be required, and in the absence of information regarding the nature of the deformation from regular close-packing this procedure might be very laborious. In anatase the oxygen ions approximate cubic close-packing; the axial ratio is, however, increased from 2,0 to 2,5 by deformation, and a knowledge of the size of the unit of structure would not suggest the close-packed arrangement with much certainty. Rutile provides an example of a structure which is easily derivable by means of the coordination theory, but in which the oxygen ions do not approach any type of close-packing whatever.

The close-packing method is more generally applicable in the case of crystals containing cations smaller than the titanium ion and showing correspondingly less deformation. The method is very powerful and simple, and already in the hands of Professor **Bragg** has led to a number of interesting structure determinations. The coordination method, though also simple in principle, is somewhat less easy to apply. The two methods are not distinct and mutually exclusive, but instead supplement each other and should be used together.

VI. Summary.

Brookite, TiO_2, is found with the use of **Laue** and spectral photographs to have an orthorhombic unit of structure with $d_{100} = 9{,}166$ Å, $d_{010} = 5{,}436$ Å, and $d_{001} = 5{,}135$ Å, containing $8\,TiO_2$, and to have the symmetry of space-group V_h^{15}. A structure predicted by means of the

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[1] There are three close-packed layers from which all of the infinite number of close-packed structures can be built; namely, A, with an atom at $X = 0$, $Y = 0$ (X, Y, Z being hexagonal coordinates); B, with an atom at $X = \frac{1}{3}$, $Y = \frac{2}{3}$; and C, with an atom at $X = \frac{2}{3}$, $Y = \frac{1}{3}$. For hexagonal close-packing these layers are superposed in the order $ABABAB\ldots$, for cubic close-packing in the order $ABCABC\ldots$, and for double hexagonal close-packing in the order $ABACABAC\ldots$

coordination theory had the same unit and space-group symmetry, and gave an atomic arrangement accounting for the intensities observed on rotation photographs. In this structure the eight titanium atoms and the sixteen oxygen atoms (in two groups of eight each) are in positions 8*c* with the parameter values given in Table VI. The basic unit of the arrangement is an octahedron of oxygen ions about a titanium ion; the octahedra are combined as shown in Fig. 5 so that each shares three edges with adjoining ones. Interatomic distances are given in Table VII.

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THE CRYSTAL STRUCTURE OF TOPAZ

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Communicated July 11, 1928

An investigation of the orthorhombic crystal topaz, $Al_2SiO_4F_2$, with x-rays has been reported by Leonhardt.[1] With the aid of data from Laue and rotation photographs he found for the edges of the unit of structure, containing $4Al_2SiO_4F_2$, the values $d_{100} = 4.64$ Å, $d_{010} = 8.78$ Å, and $d_{001} = 8.37$ Å, and determined the space-group of the crystal to be V_h^{16}. A deduction of the atomic arrangement, dependent on about fifteen parameters, was not attempted; for such complicated structures cannot be treated by the usual methods.

By making use of the coördination theory of ionic crystals, I have predicted a structure for topaz which agrees satisfactorily with the experimental data. This structure is described in the following paragraphs.

The coördination theory, which has been applied successfully[2] to brookite, the orthorhombic form of titanium dioxide, is based on the assumption that the anions in a crystal are constrained to assume positions about the cations such that they indicate the corners of polyhedra of which the cations mark the centers. These polyhedra are the fundamentally important constituents of the crystal; retaining their form essentially, they are combined by sharing corners, edges, and faces in such a way as to build up a crystal with the correct stoichiometrical composition. Thus in rutile, anatase, and brookite there occur octahedra of oxygen ions about titanium ions; in rutile each octahedron shares two edges with adjoining octahedra, in anatase four, and in brookite three.

The fundamental polyhedra for topaz were assumed to be an octahedron of anions (oxygen and fluorine) about each aluminum ion and a tetrahedron of oxygen ions about each silicon ion. The anion-anion distance determining the length of a polyhedron edge was taken to be 2.72 Å throughout.[3] By piling these polyhedra together one structure was found, the unit of which approximated that observed for topaz. This structure is shown in figure 1, in which four layers of polyhedra to be superimposed are represented. On considering the distribution of microscopic symmetry elements for this predicted atomic arrangement its space-group was found to be V_h^{16}. The directions of the three axes are fixed for this space-group; using Niggli's convention (used by Leonhardt also), the c-axis is normal to reflection planes, the a-axis normal to glide planes with translational component $b/2$, and the b-axis normal to glide planes with translational component $a/2 + c/2$. The edges of the unit of structure are accordingly determined: their values, assuming the octahedra and

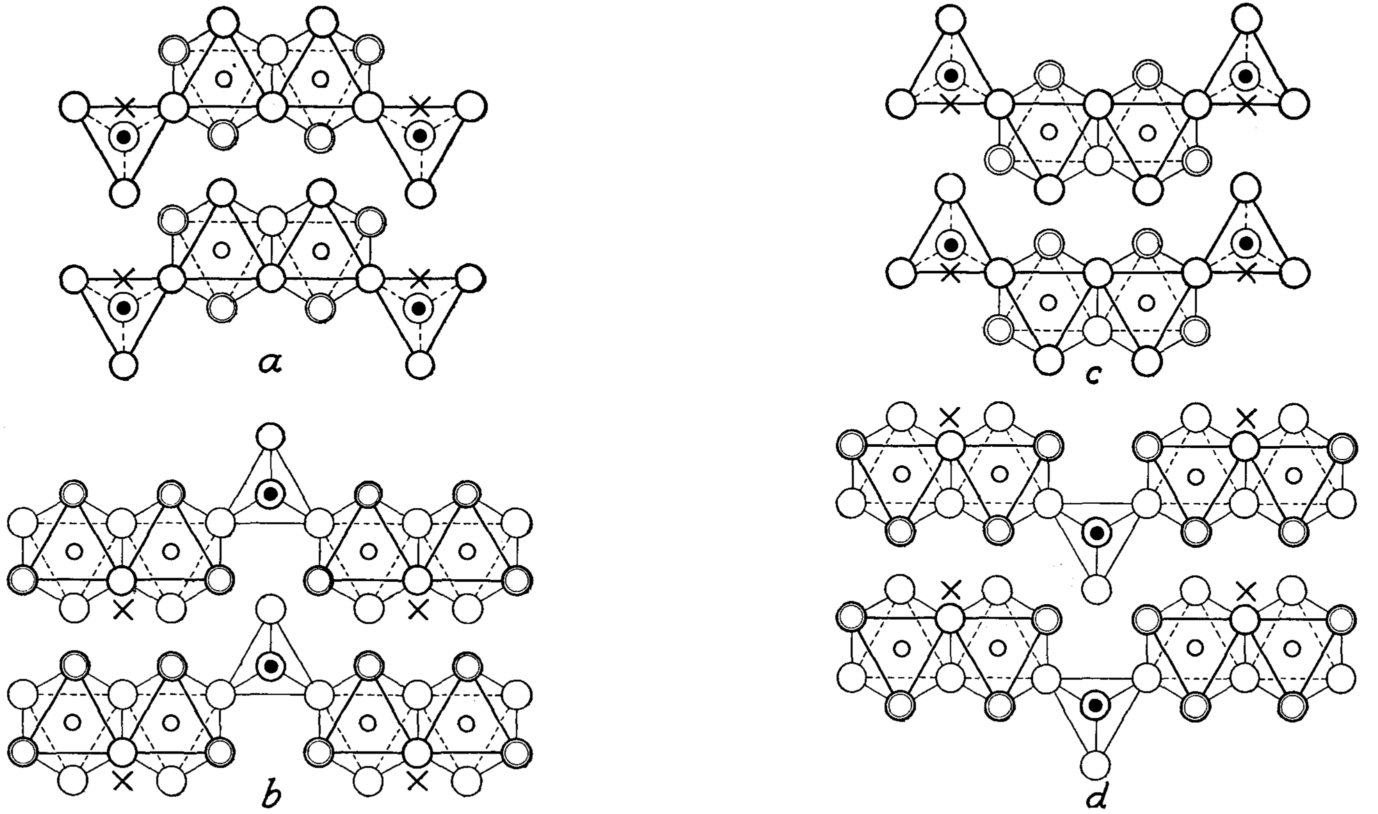

FIGURE 1

The arrangement of atoms in the crystal topaz. Large circles represent oxygen atoms, doubled large circles fluorine atoms, small open circles aluminum atoms, and small solid circles silicon atoms. The aluminum atoms are at the centers of the indicated octahedra, and the silicon atoms at the centers of tetrahedra. The four layers shown are to be superposed in the order *a*, *b*, *c*, *d*, with *d* uppermost. Crosses mark the projections of the corners of the unit of structure on the plane of the paper.

tetrahedra to be regular, are $d_{100} = 4.72$ Å, $d_{010} = 8.88$ Å and $d_{001} = 8.16$ Å. The unit contains $4Al_2SiO_4F_2$. The predicted structure leads to strong sixth order reflections from $\{100\}$ and $\{001\}$, and strong fourth and eighth order reflections from $\{010\}$, in agreement with Leonhardt's observations.

The concordance of the predicted structure and the experimental data in regard to space-group symmetry, size of unit, and intensity of reflections from the pinacoids makes it highly probable that the correct structure of topaz has been found. The effect of deformation (using the methods applied to brookite) will next be considered, leading to the more accurate determination of the atomic arrangement. It is anticipated that this consideration will result in predicted values for the edges of the unit of structure in still better agreement with the observed ones (as with brookite), and that the predicted atomic arrangement will account completely for the observed intensities of reflection of x-rays from various crystallographic planes.

The atomic positions and the parameter values for the approximate structure with undistorted polyhedra are:

$8a$: $xyz;\ x\,y\,\frac{1}{2}-z;\ \frac{1}{2}-x\,\frac{1}{2}+y\,z;\ \frac{1}{2}+x\,\frac{1}{2}-y\,\frac{1}{2}+z;\ \bar{x}\bar{y}\bar{z};\ \bar{x}\,\bar{y}\,\frac{1}{2}+z;$
$\frac{1}{2}+x\,\frac{1}{2}-y\,\bar{z};\ \frac{1}{2}-x\,\frac{1}{2}+y\,\frac{1}{2}-z.$

$4c$: $u\,v\,\frac{1}{4};\ \bar{u}\,\bar{v}\,\frac{3}{4};\ \frac{1}{2}-u\,\frac{1}{2}+v\,\frac{1}{4};\ \frac{1}{2}+u\,\frac{1}{2}-v\,\frac{3}{4}.$

4Si in $4c$ with $u = \frac{11}{12}$, $v = \frac{1}{16}$;
8Al in $8a$ with $x = \frac{1}{12}$, $y = \frac{3}{8}$, $z = \frac{1}{12}$;
8F in $8a$ with $x = \frac{1}{12}$, $y = \frac{3}{4}$, $z = \frac{1}{12}$;
8O in $8a$ with $x = \frac{3}{4}$, $y = 0$, $z = \frac{1}{12}$;
4O in $4c$ with $u = \frac{1}{4}$, $v = 0$;
4O in $4c$ with $u = \frac{11}{12}$, $v = \frac{1}{4}$.

Each aluminum octahedron shares two edges with adjoining octahedra, and the four corners (oxygen ions) defining these edges are shared with tetrahedra. The other two corners, occupied by fluorine ions, are shared with octahedra. There are present in the structure SiO_4 groups; that is, tetrahedra having no elements in common with other tetrahedra; these tetrahedra share corners alone with octahedra. The oxygen ions, although crystallographically of three kinds, are from the standpoint of the coördination theory alike, for each is attached to two aluminum octahedra and one silicon tetrahedron. Each fluorine ion is shared between two octahedra.

The arrangement of the oxygen and fluorine ions is that of double hexagonal close-packing, so that Professor W. L. Bragg's methods of close-packing the large anions[4] could be applied to this crystal. But there are very many ways of distributing the cations with this anion arrangement, and the decision among them would have to be made by the laborious comparison of observed and predicted intensities of reflection, possibly involving the consideration of distortion of the anions from the close-packed positions. Furthermore (as for brookite also), both hexagonal and double hexagonal close-packing are roughly compatible with the observed unit, increasing the number of possibilities to be considered. Bragg and West have, indeed, suggested with some reserve[4] that the anions in topaz are close-packed; their proposed type of close-packing is, however, incorrect, for it involves the identification of the hexagonal axis of the close-packed structure with the a-axis rather than the b-axis of topaz, and is, moreover, simple rather than double hexagonal close-packing.[5]

The further discussion of the structure of topaz will be published in the *Zeitschrift für Kristallographie.*

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[1] J. Leonhardt, *Zeit. f. Krist.*, **59**, 216 (1924).

[2] Linus Pauling and J. H. Sturdivant, *Ibid.*, in press.

[3] Linus Pauling, *Jour. Amer. Chem. Soc.*, **49**, 763 (1927).

[4] W. L. Bragg and J. West, *Proc. Roy. Soc.*, **A114**, 450 (1927).

[5] Bragg and West report the dimensions of the unit of structure of topaz from their measurements to be d_{100} = 4.64 Å, d_{010} = 8.79 Å, and d_{001} = 8.38 Å, in good agreement with Leonhardt's values.

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THE STRUCTURE OF THE MICAS AND RELATED MINERALS

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With the aid of the general principles[1] governing the structures of complex ionic crystals I have formulated a structure for talc, pyrophillite, the micas, and the brittle micas which is substantiated by the x-ray examination of the minerals, explains their remarkable physical properties, and leads to a general chemical formula unifying the widely varying analyses reported for different specimens. This structure is described in the following paragraphs.

The monoclinic (pseudohexagonal) unit of structure of muscovite, $KSi_3Al_3O_{10}(OH,F)_2$, has been reported by Mauguin[2] to have $a = 5.17$ Å, $b = 8.94$ Å, $c = 20.01$ Å, and $\beta = 96°$. This unit contains 4 molecules of the above composition. We have verified this with oscillation and Laue photographs of fuchsite, a variety of muscovite, the unit found having $a = 5.19$ Å, $b = 8.99$ Å, $c = 20.14$ Å, and $\beta = 96°$.

The dimensions of the unit in the basal plane closely approximate those for the similarly pseudohexagonal crystal hydrargillite, $Al(OH)_3$, as well as of the hexagonal layers in two forms of silica, β-tridymite and β-cristobalite. The monoclinic (pseudohexagonal) unit of structure of hydrargillite[3] has $a = 8.70$ Å, $b = 5.09$ Å, $c = 9.76$ Å, and $\beta = 85°29'$, and contains $8Al(OH)_3$. The crystal is composed of layers of octahedra,

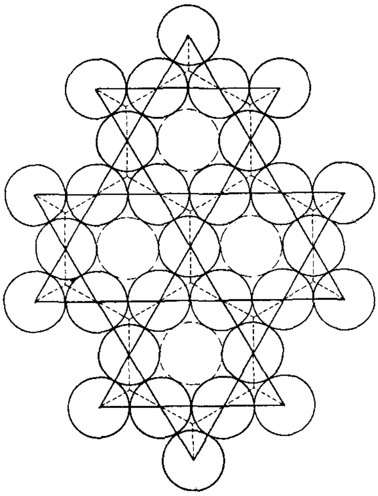

FIGURE 3

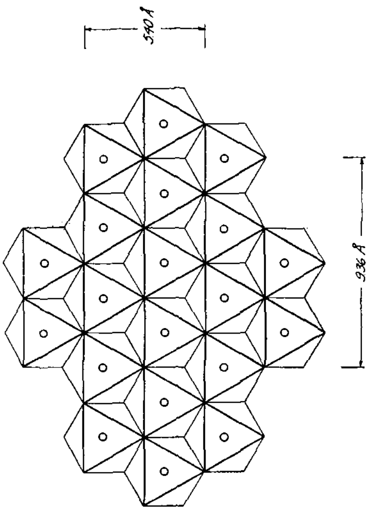

FIGURE 4

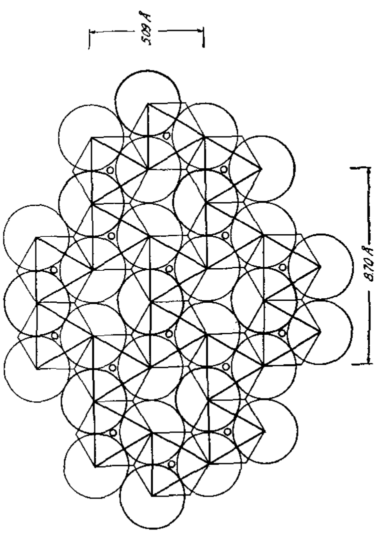

FIGURE 1

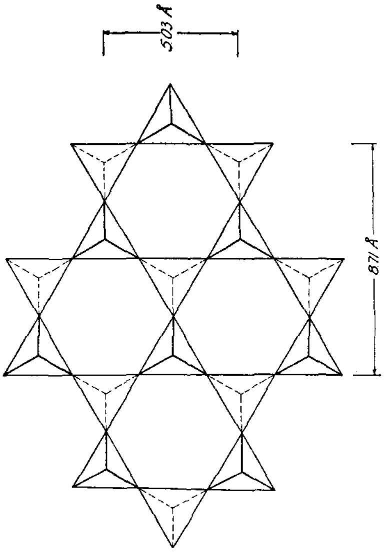

FIGURE 2

Fig. 1. A hydrargillite layer of octahedra. The light circles indicate oxygen ions, the heavier ones hydroxyl or fluorine ions in mica.

Fig. 2. A tetrahedral layer from β-cristobalite or β-tridymite. A silicon ion is located at the center of each tetrahedron, and an oxygen ion at each corner.

Fig. 3. A tetrahedral layer in which all the tetrahedra point in the same direction.

Fig. 4. A complete layer of octahedra (brucite layer).

each consisting of 6 OH^- ions grouped about an Al^{+3} ion, with each octahedron sharing three edges as shown in figure 1. The electrostatic valence rule is satisfied; each OH^- ion is held by two bonds of strength $s = {}^1/_2$. These layers are superimposed, sharing no octahedral elements with one another.

In β-tridymite and β-cristobalite[4] there are present the hexagonal layers of silicon tetrahedra shown in figure 2. Their dimensions, $a = 5.03$ Å and $b = 8.71$ Å, agree closely with those of the hydrargillite layers and of mica. Another type of tetrahedral layer with the same dimensions can be obtained by pointing all the tetrahedra in the same direction (figure 3). The oxygen ions forming the bases of the tetrahedra have their valences satisfied: the strength s of a silicon bond is 1, and each $O^=$ is held by two such bonds, giving $\Sigma s = 2$. But the oxygen ions at the unshared tetrahedral corners have $\Sigma s = 1$ only; it is hence necessary that they be held by further bonds. Now the relative positions of these tetrahedron corners are such that the tetrahedral layer can be imposed on the hydrargillite layer with the tetrahedron corners coincident with two-thirds of the shared octahedron corners; namely, those indicated in figure 1 by the large light circles. These positions are occupied by oxygen ions, which have $\Sigma s = 1 + {}^1/_2 + {}^1/_2 = 2$. The remaining positions, indicated by heavy circles, have $\Sigma s = {}^1/_2 + {}^1/_2 = 1$, and are occupied by hydroxide or fluoride ions. A similar tetrahedral layer is attached to the other side of the hydrargillite layer.

The resultant layer, with a total thickness of about 10 Å, is electrically neutral. A crystal built up by the superposition of such layers would have the composition $Si_4Al_2O_{10}(OH)_2$. It is very probable that the mineral pyrophillite, with this composition, has this structure.

Brucite, $Mg(OH)_2$, is built of complete octahedral layers such as that shown in figure 4, with dimensions not much greater than those of a hydrargillite layer, and with the octahedron corners in the same positions. A neutral layer containing tetrahedra and octahedra closely similar to that described above can be made with this complete octahedral layer in place of the hydrargillite layer; the electrostatic valence rule will be again satisfied, $O^=$ having $\Sigma s = 1 + {}^1/_3 + {}^1/_3 + {}^1/_3 = 2$ and OH^- having $\Sigma s = {}^1/_3 + {}^1/_3 + {}^1/_3 = 1$. These layers probably occur in talc, $Si_4Mg_3O_{10}(OH)_2$, which is reported to be monoclinic, pseudohexagonal, and morphologically similar to mica.

By rèplacing one-fourth of the silicon ions in a pyrophillite layer by aluminum ions, which can have the coördination number 4 as well as 6, the layers become negatively charged. To regain neutrality further positive ions must be introduced, such as K^+ or Na^+. There is room for these ions between the layers, in the pockets formed by six oxygen ions on the top of one layer and six on the bottom of the layer above. The composition of such a crystal is $K \cdot Si_3Al \cdot Al_2O_{10}(OH, F)_2$, which is the formula generally assigned to muscovite. A similar treatment of talc gives $KSi_3AlMg_3O_{10}(OH, F)_2$, which is biotite.

Pyrophillite, talc, muscovite, and biotite have the following sequence of atom-planes along the pseudo-hexagonal axes:

Pyrophillite	Talc
$6O^=$	$6O^=$
$4\ Si^{+4}$	$4\ Si^{+4}$
$4O^= + 2OH^-$	$4O^= + 2OH^-$
$4Al^{+3}$	$6Mg^{++}$
$4O^= + 2OH^-$	$4O^- + 2OH^-$
$4Si^{+4}$	$4Si^{+4}$
$6O^=$	$6O^=$

Muscovite		Biotite	
z_2 $6O^=$	Charge -2	$6O^=$	Charge -2
u $3Si^{+4} + Al^{+3}$		$3Si^{+4} + Al^{+3}$	
z_1 $4O^= + 2(OH^-, F^-)$		$4O^= + 2(OH^-, F^-)$	
Origin $4Al^{+3}$		$6Mg^{++}$	
$4O^= + 2(OH^-, F^-)$		$4O^= + 2(OH^-, F^-)$	
$3Si^{+4} + Al^{+3}$		$3Si^{+4} + Al^{+3}$	
$6O^=$		$6O^=$	
$2K^+$	$+2$	$2K^+$	$+2$
$6O^-$	-2	$6O^=$	-2
$3Si^{+4}$, etc.		$3Si^{+4}$, etc.	

The verification of the suggested structures by the comparison of the observed and calculated intensities of reflection of x-rays has been begun. So far the calculations have been carried out for 18 even orders of reflection from (001). The observed intensities given in table 2 were obtained by the visual comparison of four photographs from fuchsite, identical except for varying exposure times of 15, 90, 300, and 960 minutes. The calculated intensities were obtained from the formula

TABLE 1

ATOMIC A—VALUES

d/n =	10	5	2.5	1.0	0.75	0.60Å
A_O =	30	21	10	2.0	0.8	0.25
A_{Al} =	49	28	17	5.2	3.0	1.7
A_{Si} =	53	30	18	6.0	3.7	2.1
A_K =	72	45	24	7.8	5.0	3.2

$$I = \text{constant}\cdot A^2,$$

$$\text{with } A = \Sigma_n A_n e^{2\pi i\,(hx_n + ky + lz_n)}, \qquad (1)$$

the summation being taken over all the atoms in the unit. Values of the atomic amplitude functions[5] used are given in table 1. Assuming the group of atoms such as $4O^= + 2(OH^-, F^-)$ to depend on a single parameter, only three parameters are involved, z_1, u, and z_2. Giving the hydrargillite layer the thickness found for it in hydrargillite, and assuming the tetrahedra to be regular and 2.60 Å on an edge as in silicates in general, the parameter values $z_1 = 0.055$, $z_2 = 0.165$, and $u = 0.137$ were predicted.

The amplitude expression is

$$A = 2A_{Al} + (-1)^{l/2} A_K + (3A_{Si} + A_{Al}) \cos 2\pi lu + 6A_O(\cos 2\pi lz_1 + \cos 2\pi lz_2), \qquad (2)$$

with l having even values from 2 to 36. It was found that the values of A^2 were in general agreement with the observed intensities for the predicted parameter values. Slightly better agreement was obtained by reducing u to 0.135. The calculated intensities (the constant in equation 1 being given the arbitrary value 0.015) are included in table 2, and represented graphically together with the observed intensities in figure 5. The general agreement is striking, and lends strong support to the suggested structure.

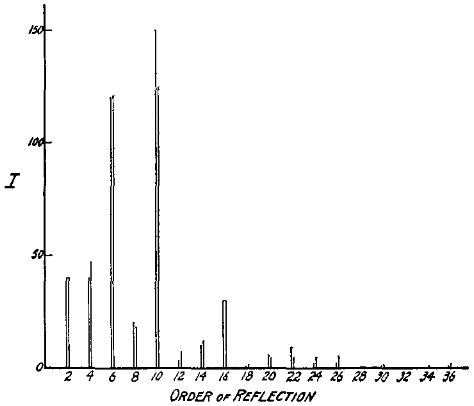

FIGURE 5

Comparison of the observed and calculated intensities of reflection of x-rays from (001) of fuchsite, in the 2nd to 36th order. In each pair of vertical lines that on the left shows the observed intensity, that on the right the calculated intensity.

TABLE 2

Observed and Calculated Intensities of Reflection from (001) of Fuchsite

ORDER OF REFLECTION	2	4	6	8	10	12	14	16	18
Observed intensity	40	40	120	20	150	3	10	30	0.5
Calculated intensity	40	47	121	18	124	7	12	30	1.4

ORDER OF REFLECTION	20	22	24	26	28	30	32	34	36
Observed intensity	6	9	2	2	0	0.8	0.1	0	1
Calculated intensity	4.3	4.5	4.8	5.2	0.0	1.6	0.2	0.6	1.7

The mica structure provides an interesting variation of the types of close-packing observed for large ions in crystals. The two central layers of $O^=$, OH^-, and F^- ions form close-packed planes with three spheres in a hexagonal unit of edge 5.2 Å, at positions 00, $^1/_3{}^2/_3$, and $^2/_3{}^1/_3$ relative to axes 120° apart. The outer layers, however, consist of oxygen ions occupying three of the four positions of a close-packed plane with four spheres in the same unit of edge 5.2 Å, at positions such as 00, $0\,^1/_2$, and $^1/_2\,0$. The insertion of a fourth sphere at $^1/_2\,^1/_2$, indicated by the dotted circles in figure 3, would complete this layer. Such a large variability in the effective dimensions of the large ions introduces some ambiguity in structure determinations involving the deduction of the type of close-packing from the size of the unit of structure.

The structure leads to a general formula for the micas: namely, $KX_nY_4O_{10}(OH,F)_2$, with $2 \leq n \leq 3$, in which X represents cations of coördination number 6 (Al^{+3}, Mg^{+}, Fe^{++}, Fe^{+3}, Mn^{++}, Mn^{+3}, Ti^{+4}, Li^{+}, etc.) and Y cations of coördination number 4 (Si^{+4}, Al^{+3}, etc.). The subscript n can have any value between 2 (hydrargillite layer) and 3 (complete octahedral layer). K^+ can be partially replaced by Na^+ and possibly to some extent by Ca^{++}. This formula represents satisfactorily the numerous recently published mica analyses almost without exception.[6] The distribution of the various ions X and Y must be such as to give general agreement with the electrostatic valence rule.

The clintonites or brittle micas have a similar structure, the layers having twice the electrical charge of those in mica, and being held together by calcium ions instead of potassium ions. The correspondingly stronger forces bring the layers closer together, the separation of adjacent layers being 9.5–9.6 Å in place of the value 9.9–10.1 Å for the micas. The general formula $CaX_nY_4O_{10}(OH, F)_2$, with $2 \leq n \leq 3$, holds for these minerals.

The physical properties of talc, pyrophillite, the micas, and the brittle micas are in agreement with the suggested structure. To tear apart one of the pseudohexagonal layers it is necessary to break the strong Si–O, Al–O, etc., bonds; as a consequence these individual layers are tough. But they can be easily separated from one another, giving rise to the pronounced basal cleavage shown by all these minerals. In talc and pyrophillite the layers are electrically neutral, and are held together only by stray electrical forces. These crystals are accordingly very soft, feeling soapy to the touch as do graphite crystals. To separate the layers in mica it is necessary to break the bonds of the univalent potassium ions, so that the micas are not so soft, thin plates being sufficiently elastic to straighten out after being bent. Separation of layers in the brittle micas involves breaking bonds of bivalent calcium ions; these minerals are hence harder, and brittle instead of elastic, but still show perfect basal cleavage. The sequence of hardness is significant; on the Mohs scale it is: talc and pyrophillite, 1–2; the micas, 2–3; the brittle micas, $3^1/_2$–6.

I wish to acknowledge the assistance of Mr. J. Sherman in the preparation and analysis of the x-ray photographs.

A further account of the x-ray investigation of these minerals and a comparison of the suggested general formulas with the reported chemical analyses will be published in the *Zeitschrift für Kristallographie.*

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[1] Linus Pauling, "Sommerfeld Festschrift," S. Hirzel, Leipzig, **1928,** p. 11; *J. Am. Chem. Soc.,* **51,** 1010 (1929).

[2] Ch. Mauguin, *Comp. Rend.,* **185,** 288 (1927).

[3] The determination of the structure of hydrargillite will be reported in a paper to be published in the *Zeits. für Krist.*

[4] For known crystal structures reference may be made to the Strukturbericht of P. P. Ewald and C. Hermann in current numbers of *Zeits. für Krist.*

[5] The atomic amplitude functions take account of the atomic F- factor, the temperature factor, the Lorentz factor, and the polarization factor.

[6] Mauguin showed that for various micas the unit of structure uniformly contains the number of atoms $O + F$ given by the above formula.

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The Structure of Sodalite and Helvite.

By

Linus Pauling in Pasadena (California).
(Contribution from Gates Chemical Laboratory, California Institute of Technology, No. 248).

(With 4 figures.)

The Unit of Structure and Space Group of Sodalite.

The mineral sodalite, $Na_4Al_3Si_3O_{12}Cl$, belongs to the cubic system, the crystals usually being dodecahedra. Etch figures strongly indicate the point-group symmetry to be T_d.

A small specimen, about $2 \times 2 \times 0.6$ mm, tabular on (110), was cleaved from a piece of light blue massive sodalite from Bancroft, Ontario. A Laue photograph was taken with the incident beam nearly normal to the cleavage face, using the radiation from a tube with tungsten anticathode operated at a peak voltage of 54 kv, the exposure being 100 mah. Two oscillation photographs were prepared, using molybdenum K radiation screened through a zirconia filter. In each case the crystal was oscillated through 45°, the incident beam varying between 90° and 45° with the normal to the cleavage face (110); the axis of rotation was $[1\bar{1}0]$ for Photograph No. 1, and [001] for Photograph No. 2.

The angles of reflection in various orders from (110), given in Table I, lead to the value $a_0 = 8.870$ Å for the edge of the cubic unit. With $2\,Na_4Al_3Si_3O_{12}Cl$ in this unit, the calculated density is 2.290, in good agreement with the experimental values[1] 2.20—2.32. On assigning indices to the spots on the Laue photograph with the aid of a gnomonic projection and calculating values of $n\lambda$, no values less than 0.24 Å, the short wave-length limit of X-rays in the incident beam, were found. Hence this unit may be accepted as the true unit of structure in the absence of any evidence requiring or indicating a larger one.

The Laue photograph showed two planes of symmetry, in agreement with the crystallographic assigment to T_d.

Examination of the Laue data of Table II shows that with only one exception first-order reflections occurred only from planes with $h + k +$ even. This would indicate the body-centered lattice Γ_c'', except for the

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[1] C. Doelter, »Handbuch der Mineralchemie«, II, 2, 230.

fact that an indubitable first-order reflection was given by $\{432\}$, eliminating this lattice. A similar observation was made on the oscillation photographs; all but one of the reflections observed were due to planes with $h+k+l$ even, but the exceptional plane, (210), gave a definite, if faint, reflection. The conclusion can be drawn that the structure is necessarily based on the simple cubic lattice Γ_c, but that it approximates very closely a body-centered atomic arrangement.

Table I.

Reflections from (110) of Sodalite.

Order of Reflection	Line	Film No. 1		Film No. 2		Estimated Intensity	Calculated A for final Structure	$\frac{A^2}{3500}$
		ϑ	d_{110}	ϑ	d_{110}			
1	MoK_β	2° 54′	6.245 Å	2° 54′	6.245 Å	7	— 148	6.3
1	α	3 14	6.275	3 15	6.263			
2	—	—	—	—	—	0	— 9	0.02
3	β	8 40	6.276	8 40.5	6.278	9	174	8.6
3	α	9 46	6.270	9 45.5	6.273			
4	β	11 32	6.308	11 35	6.284	10	187	(10.0)
4	α_1	13 2	6.276	13 4	6.268			
4	α_2	13 7.5	6.268					
5	—	—	—	—	—	0	7	0.01
6	—	—	—	—	—	0	14	0.06
7	—	—	—	—	—	0.05	25	0.2
8	α_1	26 44	6.296	26 48	6.288	0.2	59	1.0
8	α_2	26 54	6.296	27 0	6.272			

Average $d_{110} = 6.274$ Å.

Table II.

Data from a Laue Photograph of Sodalite.

(hkl)	d_{hkl}	$n\lambda$	(hkl)	d_{hkl}	$n\lambda$
$3\ \bar{2}\ \bar{3}$	1.89 Å	0.37 Å	$2\ 1\ \bar{9}$	0.95 A	0.33 A
$\bar{3}\ 4\ 1$	1.74	.43	$\bar{4}\ 7\ 5$	.93	.42
$\bar{3}\ 4\ 2$	1.64	.45	$\bar{3}\ 6\ 7$	.91	.41
$2\ \bar{1}\ \bar{5}$	1.62	.29	$\bar{1}\ 4\ 9$	.90	.45
$4\ \bar{3}\ \bar{3}$	1.52	.37	$1.1.10$	.88	.33
$3\ \bar{2}\ \bar{5}$	1.44	.26	$\bar{5}\ 9\ 0$	.86	.41
$5\ \bar{4}\ 1$	1.37	.38	$\bar{2}\ 5\ 9$	.85	.39
$2\ \bar{1}\ 7$	1.21	.36	$7\ \bar{4}\ 7$	.83	.41
$1\ 1\ 8$	1.09	.48	$\bar{1}\ 6\ \bar{9}$	.82	.44
$\bar{1}\ 4\ \bar{7}$	1.09	.44	$\bar{1}\ 5\ 10$	.79	.44
$\bar{3}\ 5\ 6$	1.06	.39	$3.2.\overline{11}$	.76	.39
$7\ \bar{5}\ 2$	1.01	.40	$\bar{3}\ 8\ 9$	.71	.43
			$\bar{1}.6.11$	.70	.44

The only space groups based on the lattice Γ_c and isomorphous with the point group T_d are T_d^1 and T_d^4. Distinction beween them should be possible through the investigation of the presence or absence of odd-order reflections from forms $\{hkl\}$ with $h = \pm k$ and l odd, these reflections not being allowed by T_d^4. No such reflections were observed. This points to T_d^4 as the correct space group; but the indication is not very certain, inasmuch as these forms are included in the general class of those giving extremely weak reflections. It was found possible, however, to deduce a satisfactory atomic arrangement with the symmetry of T_d^4, substantiating this as the correct space group.

Two previous investigations of the structure of sodalite have been reported. Barth[1]) found $a_0 = 8.85$ Å from a powder photograph of sodalite of unstated origin, while Jaeger and co-workers[2]), using powder photographs and rotation photographs, found $a_0 = 8.81$ Å for sodalite from Monte Somma. In neither case was the atomic arrangement determined.

The Atomic Arrangement.

The equivalent special positions provided by T_d^4 are[3]).

$2a$ $0\,0\,0,\ \tfrac{1}{2}\,\tfrac{1}{2}\,\tfrac{1}{2};$

$6e$ $0\,\tfrac{1}{2}\,0,\ 0\,0\,\tfrac{1}{2},\ \tfrac{1}{2}\,0\,0,\ \tfrac{1}{2}\,0\,\tfrac{1}{2},\ \tfrac{1}{2}\,\tfrac{1}{2}\,0,\ 0\,\tfrac{1}{2}\,\tfrac{1}{2};$

$6f$ $0\,\tfrac{1}{2}\,\tfrac{1}{4},\ \tfrac{1}{4}\,0\,\tfrac{1}{2},\ \tfrac{1}{2}\,\tfrac{1}{4}\,0,\ 0\,\tfrac{1}{2}\,\tfrac{3}{4},\ \tfrac{3}{4}\,0\,\tfrac{1}{2},\ \tfrac{1}{2}\,\tfrac{3}{4}\,0;$

$6g$ $\tfrac{1}{2}\,0\,\tfrac{1}{4},\ \tfrac{1}{4}\,\tfrac{1}{2}\,0,\ 0\,\tfrac{1}{4}\,\tfrac{1}{2},\ \tfrac{1}{2}\,0\,\tfrac{3}{4},\ \tfrac{3}{4}\,\tfrac{1}{2}\,0,\ 0\,\tfrac{3}{4}\,\tfrac{1}{2};$

$8a$ $u\,u\,u,\ u\,\bar{u}\,\bar{u},\ \bar{u}\,u\,\bar{u},\ \bar{u}\,\bar{u}\,u,$
$\tfrac{1}{2}+u\ \tfrac{1}{2}+u\ \tfrac{1}{2}+u,\ \tfrac{1}{2}+u\ \tfrac{1}{2}-u\ \tfrac{1}{2}-u,\ \tfrac{1}{2}-u\ \tfrac{1}{2}+u\ \tfrac{1}{2}-u,$
$\tfrac{1}{2}-u\ \tfrac{1}{2}-u\ \tfrac{1}{2}+u;$

and $12a$, $12i$, $12j$. The general case is

$$x\,y\,z,\ x\,\bar{y}\,\bar{z},\ \bar{x}\,y\,\bar{z},\ \bar{x}\,\bar{y}\,z,$$
$$z\,x\,y,\ \bar{z}\,x\,\bar{y},\ \bar{z}\,\bar{x}\,y,\ z\,\bar{x}\,\bar{y},$$
$$y\,z\,x,\ \bar{y}\,\bar{z}\,x,\ y\,\bar{z}\,\bar{x},\ \bar{y}\,z\,\bar{x},$$
$$\tfrac{1}{2}+y\ \tfrac{1}{2}+x\ \tfrac{1}{2}+z,\ \tfrac{1}{2}-y\ \tfrac{1}{2}+x\ \tfrac{1}{2}-z,\ \tfrac{1}{2}+y\ \tfrac{1}{2}-x\ \tfrac{1}{2}-z,$$
$$\tfrac{1}{2}-y\ \tfrac{1}{2}-x\ \tfrac{1}{2}+z,$$
$$\tfrac{1}{2}+x\ \tfrac{1}{2}+z\ \tfrac{1}{2}+y,\ \tfrac{1}{2}+x\ \tfrac{1}{2}-z\ \tfrac{1}{2}-y,\ \tfrac{1}{2}-x\ \tfrac{1}{2}-z\ \tfrac{1}{2}+y,$$
$$\tfrac{1}{2}-x\ \tfrac{1}{2}+z\ \tfrac{1}{2}-y,$$
$$\tfrac{1}{2}+z\ \tfrac{1}{2}+y\ \tfrac{1}{2}+x,\ \tfrac{1}{2}-z\ \tfrac{1}{2}-y\ \tfrac{1}{2}+x,\ \tfrac{1}{2}-z\ \tfrac{1}{2}+y\ \tfrac{1}{2}-x,$$
$$\tfrac{1}{2}+z\ \tfrac{1}{2}-y\ \tfrac{1}{2}-x.$$

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1) T. Barth, Norsk geol. Tidsskr., **9**, 40. 1926.

2) F. M. Jaeger, H. G. K. Westenbrink, and F. A. van Melle, Pr. Acad. Amsterdam, **30**, 249, 1927; F. M. Jaeger, Trans. Faraday Soc., **25**, 320. 1929.

3) R. W. G. Wyckhoff, "The Analytical Expression of the Results of the Theory of Space Groups", Publ. Carnegie Inst., No. 318. 1922.

The only positions possible for $2\,Cl$ and $8\,Na$ are $2a$ and $8a$ respectively. $6\,Al$ and $6\,Si$ can be in any two of the sets $6e$, $6f$, and $6g$. But with either $6\,Al$ or $6\,Si$ in $6e$ and the other in $6f$ or $6g$ strong reflections would be expected from planes with $h+k+l$ odd; with $6\,Al$ and $6\,Si$ in $6f$ and $6g$ or $6g$ and $6f$, however, the structure factor for such planes involves only the very small difference in reflecting power of Al and Si.

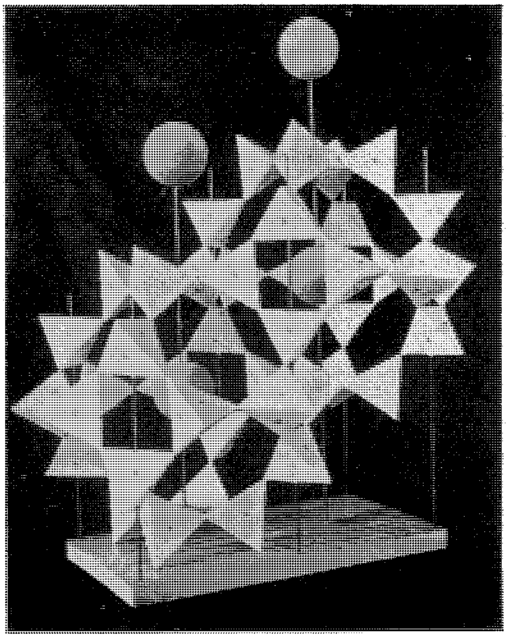

Fig. 1. A photograph of a model representing the sodalite structure. The spheres indicate chlorine ions, and the tetrahedra have an oxygen ion at each corner, and a silicon or aluminum ion at the center.

The observed small intensity of reflection of these planes in general thus rules out $6e$. We can arbitrarily place $6\,Si$ in $6f$ and $6\,Al$ in $6g$ without loss of generality.

With $24\,O$ in the general case strong reflections would be expected from some planes with $h+k+l$ odd unless two of the parameters were very nearly equal, in which case the structure factor would become very small. This limits considerably the region of parameter values to be discussed; but not sufficiently to permit the deduction of a single set of values from X-ray date alone.

It is possible to predict with some accuracy values of the four parameters determining the structure with the aid of the principles governing the structures of complex crystals[1]). The radius of the silicon ion is such that a coordination number of 4 is to be expected for Si^{+4}. This is in agreement with observation; in every silicate which has been investigated the silicon ion is surrounded by four oxygen ions at 1.60 ± 0.08 Å, forming a nearly regular tetrahedron[2]). The aluminum ion as a rule has the coordination number 6, being surrounded by six oxygen ions at a distance of about 1.90 Å. It was pointed out sometime ago[3]), however, that the coordination number 4 is also possible for Al^{+3}, and that it is, in fact, indicated for aluminosilicates of alkali metals by the electrostatic valence rule. With the composition $Al_6Si_6O_{24}$ each oxygen ion can be common to a silicon tetrahedron (bond strength 1) and an aluminum tetrahedron (bond strength $\frac{3}{4}$), giving a total bond strength of $1\frac{3}{4}$, which leaves only $\frac{1}{4}$ to be provided by the alkali (Fig. 1).

Such a structure is to be assigned to sodalite. With $6\,Si$ in $6f$ and $6\,Al$ in $6g$ each silicon ion is surrounded by four aluminum ions at the distance 3.14 Å and roughly at the corners of a regular tetrahedron, and each aluminum ion is similarly surrounded by silicon ions. With the parameter values $x = z = 0.14$ and $y = 0.50$, an oxygen ion is inserted between each Si—Al pair. These parameter values correspond to nearly regular silicon and aluminum tetrahedra, the Si—O and Al—O distances being about 1.6 Å. This is, however, rather small for the Al—O distance; the larger crystal radius of Al^{+3} as compared with Si^{+4} would indicate an Al—O distance 1.7—1.8 Å, corresponding to a 5—10% decrease from the value Al—O = 1.90 Å for Al^{+3} with the coordination number 6. The point-group symmetry of both positions $6f$ and $6g$ of T_d^4 is S_4, so that the tetrahedra can be rotated about the two-fold axes without deformation. The range of parameter values $x = 0.14 \pm 0.02$, $y = 0.44 \pm 0.03$ and $z = 0.14 \pm 0.02$ includes all reasonable structures, corresponding to Al—O distances lying between 1.6 and 1.9 Å.

We have investigated this region with the aid of the observed intensities of reflection in eight orders from (110). The value of the sodium parameter u was simultaneously determined.

The integrated intensity of reflection of an X-ray line from an extended face of a mosaic crystal is[4])

$$\varrho = \frac{\lambda^3}{2\mu}\left(\frac{Ne^2}{mc^2}\right)^2 \frac{1+\cos^2 2\vartheta}{2\sin 2\vartheta} F^2, \qquad (1)$$

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[1]) Linus Pauling, »Sommerfeld Festschrift«, S. Hirzel, Leipzig, 11, 1928; J. Am. Chem. Soc. **51**, 1010. 1929. [2]) See, for example, the summary of W. L. Bragg, Trans. Faraday Soc., **25**, 291. 1929. [3]) Linus Pauling, l. c., 1017 and 1025.

[4]) W. L. Bragg and J. West, Z. Krist., **69**, 118. 1928.

in which μ is the absorption coefficient of the X-rays and F is the structure factor

$$F = \sum_n F_n e^{2\pi i(hx_n + ky + lz_n)}. \tag{2}$$

The atomic reflecting power F_n as a function of $\sin\vartheta/\lambda$ or of d_{hkl} depends on the structure of the atom and also on the forces exerted on the atom by surrounding atoms, inasmuch as the temperature factor (also a function of d_{hkl}) is included in the F-curve. Values of F for various atoms have been tabulated by Bragg and West. Now it is convenient to introduce the concept of the atomic amplitude function A_n, defined by the equation

$$A_n = \left(\frac{1 + \cos^2 2\vartheta}{2\sin 2\vartheta}\right)^{\frac{1}{2}} F_n. \tag{3}$$

For a given wave-length (the MoK_α line in particular) the atomic amplitude function for an atom or ion is a function of the effective interplanar distance d_{hkl} only[1]. Values of atomic amplitudes for the ions in sodalite and helvite (mostly calculated from Bragg and West's F-curves) are given in Table III. For a given crystal the integrated intensities of reflection of the line MoK_α from various planes are proportional to the values of A^2, in which A is given by the equation

$$A_{hkl} = \sum_n A_n e^{2\pi i(hx_n + ky_n + lz_n)}. \tag{4}$$

Table III.

Values of the Atomic Amplitude Function.

$d/n =$	0.50	0.75	1.00	1.50	2.00	3.50	5.00 A
Be^{++}	0.0	0.1	0.3	1.0	2.0	4.1	6.0
$O^{=}$	0.4	0.8	2.0	4.8	7.6	15	21
Na^{+}	0.6	2.0	4.0	8.0	12	20	25
Al^{+3}	1.1	2.9	5.2	9.5	13	23	28
Si^{+4}	1.3	3.6	6.0	10	14	24	30
$S^{=}$	1.5	4.0	6.5	11	16	30	41
Cl^{-}	1.7	4.2	7.0	12	17	31	42
Mn^{++}	3.7	4.7	11	18	25	44	58

Using the atomic amplitudes of Table III, values of A were calculated for (110), (220), . . . (880) for various sets of values of x, y, and z in the region under consideration, and for u between 0.16 and 0.25. The region of u between 0 and 0.16 was not considered, as the corresponding

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1) d_{hkl} is to indicate the order of reflection also, h, k, l being taken to represent the orders of reinforcement of X-rays along the three crystallographic axes.

Na—*Cl* distances are too small (a maximum of 2.45 Å, as compared with 2.81 Å in *NaCl*). Complete agreement with the observed intensities (Table I) was obtained for

$$x = 0.135 \quad y = 0.440 \quad z = 0.150 \quad u = 0.175.$$

The effect of varying one of these parameters is shown in Figure 2, in which values of A as functions of u are represented. A change of

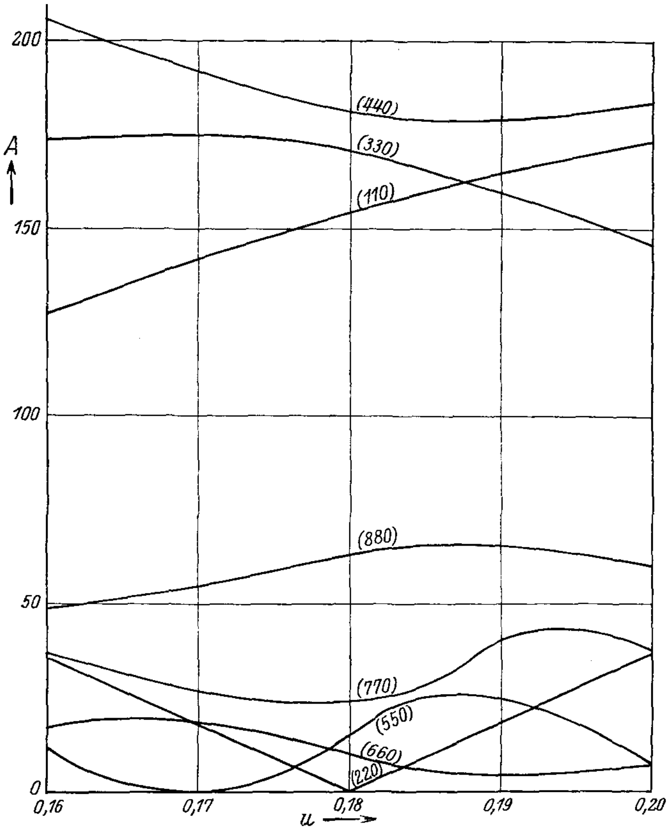

Fig. 2. Amplitude curves for eight orders of reflection from (110) of sodalite as a function of the sodium parameter u.

± 0.005 in any one of the parameters disturbs the agreement with the observed intensities, and a change of ± 0.01 spoils it; the atomic positions may accordingly be considered to be accurate to about 0.05 Å.

In Table IV are given data from oscillation photograph No. 1 of sodalite. The crystal used was a cleaved specimen with a cleaved face (110) 2 mm. square. The incident beam traversed angles between 0 and

Table IV.

Oscillation Photograph from Sodalite.

Crystal rotated about $[1\bar{1}0]$, with incident beam traversing angles between 45° and 90° to $[110]$.

Equator $h-k=0$		(110)	(220)	(330)	(440)	(550)	(660)	(770)	(880)
	$I=$	7	0	9	10	0	0	0.05	0.2
	$A^2/3500=$	6.3	0.02	8.6	(10)	0.01	0.06	0.2	1.0
	$A=$	−148	−9	174	187	7	14	25	59
Second Layer $h-k=2$		(200)	(310)	(420)	(530)	(640)	(750)		
	$I=$	6 × 0.7	1.5 × 0.9	1.0 × 0.95	0.8	0.1	0		
	$A^2/3500=$	4.4	2.2	1.7	1.0	0.4	0.00		
	$A=$	124	−87	78	−59	38	3		
Fourth Layer $h-k=4$		(310)	(400)	(510)	(620)	(730)	(840)		
	$I=$	4 × 0.4	1.5 × 0.7	0.02 × 0.8	0.1 × 0.9	0.4 × 0.9	1 × 0.95		
	$A^2/3500=$	2.2	1.4	0.16	0.26	1.2	2.6		
	$A=$	−87	71	24	−30	−66	95		
Sixth Layer $h-k=6$				(600)	(710)	(820)	(930)		
	$I=$			8 × 0.7	0	0.4 × 0.85	0		
	$A^2/3500=$			9.4	0.00	1.3	0.00		
	$A=$			182	−2	68	5		

45° with this face, the axis of rotation being $[1\bar{1}0]$. The photograph showed reflections from planes of about 20 forms in addition to those listed in the table; on account of uncertainty in a possible correction for absorption of X-rays reflected from these planes, whose traces in the large face (110) are not normal to the axis of rotation, no attempt was made to correlate their reflections with calculated amplitudes. In the table there are given under the symbol (hkl) for the reflecting plane the estimated intensity multiplied by the correction $\sqrt{1-\left(\frac{\sin\mu}{\sin 2\vartheta}\right)^2}$ for varying time of reflection[1], and below that the amplitude values calculated as before. The intensities were visually estimated; the numbers used to designate them, varying from 0.02 to 10, are not intended to be more than roughly quantitatively correct, but they do give the correct relative order of the intensities of the various reflections. It is seen from the table that the agreement between observed and calculated intensities is excellent. This provides further verification for the suggested structure; for, as before, the agreement is seriously affected by changing the parameters by as much as 0.01. It is worthy of mention that the intensities of reflections other than the various orders from (110) were

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[1] H. Ott, Z. Physik, **22**, 201. 1924.

not used at all in fixing the parameters, and the final set of parameter values was found before amplitude values were calculated for any of the planes reflecting in the second, fourth, and sixth layers; so that their ultimate calculation provided an excellent test of the correctness of the structure.

Description of the Structure.

The structure found for sodalite is represented in Fig. 3 projected on a cube face. Each silicon ion is surrounded by four oxygen ions at the corners of a nearly regular tetrahedron, the $Si—O$ distance being 1.60 Å, and the $O—O$ distances (the edges of the tetrahedron) being 2.65 Å for the two edges forming part of the squares normal to the two-fold axes of the structure, and 2.58 Å for the other four edges. Each aluminum ion is surrounded by four oxygen ions at the corners of a nearly regular tetrahedron, the $Al—O$ distance being 1.74 Å, and the six $O—O$ distances 2.85 Å. Each sodium ion is surrounded by four anions, one chlorine ion at 2.70 Å (as compared with 2.81 Å in $NaCl$, in which the sodium ion has the coordination number 6 rather than 4), and three oxygen ions at 2.36 Å, in satisfactory agreement with the sum of the crystal radii, 2.35 Å.

The electrostatic valence rule is satisfied. The bond strength from Si^{+4}, Al^{+3}, and Na^{+} are 1, $\frac{3}{4}$, and $\frac{1}{4}$ respectively, since the cations all have the coordination number 4. Each oxygen ion is in contact with 1 Si^{+4}, 1 Al^{+3}, and 1 Na^{+}, giving $\sum s_i = 2$, and each chlorine ion in contact with 4 Na^{+}, giving $\sum s_i = 1$, in agreement with their valences.

This crystal provides a remarkable example of a framework structure. The forces between the highly charged cations Si^{+4} and Al^{+3} and the oxygen ions are by far the strongest forces in the crystal. They cause the joined tetrahedra to form a strong framework, of composition $Al_6Si_6O_{24}$, extending throughout the crystal and essentially determining its structure. Within the framework are rooms and passages, spaces which can be occupied by other ions or atoms or molecules, in this case sodium and chlorine ions. The framework, while strong, is not rigid, for there are no strong forces tending to hold it tautly expanded. In sodalite the framework collapses, the tetrahedra rotating about the two-fold axes until the oxygen ions come into contact with the sodium ions, which themselves are in contact with the chlorine ions. This partial collapse of the framework reduces the edge of the unit from its maximum value, about 9.4 Å, to 8.87 Å.

The same framework exists in hauynite, $Na_3CaAl_3Si_3O_{12} \cdot SO_4$, and noselite, $Na_5Al_3Si_3O_{12} \cdot SO_4$, for hauynite has been converted into sodalite by heating in fused sodium chloride, and sodalite into noselite by fused sodium sulfate. (Indeed, this property of ease of exchange of the mobile constituents is characteristic of framework structures, finding especial expression in the zeolites.) The substituted group $SO_4^=$ is considerably larger than Cl^-, so that for these crystals the collapse of the framework is not so pronounced as for sodalite, the edge of the unit being 9.15 Å. As a matter of fact, Jaeger and van Melle[1]) by introducing larger alkali ions (K^+, Rb^+, Cs^+) increased a_0 to 9.4 Å, just equal to the maximum value calculated for tetrahedra of the size found in sodalite.

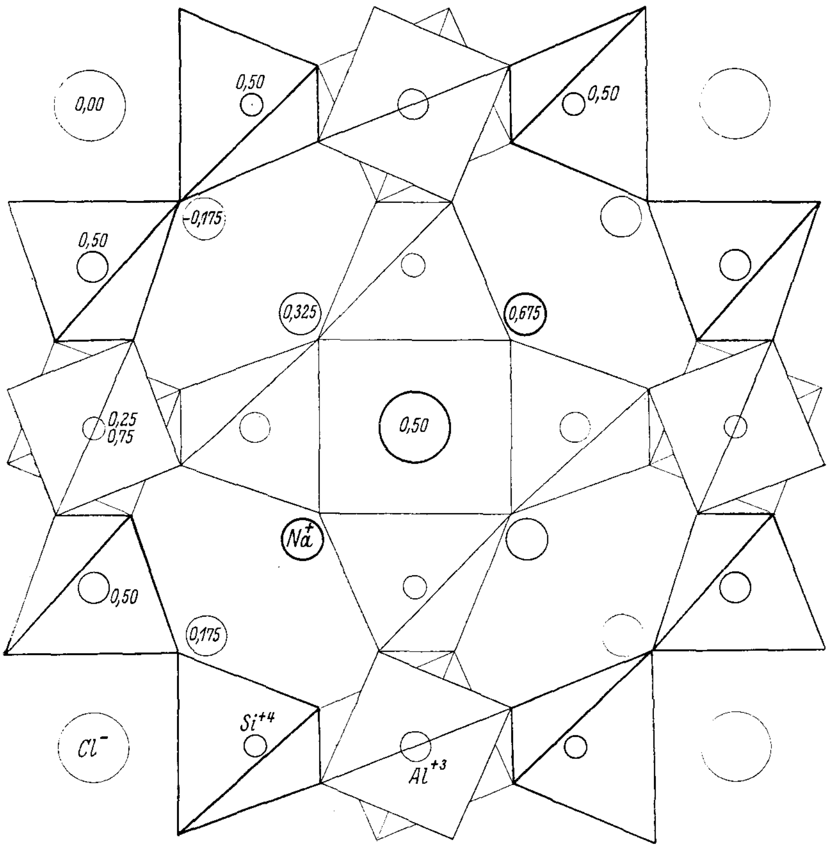

Fig. 3. The structure of sodalite projected on (001). Cl^-, Na^+, Al^{+3}, and Si^{+4} are represented by successively smaller circles. The numbers give the values of the z-coordinate of the ions. There is an oxygen ion at each corner of the tetrahedra drawn about each silicon and each aluminum ion.

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1) F. M. Jaeger and F. A. van Melle, Pr. Acad. Amsterdam, **30**, 479, 885. 1927.

The Structure of Helvite.

The mineral helvite, $(Mn, Fe, Zn)_4Be_3Si_3O_{12}S$, forms tetrahedral crystals showing face development corresponding to the point group T_d. Powder photographs of helvite from Hørtekollen, Norway, taken by Barth[1], have led to a unit with $a_0 = 8.19$ Å, containing $2(Mn, Fe, Zn)_4Be_3Si_3O_{12}S$. The observed reflections require the lattice to be Γ_c, and the absences indicate the space group T_d^4 rather than T_d^1. The similarity of the photographs with those of sodalite led Barth to suggest that the two structures are closely related.

Helvite of unstated origin has also been studied by Gottfried[2], who found the value $a_0 = 8.52$ Å from rotation photographs. His work also led to the space group T_d^1. Neither Barth nor Gottfried suggested an atomic arrangement for the crystal.

Oscillation photographs were prepared from crystals of helvite from Schwarzenberg, Saxony. The crystals available were small yellow tetrahedra about 1 mm. on an edge, and the photographs obtained showed only a few reflections. These were in reasonable agreement with Barth's data, leading, however, to a slightly different value for a_0; namely, 8.25 Å. Helvite from Schwarzenberg is reported[3] to consist of about 90% $Mn_4Be_3Si_3O_{12}S$ and 10% $Fe_4Be_3Si_3O_{12}S$. The density calculated for two molecules of this average composition in a unit 8.25 Å on edge is 3.23, in good agreement with the experimental values 3.166 and 3.202.

While the available X-ray data are not extensive enough to permit the deduction of the atomic arrangement, it is possible to use them to check a suggested one. The structure is no doubt closely related to that of sodalite, the aluminum ions being replaced by beryllium, sodium by manganese, and chlorine by sulfur. The silicon tetrahedra may be taken to have the same dimensions as in sodalite, and the beryllium tetrahedra will be only slightly larger, the $Be-O$ distance in beryllium oxide, which has the wurtzite structure, being 1.64—1.66 Å. These dimensions lead to parameter values

$$x = 0.133 \qquad y = 0.416 \qquad z = 0.137$$

for oxygen. The value $u = 0.175$ for manganese places each Mn^{++} at a distance of 2.50 Å from one $S^{=}$ and 2.08 Å from three $O^{=}$ ions. These distances are about 5% smaller than those in MnS and MnO, 2.61 Å and 2.20 Å respectively, in which Mn^{++} has a coordination number of six instead of four. Changes in the parameters greater than 0.01 would bring the ions closer together than the expected distances of closest approach.

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[1] Barth, l. c. [2] C. Gottfried, Z. Krist., **65**, 425. 1927. [3] Doelter, »Handbuch der Mineralchemie«.

Table V.

Intensities of Reflection from (100) and (110) of Helvite.

(hkl)	ϑ	d_{100}	Observed intensity[2]	A
110	—	—	absent	— 13
220	—	—	weak	93
330	10°31′	8.23 Å	strong	232
440	14 0.5	8.27	medium	173
200	—	—	very weak	— 68
400	10 0	8.17	weak	— 79
600	14 53	8.28	medium	165

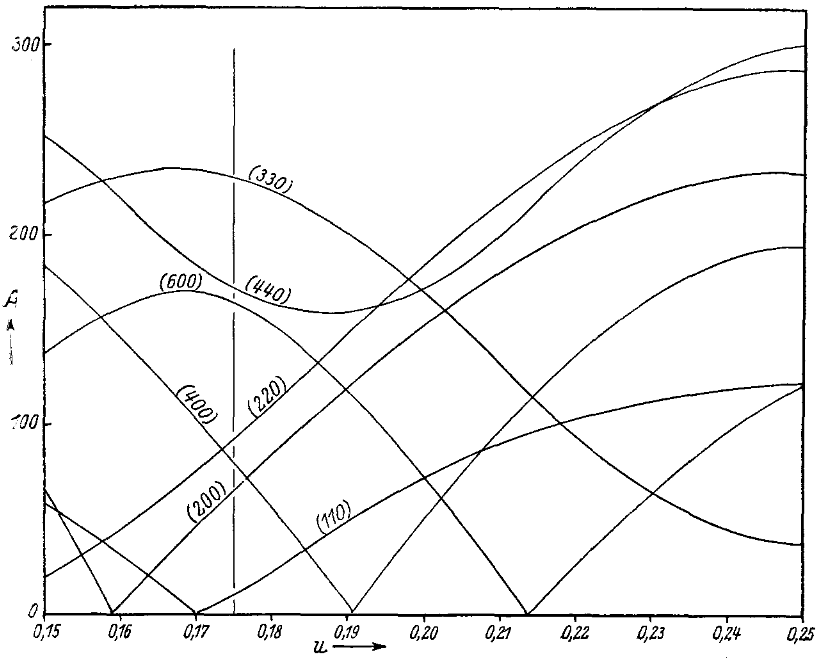

Fig. 4. Amplitude curves for helvite as a function of the manganese parameter *u*.

A-curves calculated for the above values of x, y, and z over a range of values of u are shown in Fig. 4. It is seen that the observed relative intensities of (110), (220), (330), (440), and (200), (400), (600) (Table V) limit u to the region between 0.16 and 0.19, the best value being 0.175. This evidence supports the structure proposed.

The *Zn—S* and *Zn—O* distances in *ZnS* and *ZnO*, both with the wurtzite structure, are 2.36 Å and 1.94—2.04 Å, respectively; i. e. about 5% smaller than the corresponding *Mn—S* and *Mn—O* distances. This would lead to a smaller value of a_0 for danalite (which has the composition ($(Zn, Fe, Mn)_4Be_3Si_3O_{12}S$, with about 40% $Zn_4Be_3Si_3O_{12}S$), and would explain the large value 3.427 reported for its density[1]. The helvite investigated by Barth, which also had a high density, 3.316, and a low value of a_0, 8.19 Å, was found by Goldschmidt to contain 14% $Zn_4Be_3Si_3O_{12}S$.

The very high value $a_0 = 8.525$ Å reported by Gottfried may possibly be due to partial replacement of Mn^{++} by a much larger ion.

There is no close relation between the structure of sodalite and helvite and that of the garnets.

Summary.

Using data from rotation and Laue photographs, it is shown that the unit of structure of sodalite, containing $2\,Na_4Al_3Si_3O_{12}Cl$, has $a_0 = 8.87$ Å. The lattice is the simple cubic one, Γ_c; the structure closely approximates one based on a body centered lattice, however. The atomic arrangement has

$2\,Cl$ in $2a$;
$8\,Na$ in $8a$, parameter u;
$6\,Si$ in $6f$;
$6\,Al$ in $6g$;
$24\,O$ in x, y, z, etc.

The comparison of observed intensities of reflection in eight orders from (110) and intensities calculated for a range of parameter values suggested by assumed minimum interionic distances led to the values $u = 0.175$, $x = 0.135$, $y = 0.440$, $z = 0.150$. These values were verified by a large number of other reflections. The resultant structure is shown in Fig. 1 and 3.

Helvite was found to have a unit of structure with $a_0 = 8.25$ Å, containing $2\,(Mn, Fe)_4Be_3Si_3O_{12}S$. The structure is similar to that of sodalite, the parameters having the values $u = 0.175$, $x = 0.113$, $y = 0.446$, $z = 0.137$. Both structures satisfy the electrostatic valence rule.

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[1] Dana, "A System of Mineralogy", 435.

[2] (200), (400), and (600) are from a different photograph than (110), etc., so that intercomparisons are not to be made.

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Akademische Verlagsgesellschaft m. b. H. in Leipzig, 1930.

The Crystal Structure of Bixbyite and the *C*-Modification of the Sesquioxides.

By

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(With six figures.)

1. Introduction.

It was discovered in 1925 by Goldschmidt[1]) that an extensive series of sesquioxides form cubic crystals with the unit of structure containing $16\,M_2O_3$, the value of a varying between 9.3 Å and 10.9 Å. An atomic arrangement based on the space group T^5 was assigned this C-modification of the sesquioxides by Zachariasen[2]), who studied crystals of Sc_2O_3, Mn_2O_3, Y_2O_3, In_2O_3, Tl_2O_3, Sm_2O_3, Eu_2O_3, Gd_2O_3, Tb_2O_3, Dy_2O_3, Ho_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, Lu_2O_3, and the mineral bixbyite, $(Fe, Mn)_2O_3$. Zachariasen's procedure was the following. Using data from powder and Laue photographs of Tl_2O_3, and neglecting the contribution of the oxygen atoms to the reflections, he decided that the space group is T^5, with the $32\,Tl$ in $8b$ with parameter $t = 0.25$, in $12c$ with parameter $u = 0.021$, and in $12c$ with parameter $v = 0.542$. These parameter values were assumed to hold for all members of the series. The consideration of intensities of reflection of Sc_2O_3 then was found to indicate the $48\,O$ to be in two groups of 24 in the general position of T^5, with parameters $x_1 \sim \frac{1}{8}$, $y_1 \sim \frac{1}{8}$, $z_1 \sim \frac{3}{8}$ and $x_2 \sim \frac{1}{8}$, $y_2 \sim \frac{3}{8}$, $z_2 \sim \frac{3}{8}$. The same structure was also assigned bixbyite, with $16\,(Mn, Fe)_2O_3$ in a unit 9.35 ± 0.02 Å on edge.

On beginning the investigation of the tetragonal pseudo-cubic mineral braunite, $3\,Mn_2O_3 . MnSiO_3$, we found the unit of structure to be closely related to that of bixbyite, and, indeed, to have dimensions nearly the same as those for two superimposed bixbyite cubes. This led us to

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1) V. M. Goldschmidt, »Geochem. Vert.-Ges. d. El.« IV, V, Videnskapsselsk. Skr., **5**, 7, Oslo. 1925. 2) W. Zachariasen, Z. Krist. **67**, 455. 1928; »Untersuchungen über die Kristallstruktur von Sesquioxyden und Verbindungen ABO_3«, Videnskapsselsk. Skr. **4**, Oslo. 1928.

make a study of Zachariasen's structure, leading to the observation that not only are the interatomic distances reported abnormally small, but also the structure does not fall in line with the set of principles found to hold for coordinated structures in general¹). It was further noted that Zachariasen's atomic arrangement, with the symmetry of space group T^5, approximates very closely an arrangement with the symmetry of $T_h{}^7$ (of which T^5 is a sub-group), and it is difficult to find a physical explanation of this distortion from a more symmetrical structure. This led to the reinvestigation of this mineral and the determination of a new and satisfactory structure for the C-modification of the sesquioxides.

2. The Unit of Structure and Space-group Symmetry of Bixbyite.

Bixbyite, found only in Utah, about 35 miles southwest of Simpson, is described by Penfield and Foote²) as forming shiny black cubic crystals with a trace of octahedral cleavage. The composition assigned it by them was $Fe^{++}Mn^{+4}O_3$, with a little isomorphous replacement of Fe^{++} by Mg^{++} and Mn^{++} and of Mn^{+4} by Ti^{+4}. It was shown by Zachariasen that the X-ray data exclude this formulation, and indicate instead that the mineral is a solid solution of Mn_2O_3 and Fe_2O_3. We shall reach a similar conclusion.

Table I.

Spectral Data from (100) of Bixbyite (with rock salt comparison).

hkl	Line	d/n	Estimated Intensity	$S^2/10{,}000$
200	$MoK\alpha_1$	$\frac{1}{2} \times 9.40$ Å	0.05	0.26
400	α_1	$\frac{1}{4} \times 9.38$	7	21.16
400	α_2	$\frac{1}{4} \times 9.37$		
600	α_1	$\frac{1}{6} \times 9.38$	0.2	0.61
600	α_2	$\frac{1}{6} \times 9.36$		
800	α_1	$\frac{1}{8} \times 9.36$	5	20.0
800	α_2	$\frac{1}{8} \times 9.34$		
10.0.0	α_1	$\frac{1}{10} \times 9.38$	0.1	0.23
10.0.0	α_2	$\frac{1}{10} \times 9.34$		
12.0.0	α_1	$\frac{1}{12} \times 9.36$	0.4	1.80
14.0.0	α_1	$\frac{1}{14} \times 9.37$	0.3	0.71
16.0.0	—	—	0.1	0.71

Average: $a = 9.365 \pm 0.020$ Å.

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1) Linus Pauling, J. Am. chem. Soc, **51**, 1010. 1929.

2) S. L. Penfield and H. W. Foote, Z. Krist. **28**, 592. 1897.

Data from oscillation photographs of bixbyite show a to be a multiple of 4.68 Å (Table I). The Polanyi layer-line relation applied to photographs with [100] as rotation axis showed that this multiple must be 2, giving a unit with

$$a = 9.365 \pm 0.020\ \text{Å}.$$

This unit sufficed to account for the occurrence of all spots observed on several Laue photographs taken with a tube operated at a peak voltage of 54 kv. (the incident beam making small angles with [100] or [110]), and may be accepted as the true unit.

Table II.
Laue Data for Bixbyite.
Incident beam nearly normal to (100).

$\{hkl\}$	d_{hkl} Å	Estimated Intensity. $n\lambda =$				S Calculated	$S^2/10{,}000$
		0.25—0.29 Å	0.30—0.34 Å	0.35—0.39 Å	0.40—0.45 Å		
611	1.51				10.0	209	4.37
451	1.44				10.0	172	2.96
415					10.0	157	2.46
631	1.38			7.0	7.0	218	4.75
613				7.0	10.0	—233	5.43
271	1.27		0.4	1.0		119	1.42
217			2.5	3.0		—154	2.37
651	1.18	0.1	0.4			139	1.93
615		0.2	0.4			142	2.02
417	1.15	0.1	0.1			— 84	0.71
471			0.8			107	1.14
811	1.15	1.0	1.6			180	3.24
275	1.06				0.0	18	0.03
257					0.1	25	0.06
219	1.01				0.0	11	0.01
291					0.2	30	0.09
293	0.96			0.1	0.1	43	0.18
239				0.1	0.2	43	0.18
277	.93			0.3	0.4	—103	1.06
837	.85				0.6	—102	1.04
873					0.6	—107	1.14
10.5.3	.81			0.1	0.05	— 93	0.86
10.3.5					0.1	93	0.86
4.11.3	.77			0.1	0.1	— 63	0.40
4.3.11				0.1	0.1	— 68	0.46

The value 4.945 for the density of bixbyite reported by Penfield and Foote leads to 16 $(Mn, Fe)_2O_3$ in the unit.

It was observed that the only planes giving odd-order reflections (see Table II) were those with $h+k+l$ even, indicating strongly that the structure is based on the body-centered cubic lattice Γ_c''. Moreover, a Laue photograph taken with the incident beam normal to (100) showed only two symmetry planes and a two-fold axis, requiring that the point-group symmetry of the crystal be that of T or T_h. The only space groups compatible with these conditions are T^3, T^5, T_h^5, and T_h^7. Of these T_h^7 requires that planes $(0kl)$ with k and l odd give no odd-order reflections, while T^3, T^5, and T_h^5 allow such reflections to occur. On our photographs no such reflections were found, although a number of planes of this type were in positions favorable to reflection (Table III). This makes it highly probable that T_h^7 is the correct space group, for it would be very difficult to account for the absence of these reflections with an atomic arrangement derived from T^3, T^5, or T_h^5 which at the same time did not come indistinguishably close to an arrangement derivable from T_h^7. In view of these considerations we have assumed T_h^7 to be the correct space group.

Table III.

Data for Prism Forms from Bixbyite.

A. Forms not reflecting on Laue photographs:

{hkl}	nλ	
{071}	0.35,	0.39 Å
{701}	0.34,	0.40
{11.0.3}	0.40,	0.45
{0.11.3}	0.41,	0.44
{13.0.3}	0.30,	0.33
{0.13.3}	0.31,	0.32

B. Forms not reflecting on oscillation photographs:

{031}, {013}, {033}, {051}, {015}, {053}, {035}, {055},
{071}, {017}, {073}, {037}, {075}, {057}, {091}, {019},
{093}, {039}, {095}, {059}.

This choice of space group is further substantiated by Zachariasen's data for the other substances as well as bixbyite. His reproduced Laue photographs of Tl_2O_3 and of bixbyite show no spots due to {071}, {017}, {091}, {019}, {0.11.1} or {0.1.11}, although planes of these forms were in positions favorable to reflection, while the powder data show that {031}, {013}, {073}, and {037} gave no reflections for any of the sesquioxides studied. Zachariasen's rejection of T_h^7 arose from his assumption that the oxygen contribution to the intensities was negligible, and his consequent inability to account for the observed inequalities in intensity of pairs of forms such as {271} and {217} with the metal atoms in positions provided by T_h^7. But actually the oxygen contribution is by no means negligible. For example, the structure which we find gives for the metal contributions to the structure factor for {271} and {217} the values + 66.2 and — 66.2, which are changed by the oxygen contribution to + 119.6 and — 154.2, respectively. For Tl_2O_3 the effect of the oxygen would be only about one-fourth as great, which is, however, still sufficient to account for the observed inequalities[1].

3. The Arrangement of the Metal Atoms.

The equivalent positions provided by T_h^7 are:

8*i*: $0\,0\,0;\ \frac{1}{2}\,\frac{1}{2}\,0;\ \frac{1}{2}\,0\,\frac{1}{2};\ 0\,\frac{1}{2}\,\frac{1}{2};$
$\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2};\ 0\,0\,\frac{1}{2};\ 0\,\frac{1}{2}\,0;\ \frac{1}{2}\,0\,0.$

8*e*: $\frac{1}{4}\,\frac{1}{4}\,\frac{1}{4};\ \frac{1}{4}\,\frac{3}{4}\,\frac{3}{4};\ \frac{3}{4}\,\frac{1}{4}\,\frac{3}{4};\ \frac{3}{4}\,\frac{3}{4}\,\frac{1}{4};$
$\frac{3}{4}\,\frac{3}{4}\,\frac{3}{4};\ \frac{3}{4}\,\frac{1}{4}\,\frac{1}{4};\ \frac{1}{4}\,\frac{3}{4}\,\frac{1}{4};\ \frac{1}{4}\,\frac{1}{4}\,\frac{3}{4}.$

16*e*: $u\,u\,u;\ u, \bar{u}, \frac{1}{2}-u;\ \frac{1}{2}-u, u, \bar{u};\ \bar{u}, \frac{1}{2}-u, u;$
$\bar{u}\,\bar{u}\,\bar{u};\ \bar{u}, u, u+\frac{1}{2};\ u+\frac{1}{2}, \bar{u}, u;\ u, u+\frac{1}{2}, \bar{u};$
$u+\frac{1}{2}, u+\frac{1}{2}, u+\frac{1}{2};\ u+\frac{1}{2}, \frac{1}{2}-u, \bar{u};\ \bar{u}, u+\frac{1}{2}, \frac{1}{2}-u;\ \frac{1}{2}-u, \bar{u}, u+\frac{1}{2};$
$\frac{1}{2}-u, \frac{1}{2}-u, \frac{1}{2}-u;\ \frac{1}{2}-u, u+\frac{1}{2}, u;\ u, \frac{1}{2}-u, u+\frac{1}{2};\ u+\frac{1}{2}, u, \frac{1}{2}-u.$

24*e*: $u\,0\,\frac{1}{4};\ \bar{u}\,\frac{1}{2}\,\frac{1}{4};\ \frac{1}{2}-u, 0, \frac{3}{4};\ u+\frac{1}{2}, \frac{1}{2}, \frac{3}{4};$
$\frac{1}{4}\,u\,0;\ \frac{1}{2}\,\bar{u}\,\frac{1}{2};\ \frac{3}{4}, \frac{1}{2}-u, 0;\ \frac{3}{4}, u+\frac{1}{2}, \frac{1}{2};$
$0\,\frac{1}{4}\,u;\ \frac{1}{2}\,\frac{1}{4}\,\bar{u};\ 0, \frac{3}{4}, \frac{1}{2}-u;\ \frac{1}{2}, \frac{3}{4}, u+\frac{1}{2};$
$\bar{u}\,0\,\frac{3}{4};\ u\,\frac{1}{2}\,\frac{3}{4};\ u+\frac{1}{2}, 0, \frac{1}{4};\ \frac{1}{2}-u, \frac{1}{2}, \frac{1}{4};$
$\frac{3}{4}\,\bar{u}\,0;\ \frac{3}{4}\,u\,\frac{1}{2};\ \frac{1}{4}, u+\frac{1}{2}, 0;\ \frac{1}{4}, \frac{1}{2}-u, \frac{1}{2};$
$0\,\frac{3}{4}\,\bar{u};\ \frac{1}{2}\,\frac{3}{4}\,u;\ 0, \frac{1}{4}, u+\frac{1}{2};\ \frac{1}{2}, \frac{1}{4}, \frac{1}{2}-u.$

48: $x\,y\,z;\ x, \bar{y}, \frac{1}{2}-z;\ \frac{1}{2}-x, y, \bar{z};\ \bar{x}, \frac{1}{2}-y, z;$
$z\,x\,y;\ \frac{1}{2}-z, x, \bar{y};\ \bar{z}, \frac{1}{2}-x, y;\ z, \bar{x}, \frac{1}{2}-y;$
$y\,z\,x;\ \bar{y}, \frac{1}{2}-z, x;\ y, \bar{z}, \frac{1}{2}-x;\ \frac{1}{2}-y, z, \bar{x};$
$\bar{x}\,\bar{y}\,\bar{z};\ \bar{x}, y, z+\frac{1}{2};\ x+\frac{1}{2}, \bar{y}, z;\ x, y+\frac{1}{2}, \bar{z};$
$\bar{z}\,\bar{x}\,\bar{y};\ z+\frac{1}{2}, \bar{x}, y;\ z, x+\frac{1}{2}, \bar{y};\ z, x, y+\frac{1}{2};$
$\bar{y}\,\bar{z}\,\bar{x};\ y, z+\frac{1}{2}, \bar{x};\ \bar{y}, z, x+\frac{1}{2};\ y+\frac{1}{2}, \bar{z}, x;$
$x+\frac{1}{2}, y+\frac{1}{2}, z+\frac{1}{2};\ x+\frac{1}{2}, \frac{1}{2}-y, z;\ \bar{x}, y+\frac{1}{2}, \frac{1}{2}-z;\ \frac{1}{2}-x, \bar{y}, z+\frac{1}{2};$
$z+\frac{1}{2}, x+\frac{1}{2}, y+\frac{1}{2};\ z, x+\frac{1}{2}, \frac{1}{2}-y;\ \frac{1}{2}-z, \bar{x}, y+\frac{1}{2};\ z+\frac{1}{2}, \frac{1}{2}-x, \bar{y};$
$y+\frac{1}{2}, z+\frac{1}{2}, x+\frac{1}{2};\ \frac{1}{2}-y, z, x+\frac{1}{2};\ y+\frac{1}{2}, \frac{1}{2}-z, \bar{x};\ \bar{y}, z+\frac{1}{2}, \frac{1}{2}-x;$
$\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z;\ \frac{1}{2}-x, y+\frac{1}{2}, z;\ x, \frac{1}{2}-y, z+\frac{1}{2};\ x+\frac{1}{2}, y, \frac{1}{2}-z;$
$\frac{1}{2}-z, \frac{1}{2}-x, \frac{1}{2}-y;\ z, \frac{1}{2}-x, y+\frac{1}{2};\ z+\frac{1}{2}, x, \frac{1}{2}-y;\ \frac{1}{2}-z, x+\frac{1}{2}, y;$
$\frac{1}{2}-y, \frac{1}{2}-z, \frac{1}{2}-x;\ y+\frac{1}{2}, z, \frac{1}{2}-x;\ \frac{1}{2}-y, z+\frac{1}{2}, x;\ y, \frac{1}{2}-z, x+\frac{1}{2}.$

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[1] Dr. Zachariasen has kindly informed us that he now agrees with our choice of the space group T_h^7.

Of these, all but the general position may be occupied by the metal atoms. The 32 metal atoms may have any one of the following arrangements:

A: Formula, $FeMnO_3$:

1a. $16\,Fe$ in $16e$, $16\,Mn$ in $16e$.
2a. $16\,Fe$ in $16e$, $8\,Mn$ in $8i$, $8\,Mn$ in $8e$.
2b. $16\,Mn$ in $16e$, $8\,Fe$ in $8i$, $8\,Fe$ in $8e$.

B: Formula, $(Mn, Fe)_2O_3$:

1b. $16(Mn, Fe)$ in $16e$, $16(Mn, Fe)$ in $16e$.
2c. $16(Mn, Fe)$ in $16e$, $8(Mn, Fe)$ in $8i$, $8(Mn, Fe)$ in $8e$.
3. $24(Mn, Fe)$ in $24e$, $8(Mn, Fe)$ in $8i$, or
$24(Mn, Fe)$ in $24e$, $8(Mn, Fe)$ in $8e$.

The reflecting powers of *Mn* and *Fe* are nearly the same, and may be taken equal without serious error. This reduces the number of distinct structures to three; namely, 1*ab*, 2*abc*, and 3, of which 1*ab* depends on two parameters and the others on one. It is possible to decide among them in the following way. Let us assume that the contribution of oxygen atoms to the intensity of reflection in various orders from (100) is small compared with the maximum possible contribution of the metal atoms; that is, with $32\,\overline{M}$. The metal atom structure factor for structure 1 for $(h00)$ is

$$S_{h00} = 16\,\overline{M}\,(\cos 2\pi h u_1 + \cos 2\pi h u_2).$$

Now (200) gave a very weak reflection, so that S_{200} must be small. This is true only for $u_1 + u_2 \cong \frac{1}{4}$, for which

$$S_{h00} \cong 0 \text{ for } h = 2,\ 6,\ 10,$$
$$S_{h00} \cong 32\,\overline{M} \cos 2\pi h u_1 \text{ for } h = 4,\ 8,\ 12.$$

Now the gradual decline in intensity for $h = 4, 8, 12$ (Table I) requires that $u_1 = \frac{1}{8}$, and hence $u_2 = \frac{1}{8}$. This puts the two sets of metal atoms in the same place, and is hence ruled out. It may also be mentioned that structure 1 would place eight metal atoms on a cube diagonal, giving a maximum metal-metal distance of 2.03 Å, which is considerably smaller than metal-metal distances observed in other crystals. Structure 2, dependent on one parameter u, has structure factors

$$S_{h00} = 16\,\overline{M} \cos 2\pi h u \text{ for } h = 2,\ 6,\ \ldots,$$
$$S_{h00} = 16\,\overline{M}\,(1 + \cos 2\pi h u) \text{ for } h = 4,\ 8,\ \ldots.$$

All values of the parameter u are eliminated by the comparisons $600 > 200$, $400 > 200$, and $10.0.0 > 200$.

There accordingly remains only structure 3. We may take 8(*Mn*, *Fe*) in 8*e* rather than 8*i*, which leads to the same arrangements. The structure factor for various orders from (100) is then

$$S_{h00} = 8\overline{M}\,(\cos 2\pi h u - 1) \text{ for } h = 2,\ 6,\ 10, \text{ etc.}$$

$$S_{h00} = 8\overline{M}\,(\cos 2\pi h u + 3) \text{ for } h = 4,\ 8,\ 12, \text{ etc.}$$

All distinct structures are included in the parameter range $-0.25 \leqslant u \leqslant 0.25$, and, moreover, positive and negative values of u give the same intensity of reflection from ($h00$). Hence we need consider only $0 \leqslant |u| \leqslant 0.25$. In Figure 1 are shown values of $|S|$ calculated over this range with a constant value for $\overline{M}$. It is seen that the observed intensity inequality $600 > 200$ rules out the region $0.125 \leqslant |u| \leqslant 0.25$, and $10.0.0 > 200$ and $14.0.0 > 200$ further limit $|u|$ to between 0.00 and 0.06. The value of $|u|$ can be more closely determined by the use of atomic amplitude curves. The intensity of the diffracted beam can be taken as

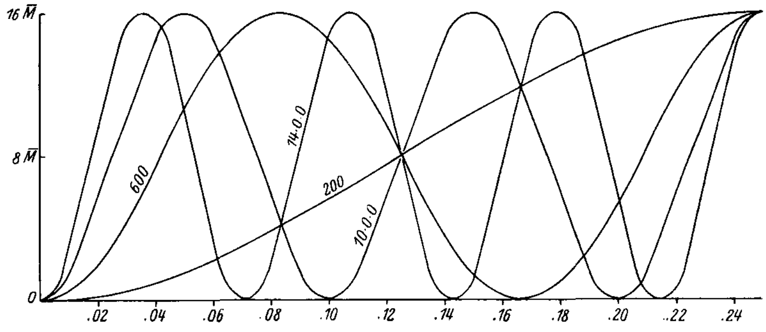

Fig. 1. Structure factor curves over the range $0 \leqslant |u| \leqslant 0.25$ with $\overline{M}$ constant.

$$I = K \cdot A_{hkl}^2, \tag{1}$$

with

$$A_{hkl} = \sum_i A_i e^{2\pi i (h x_i + k y_i + l z_i)}. \tag{2}$$

In this expression A_i, the atomic amplitude function, is given by

$$A_i = \left\{\frac{1 + \cos^2 2\theta}{2 \sin 2\theta}\right\}^{\frac{1}{2}} \cdot F_i, \tag{3}$$

in which F_i is the atomic F-function. Values of A_{Fe} and A_O calculated for MoK_α radiation and for an average wave-length of 0.40 Å effective on Laue photographs from Bragg and West's F-curves[1]) are given in

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[1]) W. L. Bragg and J. West, Z. Krist. **69**, 118. 1928.

Table IV. Figure 2 shows values of A_{h00} for $h = 2, 4 \ldots 16$ over the range of values 0 to 0.06 for $|u|$. It is seen that the value $|u| = 0.030 \pm 0.005$ is indicated by the observed intensities of Table I.

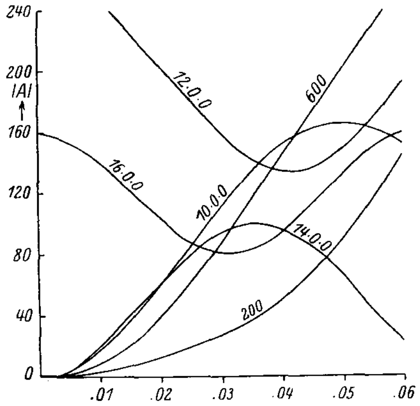

Fig. 2. A-curves over the range $0 < |u| < 0.06$.

Table IV.

Atomic A-values for Iron and Oxygen.

d_{hkl}	$\lambda = 0.40$ Å		$\lambda = 0.709$ Å	
	A_O	A_{Fe}	A_O	A_{Fe}
5.00 Å	28.0	79.0	21.2	59.8
2.50	14.5	45.0	10.4	33.6
1.67	7.5	30.1	5.8	21.7
1.25	4.4	21.8	3.5	15.6
1.00	2.7	16.8	2.1	11.6
0.83	1.5	12.5	1.2	9.0
0.72	0.9	10.3	0.6	7.3
0.63	0.6	8.4	0.4	5.9
0.55	0.4	6.6	0.2	4.6
0.50	0.3	5.2	0.1	4.0
0.45	—	4.5	—	3.6
0.42	—	3.7	—	3.4
0.39	—	3.1	—	3.2

Now there are two physically distinct arrangements of the metal atoms corresponding to $|u| = 0.030$, the first with $u = 0.030$, and the second with $u = -0.030$; and it is not possible to distinguish between them with the aid of the intensities of reflection of X-rays which they give. Let us consider the positions 24*e*. The structure factor for 24*e* is:

$$\begin{aligned} S_{hkl} &= 8\overline{M}[\cos 2\pi(hu+l/4)+\cos 2\pi(ku+h/4)+\cos 2\pi(lu+k/4)] \\ &\quad \text{for } h, k, l \text{ all even;} \\ &= 8\overline{M}\cos 2\pi(hu+l/4) \text{ for } h \text{ even, } k \text{ odd, } l \text{ odd;} \\ &= 8\overline{M}\cos 2\pi(ku+h/4) \text{ for } h \text{ odd, } k \text{ even, } l \text{ odd;} \\ &= 8\overline{M}\cos 2\pi(lu+k/4) \text{ for } h \text{ odd, } k \text{ odd, } l \text{ even.} \\ &= 0 \text{ otherwise.} \end{aligned}$$

It is seen that the value of the structure factor is the same for a given positive as for the same negative value of u, except for a difference in sign in some cases. But the positive and the negative parameter values correspond to structures which are not identical, but are distinctly different, as can be seen when the attempt to bring them into coincidence is made. This is a case where two distinct structures give the same intensity of X-ray reflections from all planes, so that they could not be distinguished from one another by X-ray methods. The presence of atoms in $8e$ or $8i$ does not change this result. In the case of bixbyite a knowledge of the positions of the oxygen atoms would enable the decision between these alternatives to be made, but the rigorous evaluation of the three oxygen parameters from the X-ray data cannot be carried out.

Zachariasen's arrangement of the metal atoms approximates the first of our two (that with the positive parameter value), and would be identical with it if his parameters were taken to be 0.030 and 0.530 rather than 0.021 and 0.542.

4. The Prediction and Verification of the Atomic Arrangement.

Recognizing the impracticability of determining the positions of the oxygen atoms from X-ray data, we have predicted a set of values for the oxygen parameters with the use of assumed minimum interatomic distances which is found to account satisfactorily for the observed intensities of a large number of reflections and which also leads to a structure which is physically reasonable.

The Fe—O distances in hematite are 1.99 and 2.06 Å. The (Mn, Fe)—O distances in bixbyite are expected to be the same in case that (Mn, Fe) has the coordination number 6, and slightly smaller, perhaps 1.90 Å, for coordination number 4. The radius of $O^{=}$ is 1.40 Å, and the average O—O distance in oxide crystals has about twice this value. When coordinated polyhedra share edges the O—O distance is decreased to a minimum value of 2.50 Å, shown by shared edges in rutile, anatase, brookite, corundum, hydrargillite, mica, chlorite, and other crystals. Our experience with complex ionic crystals leads us to believe that we may safely assume that the (*Mn*, *Fe*)—*O* and the *O*—*O* distances in bixbyite will not fall below 1.80 Å and 2.40 Å respectively.

On attempting to build up a structure on the basis of the first arrangement of the metal atoms, with $u = 0.030$, we found that there is no way in which the oxygen atoms can be introduced without causing interatomic distances smaller than the assumed minimum ones. This arrangement (which approximates Zachariasen's) is accordingly eliminated.

The second arrangement of the metal atoms, with $u = -0.030$, is such that satisfactory interatomic distances are obtained only when the oxygen atoms are in the general position with $x \cong \frac{3}{8}$, $y \cong \frac{1}{8}$, and $z \cong \frac{3}{8}$. Each oxygen atom is then at about 2 Å from four metal atoms; if it be assumed that these four metal-oxygen distances are equal, the parameters are found to have the values

$$x = 0.385, \qquad y = 0.145, \qquad z = 0.380.$$

With this structure each metal atom is surrounded by six oxygen atoms at a distance of 2.01 Å, and the minimum *O*—*O* distance is 2.50 Å. These dimensions are entirely reasonable.

It is probable that the various metal-oxygen distances are not exactly equal, but show variations of possibly ± 0.05 Å. The predicted parameter values may correspondingly be assumed to be accurate to only about ± 0.005.

Table V. Data from an Oscillation Photograph of Bixbyite[1]).

$\{h0l\}$	Estimated Intensity	$S^2/10{,}000$
202	0.00	0.01
402	0.01	0.28
404	10	67.00
602	0.2	0.68
604	0.6	1.69
802	0.2	0.74
804	2	3.34
806	0.05	0.19

The predicted structure has been verified by the comparison of the observed intensities of reflection for a large number of planes and those calculated with the use of Equation 1. Data for such comparisons for planes $(h00)$ and $(h0l)$ reflecting on oscillation photographs are given in Tables I and V, and for other planes giving Laue reflections in

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1) These reflections are from the first, second, and third layer lines of the same photograph as that from which the data of Table I were obtained, so that intercomparisons between Tables I and V may be made.

Table II. It is seen that the agreement between calculated and observed intensities is almost complete; the existent discrepancies are generally explicable as resulting from small errors in the parameter values (within the limits ± 0.005) or from errors in the assumed F-curves, for which an accuracy greater than ± 20% is not claimed.

5. Description of the Structure.

The structure found by the methods just described agrees well with the general principles underlying complex ionic crystals. The arrangement of the metal ions is shown in Fig. 3. These ions are nearly in cubic close-packing, so that the structure gives nearly the maximum dispersion of cations with given molal volume. Each cation is surrounded by six oxygen ions at a distance of 2.01 Å, at the corners of a highly distorted octahedron. These octahedra are of two types, corresponding to the two positions $8e$ and $24e$. Each $8e$ octahedron (with point-group symmetry C_{3i}) shares six edges with adjoining $24e$ octahedra, and each $24e$ octahedron shares six edges also, two with $8e$ and four with other $24e$ octahedra. Every shared edge is 2.50—2.52 Å long, in striking agreement with the minimum dimensions found in other crystals for shared edges and the theoretical values obtained for rutile and anatase[1]. These shared edges are arranged differently for $8e$ and $24e$; the distortion accompanying their shortening leads to octahedra of the shapes shown in Fig. 4 and 5. Various interatomic distances are given in Table VI.

Table VI.

Interatomic Distances in Bixbyite.

$(Fe, Mn) - O_A = 2.01$ Å	$(Fe, Mn) - O_K = 2.01$ Å	$O_A - O_F = 2.52$ Å	$O_H - O_E = 3.29$Å
$(Fe, Mn) - O_B = 2.01$	$(Fe, Mn) - O_L = 2.01$	$O_B - O_E = 2.52$	$O_L - O_G = 3.29$
$(Fe, Mn) - O_C = 2.01$	$O_A - O_B = 3.13$	$O_B - O_F = 2.52$	$O_H - O_I = 2.50$
$(Fe, Mn) - O_D = 2.01$	$O_B - O_C = 3.13$	$O_C - O_D = 2.52$	$O_K - O_L = 2.50$
$(Fe, Mn) - O_E = 2.01$	$O_D - O_E = 3.13$	$O_C - O_E = 2.52$	$O_H - O_K = 2.51$
$(Fe, Mn) - O_F = 2.01$	$O_D - O_F = 3.13$	$O_K - O_I = 3.38$	$O_I - O_L = 2.51$
$(Fe, Mn) - O_G = 2.01$	$O_E - O_F = 3.13$	$O_G - O_E = 2.92$	$O_G - O_K = 2.50$
$(Fe, Mn) - O_H = 2.01$	$O_A - O_C = 3.13$	$O_H - O_G = 3.12$	$O_E - O_I = 2.50$
$(Fe, Mn) - O_I = 2.01$	$O_A - O_D = 2.52$	$O_L - O_E = 3.12$	

Each oxygen ion is common to four octahedra, and has $\sum_i' s_i = 2$, in accordance with the electrostatic valence rule.

The structure can be instructively compared with that of fluorite, CaF_2. In fluorite the calcium ions are arranged at face-centered lattice points, and each is surrounded by eight fluorine ions at cube corners.

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[1] Linus Pauling, Z. Krist. **67**, 377. 1928.

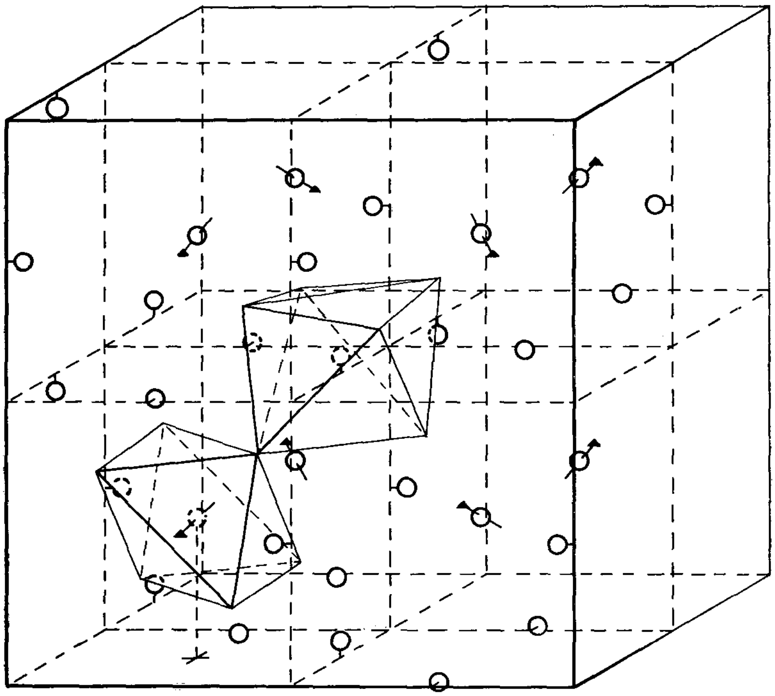

Fig. 3. The structure of bixbyite. The metal ions are shown, together with one of each kind of distorted octahedron.

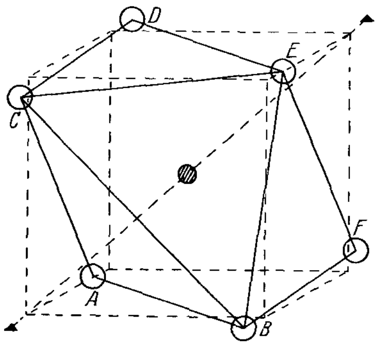

Fig. 4. The $8e$ octahedron, showing its relation to a cube.

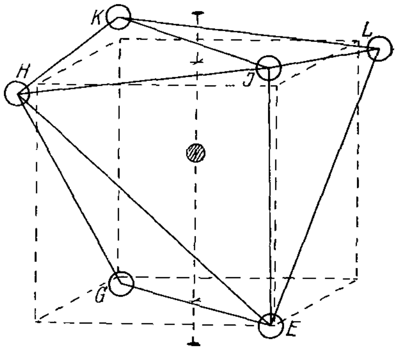

Fig. 5. The $24e$ octahedron, showing its relation to a cube.

If one-fourth of the fluorine ions are removed and the others are replaced by oxygen ions, calcium being replaced by (*Mn*, *Fe*), a structure is obtained which approximates that of bixbyite, which differs from it only in small displacements of the ions. This similarity is shown by the fact that the highly distorted octahedra have corners which are nearly at six of the eight corners of a cube, the six being chosen differently for the 8*e* and the 24*e* octahedra, as is seen from Fig. 4 and 5. This analogy was, indeed, pointed out by Zachariasen for his incorrect structure. As a matter of fact the "ideal" structure, with $u = 0$ and $x = \frac{3}{8}$, $y = \frac{1}{8}$, $z = \frac{3}{8}$, corresponding to Zachariasen's original atomic arrangement also corresponds to ours. Zachariasen very instructively pointed out that this ideal structure lies midway between the fluorite and the sphalerite arrangements, being obtained either by removing certain anions from fluorite, or by adding anions to sphalerite, the positions of the other ions remaining unchanged in either case. With the ideal structure the coordinated polyhedra are cubes with two truncated corners; for 8*e* these corners are at the ends of a body diagonal, for 24*e* at the ends of a face diagonal. The actual structure is distorted from the ideal one, which leads to too small interionic distances, in such a way as to give a constant metal-oxygen distance and a minimum oxygen-oxygen distance (for shared edges) of 2.50 Å. In Zachariasen's arrangement the distortion was in the opposite direction.

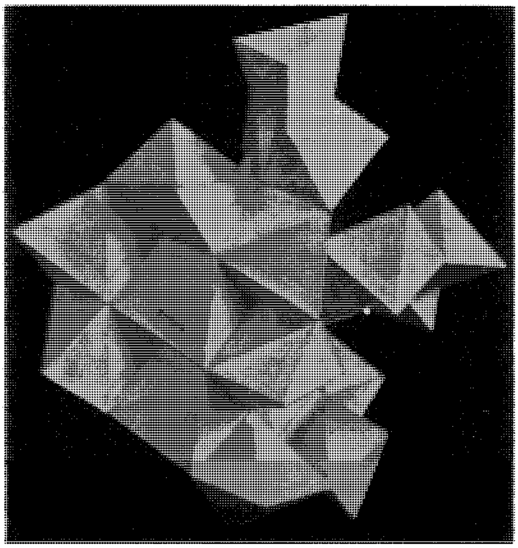

Fig. 6. A photograph of a model representing one half of the unit cube. The arrangement of the six 24*e* octahedra sharing edges with an 8*e* octahedron is clearly shown.

Table VII. Interatomic Distances in Sesquioxides.

Substance	a	$M—O$
$(Fe, Mn)_2O_3$	9.365 Å	2.01 Å
Mn_2O_3	9.41	2.02
Sc_2O_3	9.79	2.10
Y_2O_3	10.60	2.27
In_2O_3	10.12	2.17
Tl_2O_3	10.57	2.26
Sm_2O_3	10.85	2.33
Eu_2O_3	10.84	2.33
Gd_2O_3	10.79	2.32
Tb_2O_3	10.70	2.30
Dy_2O_3	10.63	2.28
Ho_2O_3	10.58	2.27
Er_2O_3	10.54	2.26
Tm_2O_3	10.52	2.26
Yb_2O_3	10.39	2.23
Lu_2O_3	10.37	2.22

As mentioned by Zachariasen, Goldschmidt[1]) found that the range of radius-ratio values leading to stability of the C-modification is about $0.60 < \frac{R_{M^{+3}}}{R_{O^{=}}} < 0.88$, which is high[2]) for a structure in which the coordination number is 6. The explanation of this is obvious; the coordinated octahedra are deformed so that the anions are nearly at six cube corners, and the radius ratio will accordingly tend to the range of values giving the coordination number 8.

A photograph of a model representing the structure is shown in Fig. 6.

Zachariasen's investigation makes it highly probable that the sesquioxides forming crystals of the C-modification have the same structure as that which we have found for bixbyite, and the similarity in intensities on powder photographs of the different substances which he reports indicates that the parameter values do not change very much throughout the series. Thus in all these crystals the cations are attributed the coordination number 6. Values of interionic distances calculated from Zachariasen's values of a with the bixbyite parameters are given in Table VII. It is probable, however, that the oxygen parameters do change as a increases in such a way as to keep shared edges short, for with the bixbyite parameters the shared edges increase from 2.50 Å to about 2.90 Å in Sm_2O_3 and Eu_2O_3. As a consequence the metal-oxygen dis-

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[1]) V. M. Goldschmidt, »Geochem. Vert.-Ges. d. El.«, VII, p. 76.

[2]) Linus Pauling, J. Am. chem. Soc. **51**, 1010. 1929.

tances in Table VII are probably a little larger than the true ones, the maximum error being 0.10 Å. It is worthy of mention that the *C*-structure and the corundum structure correspond to nearly the same interionic distances (1.99—2.06 A in hematite as compared with 2.01 Å in bixbyite), as is to be expected from the equality in coordination number of the cation.

Summary.

With the use of data from oscillation and Laue photographs it is shown that the unit of structure of bixbyite has $a = 9.365$ Å and contains $16(Mn, Fe)_2O_3$. The lattice is the body-centered cubic one, Γ_c'', and the space group is T_h^7. Two possible arrangements alone of the metal atoms are found to be compatible with the X-ray data (oxygen atoms being neglected), the first with $8(Mn, Fe)$ in $8e$, $24(Mn, Fe)$ in $24e$ with $u = 0.030$, and the second the same except with $u = -0.030$. It is pointed out that these two physically distinct arrangements give the same intensities of reflection of X-rays from all planes, so that an unambiguous structure determination for a crystal containing only atoms in $24e$ (or $24e$, $8e$, $8i$) could not be made with X-ray methods alone, despite the dependence on only one parameter.

The assumption that tbe (Mn, Fe)—O and O—O distances can not fall below 1.80 Å and 2.40 Å, respectively, eliminates the first metal atom arrangement, for there are no positions for oxygen satisfying it. With the second arrangement of metal atoms this assumption requires $48\,O$ to be in the general position of T_h^7, with $x \cong \frac{3}{8}$, $y \cong \frac{1}{8}$, $z \cong \frac{3}{8}$. Each oxygen ion is then nearly equidistant from four cations. Making the four (Mn, Fe)—O distances equal, values of the parameters are predicted which lead to good agreement between observed and calculated intensities of reflection from a large number of planes. The structure found for bixbyite has

$8(Mn, Fe)$ in $8e$
$24(Mn, Fe)$ in $24e$ with $u = -0.030 \pm 0.005$
$48\,O$ in x, y, z, etc. with $x = 0.385 \pm 0.005$,
$y = 0.145 \pm 0.005$,
$z = 0.380 \pm 0.005$.

A description of the structure with values of interatomic distances for bixbyite and for Sc_2O_3, Mn_2O_3, Y_2O_3, In_2O_3, Tl_2O_3, Sm_2O_3, Eu_2O_3, Gd_2O_3, Tb_2O_3, Dy_2O_3, Ho_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, and Lu_2O_3, which are shown to have the same structure by Zachariasen's investigation, is given in Section 5.

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The Crystal Structure of Zunyite, $Al_{13}Si_5O_{20}(OH,F)_{18}Cl$

By

Linus Pauling

With 6 figures

1933
AKADEMISCHE VERLAGSGESELLSCHAFT M. B. H.
LEIPZIG

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The Crystal Structure of Zunyite, $Al_{13}Si_5O_{20}(OH,F)_{18}Cl$.

By

Linus Pauling in Pasadena.

(With 6 figures.)

Zunyite has been found as isometric tetrahedra at the Zuñi Mine, San Juan Co., Colorado, intimately mixed with guitermanite; at Red Mountain, Ouray Co., Colorado, in an altered porphyrite; and recently[1]) near Postmasburg, South Africa. Hillebrand assigned it the empirical formula $H_{18}Al_{16}Si_6(O, F, Cl)_{45}$, and Groth adopted the formula $Al_8Si_3O_{12}(OH, F, Cl)_{12}$. The crystals are usually colorless and transparent, hardness 7, density 2.873—2.904.

Gossner[2]) prepared powder, rotation, and Laue photographs of zunyite crystals from the Zuñi Mine, reporting values for a_0 of 13.80, 13.93, and 13.98 Å. He suggested the formula $SiAl_3O_5(OH)_2(F, Cl) \cdot \frac{12}{19} H_2O$ or $Si_3Al_9O_{13}(OH)_{10}(F, Cl)_3$, and assigned the crystal the symmetry of space group T_d^1, although his data indicated a face-centered lattice.

Our investigation of zunyite has shown the cubic unit of structure with $a_0 = 13.82$ Å to contain four molecules of composition $Al_{13}Si_5O_{20}(OH, F)_{18}Cl$ and to have the space-group symmetry T_d^2, and has led to the formulation of a detailed atomic arrangement.

The Unit of Structure and Space-group Symmetry.

Oscillation and Laue photographs were prepared with tetrahedra 1—2 mm. on edge of zunyite from the Zuñi Mine. A Laue photograph taken with the incident beam of X-rays normal to (111), reproduced in Fig. 1, shows three planes of symmetry and a three-fold axis, requiring the point-group symmetry of the crystal to be T_d, O, or O_h, of which

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[1]) L. T. Nel, Min. Mag. **23**, 207. 1931. Synthetic crystals identified with zunyite have been prepared by M. Schlaepfer and P. Niggli, Z. anorg. Chem. **87**, 52. 1914. C. Palache, Am. Min. **17**, 304. 1932, has reported finding sharp crystals of zunyite (0.1—1.0 mm) with hematite in powder in pots from graves in Uaxactun, Guatemala.

[2]) B. Gossner, N. Jb. Min., Beil.-Bd. **55** A, 319. 1927. I have had available only the Strukturbericht — abstract of this work.

only T_d is compatible with the observed tetrahedral face development. An oscillation photograph with [100] as axis of rotation gave the value 14 Å for I_{100}, and an accurate value of

$$a_0 = 13.820 \pm 0.005 \text{ Å}$$

was obtained as the mean of thirteen reflections of $MoK\alpha_1$, α_2, β, and γ on a plate calibrated by simultaneous reflection from (0001) of β-alumina, for which the spacing 11.225 Å was assumed. On assigning indices to the spots on a Laue photograph with the aid of a gnomonic projection and calculating $n\lambda$-values on the basis of this unit, no values smaller than the short wave-length limit of 0.24 Å were found; there is accordingly no evidence requiring that the unit of structure be larger than that indicated by the oscillation photograph.

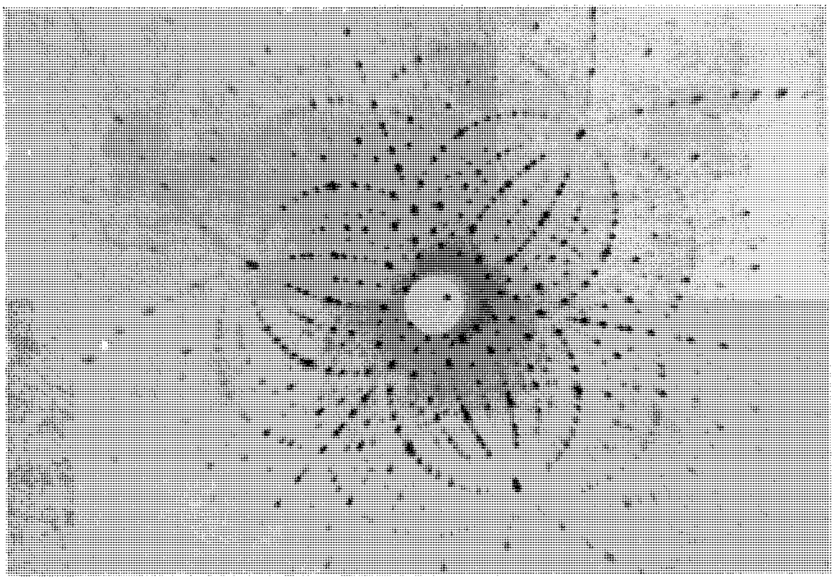

Fig. 1. Laue photograph from zunyite, incident beam nearly parallel to [111]. Short wave-length limit 0.24 Å.

The Laue data (Table I) contain first-order reflections only from planes with all indices odd. This fact, together with the absence of reflections with mixed indices on oscillation photographs, shows the lattice to be face-centered. Of the two face-centered space groups isomorphous with point group T_d, T_d^2 and T_d^5, the latter requires that no odd-order reflections occur from planes (khl) with $h = \pm k$. The numerous observed reflections of this type (Table I) consequently determine the space group to be

$$T_d^2 - F\,\bar{4}3\,m.$$

Table I.
Laue Photographic Data for Zunyite.
Incident beam normal to (111).

Forms giving first-order reflections:

{h k l}	n λ	{h k l}	n λ	{h k l}	n λ
531	0.438 Å	977	0.444 Å	13.9.3	0.427 Å
533	.372	995	.424	11.11.5	.296
551	.312	13.5.3	.386	15.7.1	.402
951	.441	11.9.3	.372	15.9.1	.360
773	.443	13.7.1	.356	17.7.1	.418
971	.357	11.9.7	.311	13.11.7	.420
11.7.1	.266	15.5.3	.421	15.11.5	.387

Forms giving second-order reflections:

{h k l}	n λ	{h k l}	n λ	{h k l}	n λ
322	0.916 Å	740	0.803 Å	652	0.727 Å
430	.618	641	.894	851	.662
530	.929	552	.575	922	.890
541	.745	722	.828	932	.662
631	.676	544	.843	10.4.1	.671

The Chemical Formula and the Atomic Arrangement.

Using the values $a_0 = 13.82$ Å and density $= 2.89$ g/cm^2, the numbers of atoms contained in a fundamental unit (one-fourth of the unit cube) given in Table II are calculated from published analyses. Of these analyses greatest weight can probably be laid on No. 1, 2, and 3; No. 6 is probably untrustworthy (very high sum).

Bearing in mind that the relative sizes of the ions permit isomorphous replacement of OH' by F' but not by Cl', we write with considerable confidence the formula $(Si, Al, Fe, P)_{18}O_{20}(OH, F)_{18}Cl$, which agrees well with analyses 1, 2, and 3. Inasmuch as aluminium (as well as phosphorus) may replace silicon with coordination number 4, it is evident that there are at least five silicon atoms in the unit, corresponding to the chemical formula

$$Al_{13}Si_5O_{20}(OH, F)_{18}Cl.$$

It will be shown that a detailed consideration of the X-ray data confirms this formula.

Table II.
Analyses of Zunyite.

	1	2	3	4	5	6
Si	4.66	4.62	4.63	4.65	4.62	5.58
Al	13.21	13.05	13.17	12.97	13.00	12.39
Fe	0.03	0.09	0.03	0.19	0.21	0.07
P	0.10	0.11	0.09	0.04	0.04	0.03
Ca	—	0.02	—	0.07	0.04	—
Mg	—	—	—	0.12	0.09	—
Na	0.09	0.18	0.12	0.62	0.55	—
K	0.02	—	0.04	—	—	—
Cl	0.96	0.86	0.96	1.15	1.58	0.81
F	3.44	3.56	3.17	0.31	0.25	0.49
OH	14.04	14.37	14.37	14.71	15.05	17.39
O	20.28	20.45	20.08	21.54	21.11	20.57
$Si+Al+Fe+P$	18.00	17.87	17.92	17.85	17.87	18.07
$F+OH$	17.48	17.93	17.54	15.02	15.30	17.88
Density	2.875	2.876/ 2.904	2.878	2.884	2.873	—

1. W. F. Hillebrand, Zuñi Mine, Colorado.
2. S. L. Penfield, Charter Oak Mine, Red Mountain, Colorado.
3. Gossner and Mussgnug, Zuñi Mine, Colorado.
4. 5. H. G. Weall, Dornfontein Farm, South Africa. 4, small crystals; 5, large crystals.
6. J. McCrae, Dornfontein Farm, South Africa.

The density calculated for four molecules of composition $Al_{13}Si_5O_{20}(OH)_{15}F_3Cl$ in a cube with $a_0 = 13.820$ Å is 2.897 $\mathrm{g/cm}^2$.

The large size of the unit of structure and the complexity of the chemical formula make the deduction of the atomic arrangement from X-ray data alone impractical if not impossible. We consequently make use also of arguments based on analogy with other structures, semi-empirical structural rules regarding ionic sizes and ionic environments, etc., with ultimate recourse to the stochastic[1]) method, which has already

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[1]) I am indebted to Dr. Karl K. Darrow of the Bell Telephone Laboratories for acquainting me with this word and with its use by Alexander Smith, who wrote in his "Inorganic Chemistry", 1909, p. 142, the following: "... When Mitscherlich discovered that Glauber's salt gave a definite pressure of water vapor, he at once formed the hypothesis, that is, supposition, that other hydrates would be found to do likewise. Experiments showed this supposition to be correct. The hypothesis was at once displaced by the fact. This sort of hypothesis predicts the probable existence of certain facts or connections of facts, hence, reviving a disused word, we call it a stochastic hypothesis (Greek στοχάστικος, apt to divine

been applied to brookite, topaz, mica, natrolite, and many other crystals — a detailed structure being suggested, and then tested by a comparison of observed and calculated intensities of reflection.

It was found possible to devise a satisfactory atomic arrangement by making the following assumptions.

1. The space group is T_d^2, and the unit cube has $a_0 = 13.82$ Å.

2. The framework of the structure consists of silicon tetrahedra (four oxygen ions coordinated about a silicon ion at the corners of an approximately regular tetrahedron) and aluminium octahedra and (or) tetrahedra, with $Si\text{-}O = 1.59$ Å, $Al\text{-}O = 1.89$ Å in octahedra, 1.75 Å in tetrahedra, as observed in other aluminosilicate crystals.

3. The electrostatic valence rule[1]) is approximately satisfied, deviations of $\frac{1}{2}$ not being allowed. Sharing of polyhedra must consequently be such as to have each OH' or F' common to two octahedra or attached to one silicon or aluminum tetrahedron only, and each $O^=$ common to two silicon tetrahedra, four aluminum octahedra, two octahedra and one silicon tetrahedron, two or three octahedra and one aluminum tetrahedron, etc.; structures with $O^=$ common to three silicon tetrahedra or to one silicon tetrahedron and three octahedra are not satisfactory.

4. The chemical composition is approximately $Al_{13}Si_5O_{20}(OH, F)_{18}Cl$, the ideal formula containing at least five silicon atoms.

5. The distance between any two oxygen atoms cannot fall below 2.4 Å.

Let us first assume that there are six equivalent silicon atoms in the fundamental unit, that is, 24 or more in the unit cube. (a) If there are 24 equivalent and distinct tetrahedra, the 24 Si occupy 24a or 24b (in Wyckoff's notation). No value of the parameter prevents infraction of the condition $O\text{-}O \geqq 2.4$ Å, eliminating this possibility. (b) If the 24 equivalent silicon tetrahedra share corners, these corners lie on threefold axes, which makes $O^=$ common to three silicon tetrahedra, contradicting assumption 3.

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the truth by conjecture). It differs from the other kind in that it professes to be composed entirely of verifiable facts and is subjected to verification as quickly as possible . . ." The method of treating very complex crystals which has been used recently, in which a plausible structure is guessed with the aid of hints provided by the observed size of unit and space-group symmetry, and the stochastic hypothesis that this is the actual structure of the crystal thereupon is either verified or disproved by intensity observations, may well be called the stochastic method, in contradistinction to the "rigorous" method, which latter involves the straightforward testing by intensity data of all of the possible arrangements provided by the theory of space groups.

[1]) Linus Pauling, J. Am. chem. Soc. **51**, 1010. 1929.

The only remaining positions for 20 or 24 silicon atoms are 16a plus one or two of the positions 4b, 4c, 4d, and 4e. Agreement with the electrostatic valence rule with silicon tetrahedra in 4b (or c, d, e) is reached only when the corners are shared with other tetrahedra. The crystals must consequently contain groups of five tetrahedra such as shown in Fig. 2.

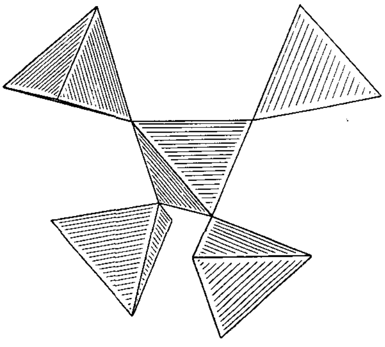

Fig. 2. Group of five silicon tetrahedra, $[Si_5O_{16}]$, occurring in zunyite.

The formula suggests that the unit contains four groups of twelve octahedra, with point-group symmetry T_d (positions 4b, c, d, e). Such groups, shown in Fig. 3, occur in spinel. A framework might be constructed by sharing the tetrahedral groups of Fig. 2 with these, the three oxygen atoms labeled *A* in Fig. 3 forming the base of a tetrahedron. The chemical formula and the electrostatic valence rule require, however, that the atoms labeled *B* be shared with similar octahedra in a neighboring group, and it is found that this sharing is not geometrically possible.

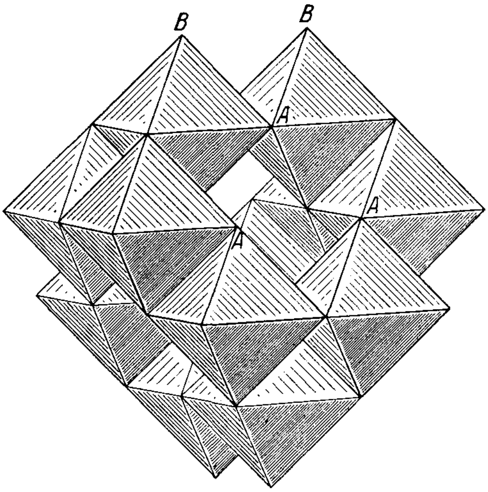

Fig. 3. Group of twelve aluminum octahedra, point-group symmetry T_d, occurring in spinel.

If the groups of three octahedra be inverted, the group of twelve shown in Fig. 4, also with point-group symmetry T_d, is obtained. When four such groups are placed in the positions 4b, it is found that the corners *B* of one group (at 000, say) can be shared with the corners *B'* of an adjacent group (at $\frac{1}{2}0\frac{1}{2}$), and that such sharing for regular octahedra with $Al\text{-}O = 1.89$ Å leads to a value of 13.82 Å for a_0, in exact agreement with the observed value. Moreover, the groups of five tetrahedra can be placed in position 4d, and tetrahedron corners shared with corners *A* with only a slight distortion (of a few hundredths of an Ångström).

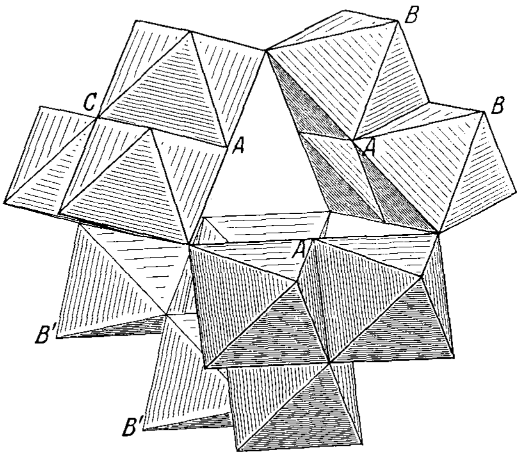

Fig. 4. Group of twelve aluminum octahedra, point-group symmetry T_d, occurring in zunyite.

This agreement in dimensions makes it highly probable that this is the framework of zunyite.

Agreement with the electrostatic valence rule is satisfactory except for the oxygen atoms C (Fig. 4), common to only three octahedra. It is seen, however, that these atoms occur in groups of four, which can be combined to tetrahedra by placing aluminum ions in positions 4e, the total bond strengths then becoming $2\frac{1}{4}$. The four chlorine ions occupy positions 4c, 4b being ruled out by the small Cl^{-}-$O^{=}$ distance it leads to (2.72 Å, sum of radii 3.21 Å).

The resultant atomic arrangement of $4\,Al_{13}Si_5O_{20}(OH,F)_{18}Cl$ in the unit cube has the following analytical description, the parameter values being so chosen as to distort the octahedra slightly in order to join them to undistorted silicon tetrahedra:

$4\,Cl$ in 4c;
$4\,Si_{\mathrm{I}}$ in 4d;
$16\,Si_{\mathrm{II}}$ in 16a, $u_{Si} = 0.117$;
$4\,Al_{\mathrm{I}}$ in 4e;
$48\,Al_{\mathrm{II}}$ in 48d, $u_{Al} = 0.089$, $v_{Al} = -0.228$;
$16\,O_{\mathrm{I}}$ in 16a, $u_{\mathrm{I}} = -0.177$;
$16\,O_{\mathrm{II}}$ in 16a, $u_{\mathrm{II}} = 0.184$;
$24\,O_{\mathrm{III}}$ (OH,F) in 24a, $u_{\mathrm{III}} = 0.273$;
$48\,O_{\mathrm{IV}}$ (OH,F) in 48d, $u_{\mathrm{IV}} = 0.181$, $v_{\mathrm{IV}} = 0.545$;
$48\,O_{\mathrm{V}}$ in 48d, $u_{\mathrm{V}} = 0.139$, $v_{\mathrm{V}} = 0.006$.

The special positions include the following points and those obtained from them by the translational operations of the face-centered lattice:

4c: $\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}$;
4d: $\frac{1}{4}\,\frac{1}{4}\,\frac{1}{4}$;
4e: $\frac{3}{4}\,\frac{3}{4}\,\frac{3}{4}$;
16a: $u\,u\,u$, $u\,\bar{u}\,\bar{u}$, $\circlearrowleft$);
24a: $u\,0\,0$, $\circlearrowleft$), $\bar{u}\,0\,0$, $\circlearrowleft$);
48d: $u\,u\,v$, $\circlearrowleft$), $u\,\bar{u}\,\bar{v}$, $\circlearrowleft$), $\bar{u}\,u\,\bar{v}$, $\circlearrowleft$) $\bar{u}\,\bar{u}\,v$, $\circlearrowleft$).

Observed and calculated intensities of reflections on two oscillation photographs, one of which is reproduced in Fig. 5, are given in Table III. The first number below each set of indices (*hkl*) is the visually estimated observed intensity, and the second the intensity calculated by the usual Bade-methode formula with the use of the Pauling-Sherman f_0-values[1], the Lorentz and polarization factors being included and the temperature factor omitted. No correction for position on the film has been made. It is seen that the agreement is satisfactory for most of the 56 forms included in the table, providing strong support for the suggested structure, inasmuch as the calculated intensities relate to a structure constructed entirely without reference to the intensity data, and no variation of parameters to improve the agreement has been made. Rather small changes in the parameters or f_0 values produce large changes in the calculated intensities, which are sensitive to these changes because they are small, the calculated intensity 0.20 for (220), for example, being only 0.05% of the maximum intensity possible for this reflection, with all the atoms in the unit reflecting in phase. It is probable that complete agreement with the observed intensities could be obtained with the use of parameter values differing only slightly from those given above; but the large number of the parameters and the labor involved in the

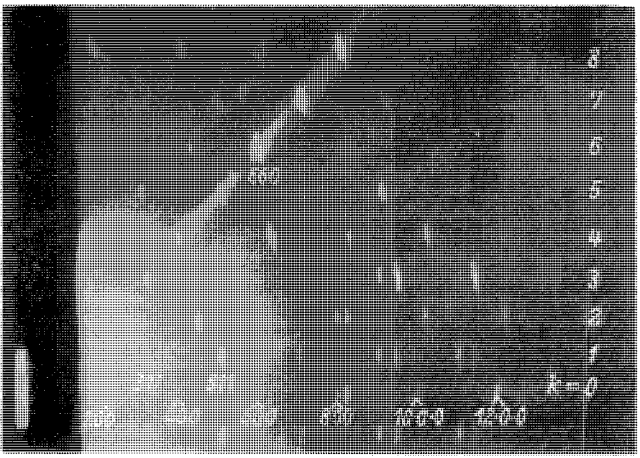

Fig. 5. Oscillation photograph No. 4 from zunyite. Axis of oscillation [010], crystal oscillated 45° from (100). Molybdenum *K* radiation filtered through zirconia.

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[1] Linus Pauling and J. Sherman, Z. Krist. **81**, 1. 1932.

Table III.

Observed and Calculated Intensities on 45° Oscillation Photographs.

Photograph No. 4. (100), with [010] as axis of rotation. *MoKa* radiation.

(200) 0.5—1.1		(220) 0.6—0.2						
	(311) 5—4.4		(331) 2—1.1					
(400) 0.0—0.1		(420) 0.0—0.0 (422) 4—2.6		(440) 2—1.7 (442) 0.0—0.1				
	(511) 5—2.8		(531) 0.5—0.2		(551) 1.2—1.3			
(600) 0.1—1.4 (602) 0.1—0.1		(620) 0.1—0.1 (622) 0.5—0.6		(640) 0.0—0.0 (642) 1.1—1.3		(660) 10—10.9 (662) 0.6—1.2		
	(711) 0.4—0.3		(731) 0.1—0.5		(751) 0.6—0.4		(771) 3—2.4	
(800) 0.4—0.8 (802) 1.0—1.1		(820) 1.0—1.1 (822) 1.0—0.9		(840) 0.0—0.0 (842) 0.8—0.3		(860) 0.2—0.3 (862) 0.6—0.6		(880) 3—3.8
	(911) 1.1—0.9 (913) 0.9—1.1		(931) 1.0—1.1 (933) 1.4—1.2		(951) 1.6—1.3		(971) 0.4—0.3	
(10.0.0) 0.2—1.3 (10.0.2) 0.0—0.0		(10.2.0) 0.0—0.0 (10.2.2) 1.0—0.7		(10.4.0) 0.0—0.0 (10.4.2) 1.1—1.1				
	(11.1.1) 1.1—0.6 (11.1.3) 0.4—0.2		(11.3.1) 0.4—0.2 (11.3.3) 1.4—2.2					
(12.0.0) 1.0—1.1 (12.0.2) 0.0—0.2		(12.2.0) 0.0—0.2 (12.2.2) 0.8—0.5						

Photograph No. 1. (111).

(111)	(222)	(333)	(444)	(555)	(666)	(777)	(888)	(999)
5—8	6—6	15—11	10—12	0.3—0.5	1—0.9	0.2—0.2	0.5—1.0	0.2—0.1

structure-factor calculations makes the determination of the parameter variations impracticable.

The structure of zunyite is shown in Fig. 6. It may be considered as a sphalerite-type arrangement of the tetrahedral and octahedral groups, the group of twelve octahedra (Fig. 4) replacing *Zn* and the group of five tetrahedra (Fig. 2) replacing *S*. The interatomic distances, which are probably accurate to ± 0.05 Å for *K*-*O* and ± 0.10 Å for *O*—*O*, (*O* = *O*, *OH*, *F*), are given in Table IV. The interatomic distances given by ionic radii1) are: Al^{3+}-$O^{=}$ = 1.90 Å in octahedron, 1.67 Å in tetrahedron (using correction factor 0.88 for octahedron-tetrahedron transition), Si^{4+}-$O^{=}$ = 1.59 Å, $O^{=}$-$O^{=}$ = 2.80 Å on the average. The radius of F' (1.36 Å) is very close to that of $O^{=}$ (1.40 Å). The sum of the ionic radii Cl'-$O^{=}$ = 3.21 Å and Cl'-F' = 3.17 Å are in satisfactory agreement with value 3.14 Å of Table IV for the six nearest neighbors of *Cl*, there being twelve other $(OH,F)'$ ions at 3.59 Å.

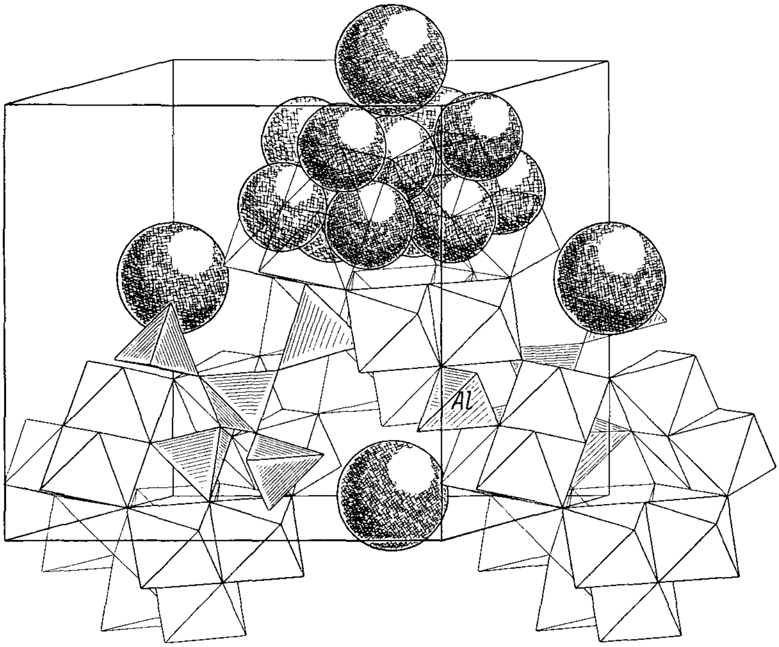

Fig. 6. A portion of the zunyite structure. AlO_6 groups are represented by octahedra, and SiO_4 and AlO_4 groups by tetrahedra, the last being marked *Al*. Smaller spheres represent oxygen, larger chlorine ions. Groups of five tetrahedra (Fig. 2) and twelve octahedra (Fig. 4) preserve their identity in the structure.

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1) Linus Pauling, J. Am. chem. Soc. **49**, 765. 1927.

Table IV.
Interatomic Distances.

Tetrahedra:

$Si\text{-}O = 1.59$ Å
$Al_I\text{-}O = 1.74$

Octahedra:

$Al_{II}\text{-}O_I = 1.86$
$Al_{II}\text{-}O_{III} = 1.85$
$Al_{II}\text{-}O_{IV} = 1.89$
$Al_{II}\text{-}O_V = 1.93$

$Cl\text{-}O_{III} = 3.14$
$Cl\text{-}O_{IV} = 3.59$

Tetrahedron edges:

$O\text{-}O = 2.60$ Å, Si tetrahedra
$O_I\text{-}O_I = 2.84$, Al tetrahedra.

Octahedron edges:

$O_I\text{-}O_V = 2.64$
$O_{IV}\text{-}O_V = 2.64$
$O_{IV}\text{-}O_I = 2.68$
$O_V\text{-}O_V = 2.84$
$O_{III}\text{-}O_V = 2.67$
$O_{IV}\text{-}O_{IV} = 2.67$
$O_{III}\text{-}O_{IV} = 2.67$

I wish to thank Dr. J. L. Hoard for assistance in preparing the photographs and Dr. J. Sherman for the intensity calculations of Table III.

Summary.

The X-ray examination of zunyite with the use of Laue and oscillation photographs has shown the cubic unit of structure to have $a_0 = 13.820 \pm 0.005$ Å, and the symmetry of space group $T_d^2\text{-}F\bar{4}3m$. The unit contains $4\,Al_{13}Si_5O_{20}(OH, F)_{18}Cl$, the calculated density being 2.897 g/cm^2. An atomic arrangement suggested by general structural principles applicable to complex ionic crystals was found to account satisfactorily for the observed intensities of the X-ray reflections on oscillation photographs. This structure, consisting of a framework of silicon tetrahedra and aluminum octahedra and tetrahedra, with chlorine ions occupying cavities in the framework, is described in the foregoing section.

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Chapter 6

COVALENT, INTERMETALLIC AND MOLECULAR CRYSTALS

Contents

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[Contribution from the Gates Chemical Laboratory, California Institute of Technology, No. 27]

THE CRYSTAL STRUCTURE OF MOLYBDENITE

By Roscoe G. Dickinson[1] and Linus Pauling

Received April 24, 1923

The mineral molybdenite, MoS_2, is described[2] as occurring in hexagonal crystals with a very complete basal cleavage. A study of its crystal structure has been carried out using X-ray spectral photographs and Laue photographs treated as previously described.[3] Since the crystals bend very easily and inelastically, some difficulty was experienced in obtaining good Laue photographs. However, the following procedure resulted in very satisfactory photographs: a crystal considerably thicker than the desired section was selected and one surface cleaved away; the cleavage face was then cemented to a cover glass and the specimen thus supported cleaved to the desired thickness and photographed without removal from the glass. A Laue photograph taken with the incident beam normal to the basal plane possessed a hexagonal axis and 6 symmetry planes. Several photographs were made with the beam somewhat inclined to this position.

The Unit of Structure

Angles of reflection of the molybdenum Kα radiation from the faces (0001), $(10\bar{1}0)$, and $(11\bar{2}0)$ are given in Table I. The reflections from the last two faces were obtained by transmission of the beam through the crystal; in these cases the α doublet was not resolved. A density determination carried out with a pycnometer using benzene gave the value 4.92 g./cc. From this the number of molecules in a unit having $d_{0001} = 6.15$ Å. and $d_{10\bar{1}0} = 2.73$ is found to be 0.988. The axial ratio of this unit is 1.95; correspondingly the angle between the faces $(20\bar{2}1)$ and (0001) should be 77° 28.6′. Direct observations[2] have given values from 70° 28′ to 77° 13′, the last being the usually accepted value.

Table I

Reflection Data from Molybdenite

$h\,i\,k\,l$	λ	Observed angle of reflection	$\frac{1}{n} \times d_{h\,i\,k\,l}$	Relative intensities	S u = 0.621
(0001)	0.7078	3° 18′	$\frac{1}{2} \times 12.32$	strong	5.05
....	....	6° 37′	$\frac{1}{4} \times 12.28$	weak	1.27
....	....	9° 56′	$\frac{1}{6} \times 12.32$	medium	5.85
....	....	13° 19′	$\frac{1}{8} \times 12.28$	med. strong	9.17
....	....	16° 43′	$^1/_{10} \times 12.30$	med. weak	4.26
$(10\bar{1}0)$	0.7085	7° 27′	$^1/_1 \times 2.73$	....	..
$(11\bar{2}0)$	0.7085	13° 25′	$^1/_1 \times 1.53$	....	..

When indices were assigned to the Laue spots on a basis of this unit, values of $n\,\lambda$ as low as 0.13 Å. were found. As the minimum wave length

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[1] National Research Fellow in Chemistry.

[2] Hintze, "Handbuch der Mineralogie," Viet and Co., Leipzig, **1904**, vol. 1, p. 410.

[3] Dickinson, This Journal, **44**, 276 (1922).

present was about 0.24 Å., this unit is not possible. A unit having $d_{0001} = 12.30$ Å. and an axial ratio 3.90 and containing, therefore, 2 MoS_2 gave no impossible values of $n\lambda$; this unit is the smallest one possible and all of the indices used in the remainder of this paper refer to its axes.

The Arrangement of the Atoms

Reference to a tabulation[4] of the coördinates of equivalent points in space groups isomorphous with the point-groups D_{3h}, C_{6v}, D_6, and D_{6h} shows that there is a variety of ways of arranging 2 MoS_2 in an hexagonal unit in such a way that the molybdenum atoms are in equivalent positions, and likewise the sulfur atoms. Some of these arrangements can be obtained by placing 1 MoS_2 in the smaller unit shown to be impossible. Excluding these, the following distinct arrangements remain.

	Mo at	S at
1.	$(\frac{1}{3}\frac{2}{3}0)$ $(\frac{2}{3}\frac{1}{3}0)$	$(\frac{1}{3}\frac{2}{3}u)$ $(\frac{1}{3}\frac{2}{3}\bar{u})$ $(\frac{2}{3}\frac{1}{3}u)$ $(\frac{2}{3}\frac{1}{3}\bar{u})$
2.	$(00v)$ $(00\bar{v})$	$(\frac{1}{3}\frac{2}{3}u)$ $(\frac{1}{3}\frac{2}{3}\bar{u})$ $(\frac{2}{3}\frac{1}{3}u)$ $(\frac{2}{3}\frac{1}{3}\bar{u})$
3.	(000) $(00\frac{1}{2})$	$(\frac{1}{3}\frac{2}{3}u)$ $(\frac{2}{3}\frac{1}{3}\bar{u})$ $(\frac{1}{3},\frac{2}{3},\frac{1}{2}-u)$ $(\frac{2}{3},\frac{1}{3},\frac{1}{2}+u)$
4.	$(00\frac{1}{4})$ $(00\frac{3}{4})$	$(\frac{1}{3}\frac{2}{3}u)$ $(\frac{2}{3}\frac{1}{3}\bar{u})$ $(\frac{1}{3},\frac{2}{3},\frac{1}{2}-u)$ $(\frac{2}{3},\frac{1}{3},\frac{1}{2}+u)$
5.	$(\frac{1}{3}\frac{2}{3}\frac{1}{4})$ $(\frac{2}{3}\frac{1}{3}\frac{3}{4})$	$(00u)$ $(00\bar{u})$ $(0,0,\frac{1}{2}+u)$ $(0,0,\frac{1}{2}-u)$
6.	$(\frac{1}{3}\frac{2}{3}\frac{1}{4})$ $(\frac{2}{3}\frac{1}{3}\frac{3}{4})$	$(\frac{1}{3}\frac{2}{3}u)$ $(\frac{2}{3}\frac{1}{3}\bar{u})$ $(\frac{1}{3},\frac{2}{3},\frac{1}{2}-u)$ $(\frac{2}{3},\frac{1}{3},\frac{1}{2}+u)$

Arrangements 1 and 2 make it difficult to account for the absence of odd orders from (0001), and the absence of all first orders from planes having $\frac{1}{3}(h + 2i)$ integral and l odd. Any of the remaining arrangements accounts for the above observations.

The value of $S = \sqrt{A^2 + B^2}$ for planes having $\frac{1}{3}(h + 2i)$ not integral and l odd is always $2\,\overline{\text{Mo}}$ for Arrangement 3; therefore, at a given wave length such planes should always reflect more weakly the smaller the value of d/n. This is not at all in accord with the Laue photographic data, hence Arrangement 3 is impossible.

From (0001) the eight order was slightly stronger than the sixth and much stronger than the fourth. Assuming that a molybdenum atom has at least twice the reflecting power of a sulfur atom (the respective atomic numbers are 42 and 16) it can readily be shown that these (0001) intensities necessitate giving u a value between 0.11 and 0.15 or between 0.61 and 0.65 in Arrangements 4, 5, and 6. On Laue photographs, planes of the forms $\{31\bar{4}5\}$ and $\{31\bar{4}3\}$ were found to reflect much more strongly than $\{31\bar{4}1\}$ in spite of their smaller spacings. The value of S for these planes is given by $S = 2\,\bar{S}[\cos 2\pi(\frac{1}{3} + lu) + \cos 2\pi(\frac{1}{3} - lu)]$ for either Arrangment 4 or 5. The possible values of u make S differ only moderately for these 3 forms and never in such a way that the first 2 are both greater than the third. Hence Arrangements 4 and 5 are impossible.

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[4] Wyckoff, "The Analytical Expression of the Results of the Theory of Space-Groups," *Carnegie Inst. Publ.*, **318** (1922).

For Arrangement 6 the values of S are given by the following equations.

Class 1: $\frac{1}{3}(h + 2i)$ integral, l even.

$$n = 1;\ S = 2\,\overline{\mathrm{Mo}} + 4(-1)^{\frac{l}{2}}\,\overline{\mathrm{S}}\cos 2\pi l\,\mathrm{u}$$

Class 2: $\frac{1}{3}(h + 2i)$ not integral, l even.

$$n = 1;\ S = \overline{\mathrm{Mo}} - 2(-1)^{\frac{l}{2}}\,\overline{\mathrm{S}}\,[\cos 2\pi(\tfrac{1}{3} + l\,\mathrm{u}) + \cos 2\pi(\tfrac{1}{3} - l\,\mathrm{u})]$$

Class 3: $\frac{1}{3}(h + 2i)$ integral, l odd.

$$n = 1;\ S = 0.$$

$$n = 2;\ S = 2\,\overline{\mathrm{Mo}} - 4\,\overline{\mathrm{S}}\cos 4\pi\, l\,\mathrm{u}$$

Class 4: $\frac{1}{3}(h + 2i)$ not integral, l odd.

$$n = 1;\ S = \sqrt{3}\,\overline{\mathrm{Mo}} + 2(-1)^{\frac{l+1}{2}}\,\overline{\mathrm{S}}\,[\cos 2\pi(\tfrac{1}{3} + l\,\mathrm{u}) - \cos 2\pi(\tfrac{1}{3} - l\,\mathrm{u})]$$

For $0.11 < \mathrm{u} < 0.15$ the calculated value of S for $\{31\bar{4}1\}$ is much greater than for $\{31\bar{4}5\}$ and $\{31\bar{4}3\}$, but is much less in the range $0.61 < \mathrm{u} < 0.65$; this range, then, contains the only possible values of u. The value of u may be more closely fixed by the consideration of other data.

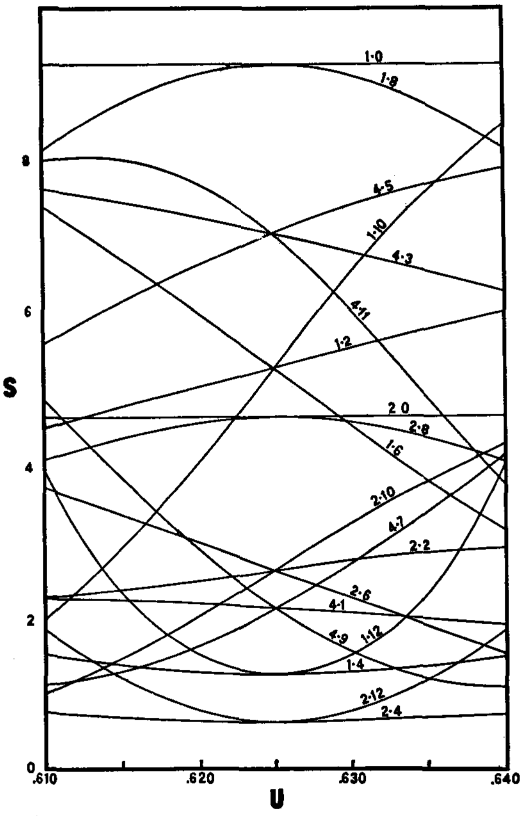

Fig. 1.—Values of S for values of u between 0.61 and 0.64 calculated for Arrangement 6, placing $\overline{\mathrm{S}} = 1$. The first number on each curve indicates the class of plane and the second the value of l. Thus 4 – 5 is the curve for any plane of Class 4 having l = 5.

In Fig. 1 are shown values of S for various planes plotted against values of u in the range $0.61 < \mathrm{u} < 0.65$; in the calculation of these, $\overline{\mathrm{Mo}}$ and $\overline{\mathrm{S}}$ have been taken proportional to the respective atomic numbers. It was found that $\{33\bar{6}.10\}$ reflected considerably more strongly than $\{14\bar{5}.12\}$; therefore, u is appreciably greater than 0.614. Also $\{23\bar{5}9\} \geqq \{23\bar{5}7\}$; therefore, u is probably slightly less than 0.625. From these and similar data the value of u is taken as 0.621 ± 0.004. All of the Laue photographic data treated in the above manner were found to be in agreement with the values of S calculated using u = 0.621; when, however, comparisons were made between planes of different classes, requiring a more accurate knowledge of $\overline{\text{Mo}}$ and $\bar{\text{S}}$, the agreement was not so good, although on the whole satisfactory. The extent of this agreement is illustrated by typical data given in Table II.

TABLE II

LAUE PHOTOGRAPHIC DATA FROM MOLYBDENITE

Incident beam 8° 20′ from normal to (0001). Crystal thickness 0.23 mm.

h i k l	Class	$n\lambda$	*d*	Estimated intensity	*S* u = 0.621
$\bar{2}021$	4	0.37	1.36	3.2	2.17
$\bar{1}\bar{2}31$	4	.40	1.03	1.4	2.17
$3\bar{1}\bar{2}2$	2	.38	1.02	0.8	2.53
$\bar{3}213$	4	.34	1.00	6.0	7.18
$\bar{2}3\bar{1}4$	2	.37	0.98	0.15	0.64
$03\bar{3}5$	3	.37	.85	0.0	0
$4\bar{2}\bar{2}3$	3	.36	.77	0.0	0
$3\bar{4}12$	2	.38	.75	0.3	2.53
$\bar{4}225$	3	.39	.75	0.0	0
$\bar{3}\bar{1}43$	4	.36	.74	2.6	7.18
$31\bar{4}5$	4	.34	.72	2.0	6.68
$24\bar{2}7$	3	.40	.72	0.0	0
$\bar{4}316$	2	.38	.71	0.3	2.93
$\bar{1}4\bar{3}7$	4	.36	.70	0.3	1.70
$2\bar{5}33$	4	.36	.62	1.0	7.18
$5\bar{3}\bar{2}5$	4	.37	.61	1.0	6.68
$1\bar{5}43$	3	.34	.59	0.0	0
$\bar{5}237$	4	.37	.59	0.15	1.70
$\bar{1}\bar{4}54$	1	.37	.59	0.15	1.27
$\bar{5}328$	2	.37	.58	0.2	4.58
$\bar{4}\bar{1}56$	1	.37	.57	0.6	5.85
$23\bar{5}9$	4	.36	.57	0.2	2.71
$\bar{5}147$	3	.36	.56	0.0	0
$41\bar{5}8$	1	.34	.56	0.8	9.17
$\bar{4}5\bar{1}.10$	1	.34	.54	0.3	4.26
$\bar{1}5\bar{4}.12$	1	.39	.52	faint	0.72
$3\bar{6}35$	3	.36	.51	0.0	0
$2\bar{6}45$	4	.35	.50	0.3	6.68
$\bar{6}33.10$	1	.34	.48	0.15	4.26
$\bar{6}24.11$	4	.37	.47	0.2	7.58

Discussion of the Structure

The arrangement found to account for X-ray data from molybdenite is shown in Fig. 2. This arrangement is derivable from the space group D_{6h}^4 as well as from the space groups D_{3h}^4, D_6^6, C_{6h}^2, and D_{3d}^2. Considering the atoms as points or spheres, the structure then has holohedral hexagonal symmetry.

Small, very thin crystals of molybdenite may be made by fusing together ammonium molybdate, sulfur and potassium carbonate.[5] We have ex-

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[5] Guichard, *Ann. chim. phys.*, [7] **23**, 552 (1901). Hintze, Ref. 2, p. 418, also mentions trigonal artificial crystals.

amined crystals made by this method and have found them to be frequently triangular rather than hexagonal plates. Such a face development is not to be expected if the symmetry is that of the hexagonal holohedry. Several explanations of this apparent discrepancy are possible: (1) The artificial crystals may have a structure different from that of the natural mineral; satisfactory Laue photographs from the artificial crystals were not obtainable to decide this point. (2) The structure may be the same in both cases and the natural crystals twinned so as to simulate the higher symmetry; however, we have not found it possible to account for the X-ray data on this hypothesis. (3) Although the structure found has holohedral symmetry for the positions of the atoms, it may have a 3-fold symmetry axis when the shapes of the atoms or the bonds between them are considered. That this is a possible explanation follows immediately from the fact that the structure is derivable from the space group D_{3h}^4 or D_{3d}^2.

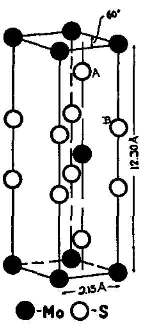

Fig. 2.—Arrangement of the atoms in molybdenite, MoS_2.

In the structure found, each sulfur atom is equidistant from 3 molybdenum atoms, and each molybdenum atom is surrounded by six equidistant sulfur atoms at the corners of a small triangular prism whose altitude is 3.17 ± 0.10 and whose edge is 3.15 ± 0.02. The distance from the molybdenum atom to these nearest sulfur atoms is then 2.41 ± 0.06. This distance is in good agreement with Bragg's hypothesis of constant atomic radii.[6] Taking the radius of molybdenum as 1.36, which is half the distance between the atoms in the metal (Wyckoff[7] has shown this to be consistent with the distances in silver molybdate, Ag_2MoO_4), and the radius of sulfur 1.05 as given by Bragg, the sum is 2.41. On the other hand, the 2 sulfur atoms marked A and B in Fig. 2, which should also be in contact on Bragg's hypothesis, are at a distance of 3.49 Å., while constant radii require 2.10. These relations are analogous to those found in cadmium iodide,[8] and in tin tetra-iodide.[9] This great distance between sulfur atoms is undoubtedly connected with the excellent basal cleavage of molybdenite.

Summary

The mineral molybdenite has been investigated by means of spectral and Laue photographs and, with the aid of the theory of space groups, the simplest structure capable of accounting for the X-ray data has been derived. This structure, which is of a new type, contains 2 MoS_2 in an hexagonal unit having d_{0001} = 12.30 Å. and an axial ratio 3.90. The molyb-

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[6] W. L. Bragg, *Phil. Mag.*, **40**, 180 (1920).

[7] Wyckoff, *Proc. Nat. Acad. Sci.*, **9**, 35 (1923).

[8] Bozorth, THIS JOURNAL, **44**, 2235 (1922).

[9] Dickinson, *ibid.*, **45**, 961 (1923).

denum atoms are at $(\frac{1}{3}\frac{2}{3}\frac{1}{4})$ $(\frac{2}{3}\frac{1}{3}\frac{3}{4})$ and the sulfur atoms at $(\frac{1}{3}\frac{2}{3}u)$ $(\frac{2}{3}\frac{1}{3}\bar{u})$ $(\frac{1}{3},\frac{2}{3},\frac{1}{2}-u)$ $(\frac{2}{3},\frac{1}{3},\frac{1}{2}+u)$ where $u = 0.621 \pm 0.004$.

Pasadena, California

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 28]

THE CRYSTAL STRUCTURE OF MAGNESIUM STANNIDE

BY LINUS PAULING

RECEIVED MAY 21, 1923

Introduction

The temperature-composition diagram[1] of the binary system, magnesium-tin, shows a pronounced maximum corresponding to the composition Mg_2Sn. This compound is described[2] as cubic with octahedral habit and complete octahedral cleavage. For the purpose of obtaining information regarding the nature of intermetallic compounds, crystals of magnesium stannide, Mg_2Sn, have been investigated by means of X-rays, resulting in a complete determination of their structure. No crystal structure determination for an intermetallic compound has been previously reported.

By melting the calculated amounts of magnesium and tin in an iron crucible under a mixture of potassium and magnesium chlorides, and cooling slowly, a mass of magnesium stannide was obtained from which individual crystals could be cleaved. The X-ray data were obtained from Laue and spectral photographs, treated as described by Dickinson.[3] I wish to express my thanks to Dr. Roscoe G. Dickinson for his advice and active interest in this research.

The Determination of the Structure

Spectral data from a (111) face of a crystal of magnesium stannide are given in Table I. Using the value of 3.591 for the density,[2] these data place $n^3/m = 0.248$ for the first reflection. No reflections were found on the Laue photographs with values of $n\lambda$ less than 0.26 Å. U., calculated for the unit containing four Mg_2Sn, with $n = 1$, and $d_{100} = 6.78 \pm 0.02$ Å. U.

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[1] Kurnakow and Stepanow, *Z. anorg. Chem.*, **46**, 177 (1905).

[2] Sustschinsky, *Z. Krist.*, **38**, 265 (1904).

[3] Dickinson, THIS JOURNAL, **44**, 276 (1922).

As the lower limit of X-rays present in the spectrum was 0.24 Å. U., a larger unit of structure is not indicated.

A symmetrical Laue photograph through the (111) face showed a trigonal axis and three reflection planes; consequently only arrangements derived from point-groups T_d, O and O_h were treated. No planes but those with all indices odd gave values of $n\lambda$ less than 0.50, although a large number of other planes were in positions favorable for reflection, so treatment was given only to arrangements based on a face-centered lattice. There are three ways[4] of arranging $4Mg_2Sn$ with these restrictions, irrespective of any assumptions regarding the equivalence of atoms of one element. These are

I Sn at 000, $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$
Mg at $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, $\frac{1}{4}\frac{1}{4}\frac{3}{4}$, $\frac{1}{4}\frac{3}{4}\frac{1}{4}$, $\frac{3}{4}\frac{1}{4}\frac{1}{4}$, $\frac{3}{4}\frac{3}{4}\frac{3}{4}$, $\frac{3}{4}\frac{3}{4}\frac{1}{4}$, $\frac{3}{4}\frac{1}{4}\frac{3}{4}$, $\frac{1}{4}\frac{3}{4}\frac{3}{4}$
II Sn at 000, $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$
Mg at $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, $\frac{3}{4}\frac{1}{4}\frac{3}{4}$, $\frac{1}{4}\frac{3}{4}\frac{3}{4}$, $\frac{3}{4}\frac{3}{4}\frac{1}{4}$, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}00$, $0\frac{1}{2}0$, $00\frac{1}{2}$
III Sn at 000, $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$
Mg at $\frac{3}{4}\frac{3}{4}\frac{3}{4}$, $\frac{3}{4}\frac{1}{4}\frac{1}{4}$, $\frac{1}{4}\frac{1}{4}\frac{3}{4}$, $\frac{1}{4}\frac{3}{4}\frac{1}{4}$, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}00$, $0\frac{1}{2}0$, $00\frac{1}{2}$

The intensity of the third order (111) reflection is greater than that of the second order, and the structure factor, $S = \sqrt{A^2 + B^2}$, must be greater for the third order. For Arrangements II and III, the corresponding values are

$$n = 2,\quad A = 4\overline{Sn},\quad B = 0;\quad n = 3,\quad A = 4\overline{Sn} - 4\overline{Mg},\quad B = \pm 4\overline{Mg}.$$

On the very safe assumption that an atom of tin scatters X-rays more strongly than an atom of magnesium, the value of S for the third order is less than that for the second order, eliminating these two arrangements.

For Arrangement I reflecting planes may be divided into three classes, which have the following values of S.

Class I: *hkl* one odd, two even; $n = 1$, $S = 0$; $n = 2$, $S = 4\overline{Sn} - 8\overline{Mg}$
Class II: *hkl* all odd; $n = 1$, $S = 4\overline{Sn}$
Class III: *hkl* two odd, one even; $n = 1$, $S = 0$; $n = 2$, $S = 4\overline{Sn} + 8\overline{Mg}$.

On the previously made assumption regarding relative reflecting powers, the values for the structure factor of the classes of planes increase in this

TABLE I

REFLECTION DATA FOR Mg_2Sn, (111) FACE

X-rays reflected Å. U.	Angle of reflection	$\frac{d_{111}}{n}$ Å. U.	I_{observed}	S
Moβ_1 = 0.6311	4° 37′	3.918	strong	$4\overline{Sn}$
Moα_1 = 0.7078	5° 11′	3.921		
Moβ_1	9° 16′	$^1/_2 \times 3.920$	weak	$4\overline{Sn} - 8\overline{Mg}$
Moα_1	10° 26′	$^1/_2 \times 3.913$		
Moβ_1	14° 3′	$^1/_3 \times 3.899$	medium	$4\overline{Sn}$
Moα_1	15° 46′	$^1/_3 \times 3.913$		
Moβ_1	18° 52′	$^1/_4 \times 3.902$	medium	$4\overline{Sn} + 8\overline{Mg}$

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[4] Wyckoff, "The Analytical Expression of the Results of the Theory of Space Groups," *Carnegie Inst. Pub.*, 1922.

order: I, II, III. Intensity data showing the extent of the agreement with this structure are given in Tables I and II. In comparing intensities of two planes reflecting at the same wave length, if the intensity of the plane with the smaller value of d/n is larger than that of the other, the structure factor of the first must be greater than that of the second. No intensity relations not accounted for by the above arrangement were observed.

TABLE II

LAUE PHOTOGRAPHIC DATA FOR Mg_2Sn. INCIDENT BEAM 12° 30′ FROM NORMAL TO (111)

hkl	$\frac{d_{kkl}}{n}$ Å. U.	λ Å. U.	$I_{observed}$	Class	hkl	$\frac{d_{kkl}}{n}$ Å. U.	λ Å. U.	$I_{observed}$	Class
$13\bar{3}$	1.52	0.28	2.8	II	$41\bar{2}$	0.74	0.29	0.08	I
$\overline{11}2$	1.38	.30	8	III	$91\bar{3}$	.71	.32	.3	II
$\bar{5}11$	1.30	.31	2.4	II	$\bar{7}71$	.68	.34	.2	II
$\bar{1}5\bar{3}$	1.15	.36	2.4	II	$50\bar{1}$	.67	.33	.4	III
$30\bar{1}$	1.07	.33	2.6	III	$\bar{1}9\bar{5}$	.66	.28	.14	II
$03\bar{2}$	0.94	.33	0.5	I	$05\bar{2}$	.63	.45	.4	I
$2\bar{3}1$	.91	.26	.4	III	$\overline{11}.1.\bar{1}$	.61	.32	.12	II
$35\bar{5}$	.88	.26	.2	II	$11.1.\bar{1}$	.61	.46	.5	II
$71\bar{3}$	.88	.31	.6	II	$11.1.\bar{3}$	.59	.31	.10	II
$\bar{3}7\bar{3}$	.83	.30	.5	II	$\bar{4}33$	.58	.48	1.0	III
$17\bar{5}$	.78	.30	.4	II					

Discussion of the Structure

The structure determined for magnesium stannide is the one known as the calcium fluoride arrangement.[5] It places eight magnesium atoms around each tin atom at the corners of a cube, and four tin atoms around each magnesium atom at tetrahedron corners. The sum of the atomic radii of magnesium[6] and tin[7] obtained from the distance between atoms in the metals is 3.01 Å. U. (from gray tin) or 2.80 (from white tin); the closest approach of tin and magnesium atoms in magnesium stannide is 2.94 ± 0.01. There is no similarity in the way in which an atom of tin or magnesium is surrounded by other atoms in the metals and in this compound.

Crystals of sodium cadmide, $NaCd_2$, reported from goniometrical measurements as cubic, were prepared by the method of Kurnakow.[8] Each of several Laue photographs taken from three different crystals with the beam perpendicular to an octahedral face showed a 3-fold symmetry axis lying in three symmetry planes. The photographs were, however, so complicated that it was not found possible to assign indices with certainty to many of the spots even on the symmetrical photographs. It was accordingly not possible to determine the apparently very complex structure.

[5] W. H. and W. L. Bragg, *Proc. Roy. Soc.*, **89A**, 474 (1913).

[6] Hull, *Phys. Rev.*, [2] **10**, 661 (1917).

[7] Bijl and Kolkmeier, *Proc. Acad. Sci. Amsterdam*, **21**, 494 (1919).

[8] Kurnakow, *Z. anorg. Chem.*, **23**, 459 (1900).

In view of the lack of a simple valence relation between the atoms, complex atom-groups may be formed in sodium cadmide in a way similar to the formation of Pb_2^- ions in a solution of sodium plumbide, $NaPb_2$, in liquid ammonia,[9] preventing a simplicity of structure.

Summary

Crystals of the intermetallic compound magnesium stannide, Mg_2Sn, have been prepared and investigated by means of Laue and spectral photographs with the aid of the theory of space-groups. The intermetallic compound has been found to have the calcium fluoride structure, with $d_{100} = 6.78 \pm 0.02$ Å. U. The closest approach of tin and magnesium atoms is 2.94 ± 0.01 Å. U.

PASADENA, CALIFORNIA

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[9] Kraus, THIS JOURNAL, **29**, 1557 (1907).

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The Crystal Structure of Sulvanite, Cu_3VS_4

By

Linus Pauling and Ralph Hultgren

With 3 figures

1933
AKADEMISCHE VERLAGSGESELLSCHAFT M. B. H.
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The Crystal Structure of Sulvanite, Cu_3VS_4.

By

Linus Pauling and **Ralph Hultgren** in Pasadena.

(With 3 figures.)

Massive sulvanite, Cu_3VS_4, from Burra Burra in Australia was recognized as cubic by Orcel[1]) and de Jong[2]) from its isotropic reflection of polarized light. De Jong prepared powder X-ray photographs of the substance, and assigned indices to the lines on the basis of a cubic unit with $a_0 = 10.75$ Å, containing $8\,Cu_3VS_4$. Assuming chemically identical atoms to be crystallographically equivalent, he suggested a complicated arrangement of the atoms within this unit.

We noticed that the experimental data published by de Jong do not require such a large unit, but can be accounted for by a unit with $a_0 = 5.375$ Å, containing $1\,Cu_3VS_4$, and we planned to study the crystal further. The opportunity to do this arose when a new find of sulvanite, from near Mercur, Utah, was made[3]), consisting of cleavable masses and a few individual crystals. Dr. W. T. Schaller of the United States Geological Survey very kindly lent us this material, enabling us to prepare excellent Laue and oscillation photographs. Data from these show conclusively that the true unit contains only one molecule. A rigorous derivation has led to a very interesting new type of atomic arrangement.

The unit of structure and space-group symmetry.

Several oscillation photographs were prepared of the radiation from a molybdenum-target tube, either unfiltered or filtered through zirconia, reflected from (100) of a crystal of sulvanite oscillating through 45° about a vertical [010] axis. A cleavage face about 2.5 mm. across and a smaller wellformed cube about 0.8 mm. on edge were used. Various orders of (100) up to (800) were observed to reflect, with the estimated relative intensities given in table I.

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1) J. Orcel, Bl. Soc. franç. Min. **51**, 205. 1928.

2) W. F. de Jong, Z. Krist. **68**, 522. 1928.

3) C. A. Schempp and W. T. Schaller, Am. Min. **16**, 557. 1931.

Table I.

Oscillation data from (100) of sulvanite.

X-ray Line	Wave Length	Order	Angle of Reflection	d_{100}	Estimated Intensity	Calculated Intensity for $u = 0.235$
MoKβ	0.6311	1	3°23′	5.348		
α	.7093	1	3°47′	5.365	5	37
γ	.6197	2	6°38′	5.361		
β		2	6°45′	5.371		
α_1	.70783	2	7°35′	5.366	3	19
α_2	.71212	2	7°37′	5.375		
β		3	10°10′	5.367		
α_1		3	11°24′	5.371	0.8	4.0
α_2		3	11°28′	5.370		
γ		4	13°20′	5.372		
β		4	13°36′	5.371		
α_1		4	15°17′	5.371	10	53
α_2		4	15°23′	5.368		
α_1		5	19°14′	5.374		
α_2		5	19°22′	5.370	1	7.4
		6			Absent	1.6
		7			Absent	0.5
		8			1	6.6

Weighted mean: $d_{100} = \underline{5.370}$ Å.

The value of $a_0 = 5.370 \pm 0.005$ Å (table I) was obtained from a photograph of radiation reflected on the same plate from (100) of sulvanite and (0001) of β-alumina, for which a spacing of 11.225 Å was assumed[1]. This agrees well with the value $\frac{1}{2} \times 10.750 = 5.375$ Å from de Jong.

Laue photographs were prepared in the usual way from two small crystals (described by Schempp and Schaller), the incident beam being normal to (100), (110), or (111), or making small angles with the normals to these faces. On assigning indices to the reflections with the aid of gnomonic projections and calculating values of $n\lambda$ on the basis of a unit with $a_0 = 5.37$ Å, it was found that none of the values was smaller than 0.24 Å, the short wave-length limit of the incident radiation. Consequently there is no evidence requiring a larger unit of structure; and in view of the excellence of the Laue photographs obtained and the

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1) Linus Pauling and A. Björkeson, Pr. Nat. Acad. Am. **11**, 445. 1925.

sensitivity of the Laue method of determining the true unit1), the unit with

$$a_0 = 5.370\ \text{Å}$$

may be confidently accepted as the true one. With 1 Cu_3VS_4 in the unit, the calculated density is 3.94 g./cm³, in satisfactory agreement with the reported values2)3) 3.98, 4.01, and 4.03.

Many observed reflections eliminate the body-centered and face-centered lattices, requiring the lattice to be simple cubic. Laue photographs through (100), (110), and (111) show the symmetry elements expected for O, T_d, and O_h, rather than T and T_h. (It may be mentioned that photographs showing a fourfold and a three-fold axis were obtained from the same crystal, which is thus proved to be cubic.) The possible space groups are thus limited to T_d^1, T_d^4, O^1, O^2, O^6, O^7, O_h^1, O_h^2, O_h^3, and O_h^4. The observed reflections (100), (300), and many others eliminate T_d^4, O^2, O^6, O^7, O_h^2, O_h^3, and O_h^4, leaving only T_d^1, O^1, and O_h^1. These three space groups are indeed the only ones which provide positions for the atoms V, 3 Cu, 4 S in a cubic unit.

The space groups O^1 and O_h^1 provide the possible positions

1a. 000
1b. $\frac{1}{2}\frac{1}{2}\frac{1}{2}$
3a. $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$
3b. $\frac{1}{2}00$, $0\frac{1}{2}0$, $00\frac{1}{2}$

for the atoms in the unit. For any atomic arrangement based on these positions the structure factor becomes $F = f_V + 3f_{Cu} + 4f_S$ for all even order reflections, which should consequently show a normal decline in intensity with decreasing interplanar distance. The observation that (400) reflects more strongly than (200) consequently eliminates all such arrangements. The space group is hence determined to be

$$T_d^1 - P\bar{4}3m.$$

The atomic arrangement.

The possible atomic positions provided by T_d^1 are 1a, 1b, 3a, 3b, and, in addition,

4a. uuu, $u\bar{u}\bar{u}$, $\bar{u}u\bar{u}$, $\bar{u}\bar{u}u$.

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1) Illustrated, for example, by the work of R. G. Dickinson, J. Am. chem. Soc. **45**, 958. 1923; Z. Krist. **64**, 400. 1926, on tin tetraiodide, and of Linus Pauling and L. O. Brockway, Z. Krist. **82**, 188. 1932, on chalcopyrite.

2) G. A. Goyder, J. chem. Soc. London **77**, 1094. 1900.

3) H. Schultze and H. Steinmetz, Z. Krist. **49**, 40. 1911.

The sulfur atoms are shown by the fore-going argument to occupy 4a. The vanadium atom may be placed in 1a rather than 1b without loss of generality. Two distinct structures are then obtained by placing 3 *Cu* in 3a or in 3b. These are the only possible atomic arrangements.

It is easily shown that the observed intensities of reflection in various orders from (100) require that for the first of these two arrangements the parameter lie in the neighborhood of $\frac{1}{4}$; at $u = 0.27 \pm 0.02$ the best agreement is obtained, though this is not very good, the observed rather strong first-order reflection not being well accounted for. This arrangement is a very simple and reasonable one, obtained from the sphalerite arrangement by replacing one of the zinc atoms by vanadium and the other three by copper. The approximation of the value of a_0 to that for sphalerite, 5.42 Å, further suggests this structure. Chalcopyrite, $CuFeS_2$, has been shown¹) to have a structure similarly related to that of sphalerite. Despite its reasonableness, however, this is not the structure of sulvanite, for many intensity comparisons on Laue photographs are incompatible with this atomic arrangement. For example, (643) is observed to reflect on Laue photographs about as intensely as (553), whereas the calculated intensity of reflection of (553) is over ten times that of (643) throughout the parameter range $0.20 < u < 0.30$. It is, indeed, evident from the nature of the photographs that the structure of sulvanite is not closely related to the sphalerite structure; for inasmuch as the f-values for V and Cu are not very different, reflections other than those with h, k, l either all odd or all even should be very weak (as was the case in chalcopyrite, where such reflections were not observed at all in the first two investigations of this crystal and appeared only as very weak Laue spots in the last study¹), whereas actually on the sulvanite Laue photographs the strongest reflections are those from planes not satisfying this condition.

The parameter for the remaining structure, with 3 *Cu* in 3b, can be limited to a narrow range of values with the aid of intensity comparisons on oscillation and Laue photographs. In Fig. 1 there are plotted the intensities of reflection in various orders from (100) for the parameter range 0.20 to 0.30 (limitation to this region being easily made) calculated from the equation

$$I_{n00} = \text{Constant} \cdot n \cdot \frac{1 + \cos^2 2\theta}{2 \sin 2\theta} \cdot \{f_{0_V} + f_{0_{Cu}} (1 + 2(-1)^n) + 4 f_{0_S} \cos 2\pi n u\}^2 \cdot e^{-0.125\, d^2_{n00}}. \qquad (1)$$

---

1) Linus Pauling and L. O. Brockway, Z. Krist. 82, 188. 1932.

The factor n is required by the experimental conditions, under which the amount of incident radiation intercepted by the face of the crystal increases linearly with the order of reflection. The temperature factor corresponds to an estimated characteristic temperature of about 530° The f_0-values used are those of Pauling and Sherman[1]). It is seen that the observed intensity relations (800) ≫ (600) and (500) > (300) limit u to between 0.223 and 0.239, the quantitative agreement being most satisfactory in the neighborhood of 0.235. The intensity relation (731) > (643) on Laue photographs further requires that u be greater than 0.230, as is seen from Figure 2, in which there are plotted some intensity curves calculated for a wave-length of 0.40 Å with the expression

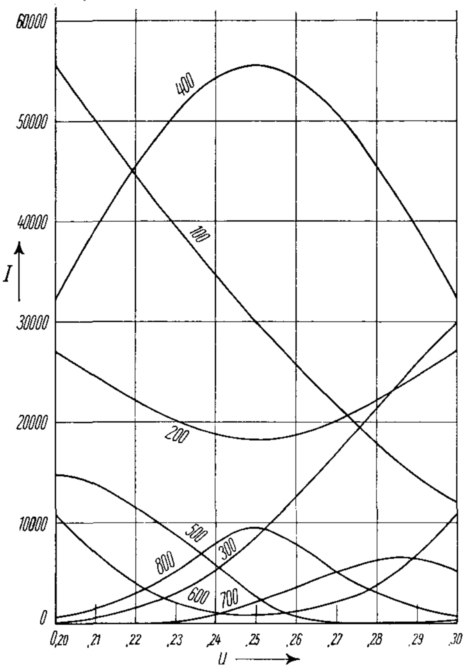

Fig. 1.

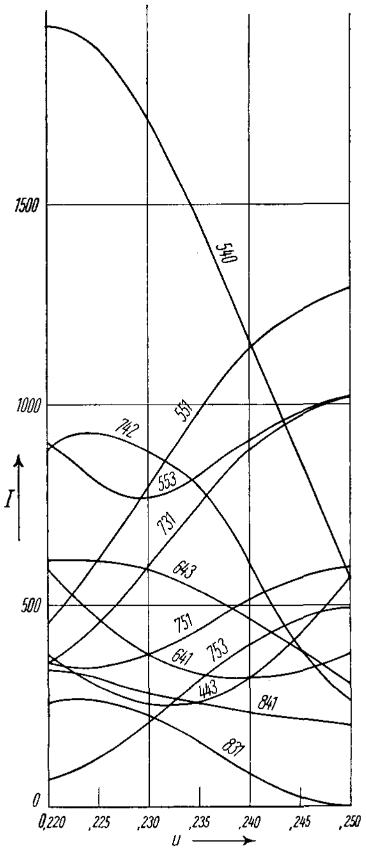

Fig. 2.

Fig. 1. Calculated intensities for various orders of reflection from (100) of sulvanite as functions of u.

Fig. 2. Calculated intensities of Laue reflections.

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1) Linus Pauling and J. Sherman, Z. Krist. 81, 1. 1932.

$$I_{hkl} = \text{Constant} \cdot \frac{1 + \cos^2 2\theta}{2 \sin 2\theta} \left| F_{0_{hkl}} \right|^2 e^{-0.125/d^2_{hkl}} \tag{2}$$

with $$F_0 = \sum_j f_{0j}\, e^{2\pi i (h x_j + k y_j + l z_j)}\,.$$

(The use of Lorentz and polarization factors not corresponding exactly to the Laue technique probably introduces no appreciable error.) The parameter accordingly has the value

$$\underline{u = 0.235 \pm 0.004.}$$

The agreement between observed and calculated intensities is shown in Tables I and II.

Table II.

Data from Laue photographs 1 and 6.

Laue 1. Incident beam 8° from [110]
Laue 6. Incident beam 2° from [110]

hkl	d_{hkl}	Calculated Intensity for $u = 0.235$	Observed Intensity Laue 1		Observed Intensity Laue 6	
211	2.19 Å	6	2.5 at $\lambda = 0.44$ Å			
221	1.79	63	25	.40		
311	1.62	126	15	.28		
320	1.53	60			25 at $\lambda = 0.39$ Å	
321	1.44	2	0.4	.41		
322	1.30	11	1.0	.30	12	.38
331	1.23	60	5	.30		
421	1.17	13	5	.42	13	.39
332	1.15	2			0.5	.39
430	1.07	5			3.5	.37
431	1.05	3	0.4	.36	0.5	.35
510	1.05	0	0.0	.32		
432	1.00	18	2.5	.35		
520	1.00	2	0.3	.38		
441	0.94	10	1.5	.44		
433	.92	2	0.1	.39		
531	.91	23	3.5	.37	10	.38
611	.87	4			0.7	.40
540	.84	15	1.4	.40		
443	.84	3	0.4	.39		
533	.82	14			7	.40
542	.80	1			0.3	.37
632	.77	2	0.4	.42	0.5	.42
551	.75	10	1.0	.43		
711	.75	10	0.6	.35		

Table II (continuation).

hkl	d_{hkl}	Calculated Intensity for $u = 0.235$	Observed Intensity Laue 1		Observed Intensity Laue 6	
641	.74	3	0.3	.38	0.7	.41
720	.74	13	0.7	.37		
553	.70	8	0.6	.37		
643	.69	5	0.4	.39	1.0	.41
652	.68	7	0.3	.37	0.7	.37
733	.66	6			0.5	.42
742	.65	8	0.4	.39	0.6	.37
821	.65	2	0.1	.36		
830	.63	1	0.05	.39		
831	.63	2			0.2	.40
751	.62	4			0.4	.42
841	.60	2			0.3	.41
753	.59	3			0.3	.39

Description of the structure.

The atomic arrangement found for sulvanite is a new type, shown in Figure 3. Each copper atom is surrounded by four sulfur atoms at the corners of a nearly regular tetrahedron. Each vanadium atom is surrounded by four sulfur atoms at the corners of a regular tetrahedron. Each sulfur atom is surrounded by three copper atoms at three of the corners of a nearly regular tetrahedron, and a vanadium atom not at the fourth corner of the tetrahedron, but in the negative position to this; that is, in the pocket formed by the three copper atoms.

It is probable that there are bonds of essentially covalent type between each atom and its four nearest neighbors. The mutual orientation of the four sulfur bonds is very surprising; for in all other sulfur-containing covalent crystals whose structures are known with certainty, such as ZnS, MoS_2, FeS_2, etc., the sulfur bonds are at approximately tetrahedral angles. It is true, however, that other angles may be expected on theoretical grounds, inasmuch as the 3d as well as 3s and 3p orbital wave functions may take part in bond formation[1]), in which case bonds at 110° and 71° may well be formed. The factors determining the stability of such bonds rather than tetrahedral bonds are not known. The following argument suggests that electrostatic interactions may be important in stabilizing the sulvanite structure. If each of the atoms in sulvanite forms four extreme covalent bonds, each consisting of two electrons

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[1]) See R. Hultgren, Physic. Rev. **40**, 891. 1932.

shared equally between two nuclei, then the average electric charges on the various atoms will correspond to the formula $Cu_3^{=} V^{+} S_4^{++}$. In the sulvanite structure the ions immediately adjacent to each ion are the same as in the sphalerite-type structure discussed above and eliminated by the X-ray data. In the next sphere of influence, however, there is a difference; in the sulvanite structure six of the negatively charged copper atoms are brought to within $\frac{1}{2}a_0$ of each positively charged vanadium atom, with a resultant stabilization of the structure because of the Coulomb terms. This is shown by the **Madelung** constants, which have the values 39.217174 for $Cu_3^{=} V^{+} S_4^{++}$ with the sulvanite structure and 37.026993 for the sphalerite-type structure (each for $u = \frac{1}{4}$, and referred to a_0), corresponding to an energy difference of 135 kcal/mole in favor of the sulvanite structure. This consideration is, of course, too idealized, for the bonds without doubt have considerable ionic character, which

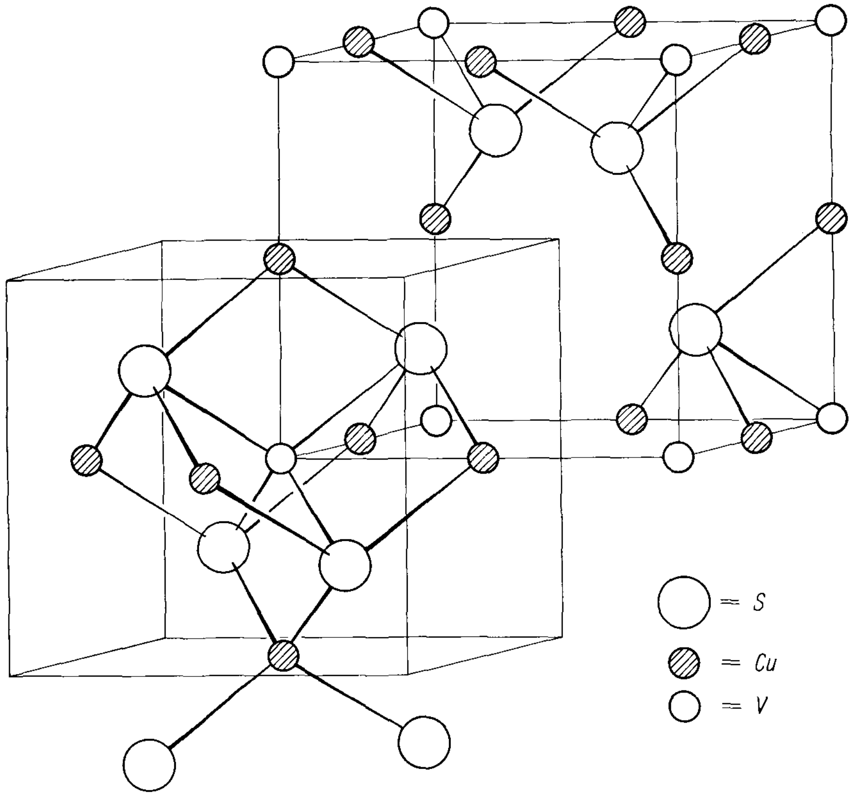

Fig. 3. The atomic arrangement in sulvanite, Cu_3VS_4.

operates in such a direction as to make the metal atoms more positive and the sulfur atoms more negative[1]). If this occurs to the extent indicated by the formula $Cu_3^{=}V^{++}S_4^{+}$, the Madelung constants become 17.249703 and 14.329462, respectively, the sulvanite structure being then favored by the energy difference 180 kcal/mole. Only if the ionic character were to become so pronounced as to make the copper atoms positive would the Madelung constant for the sulvanite structure fall below that for the sphalerite-type structure.

The interatomic distances found are $V—S = 2.186 \pm 0.040$ Å and $Cu—S = 2.285 \pm 0.014$ Å. The $Cu—S$ distance is somewhat smaller than the sum of the tetrahedral radii[2]) for sulfur and univalent copper, 2.39 Å. As in the case of chalcopyrite, this probably indicates that the valence states are not well defined as $Cu_3^I V^V S_4$, but fluctuate, the copper resonating between cuprous and cupric states and the vanadium between quinquivalent and lower states.

Summary.

The study by means of Laue and oscillation photographs of the cubic mineral sulvanite, using single crystals from Mercur, Utah, has shown the unit of structure to have $a_0 = 5.370 \pm 0.005$ Å, and to contain 1 Cu_3VS_4. The space group is $T_d^1—P\bar{4}3m$. The atomic arrangement is a new type, V at 000, 3 Cu at $\frac{1}{2}00$, $0\frac{1}{2}0$, $00\frac{1}{2}$, and 4 S at uuu, $u\bar{u}\bar{u}$, $\bar{u}u\bar{u}$, $\bar{u}\bar{u}u$, with $u = 0.235 \pm 0.004$. Smallest interatomic distances are $V—S = 2.186 \pm 0.040$ Å, and $Cu—S = 2.285 \pm 0.014$ Å.

We are indebted to Dr. W. T. Schaller of Washington, D. C., for lending us the excellent crystals of sulvanite for investigation, and to Dr. J. Sherman of this Laboratory for the calculation of the Madelung constants.

July 22nd, 1932. Contribution No. 332 from the Gates Chemical Laboratory, California Institute of Technology.

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1) For a discussion of ionic character of covalent bonds see Linus Pauling, Pr. Nat. Acad. Am. **18**, 414. 1932; J. Am. chem. Soc. **54**, 3570. 1932.

2) Linus Pauling and M. L. Huggins, Z. Krist. to be published.

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The Crystal Structure of Binnite $(Cu,Fe)_{12}As_4S_{13}$, and the Chemical Composition and Structure of Minerals of the Tetrahedrite Group

By

Linus Pauling and E. W. Neuman

With 1 figure

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(Contribution from Gates Chemical Laboratory, California Institute of Technology, No. 383.)

The Crystal Structure of Binnite, $(Cu,Fe)_{12}As_4S_{13}$, and the Chemical Composition and Structure of Minerals of the Tetrahedrite Group.

By
Linus Pauling and **E. W. Neuman** in Pasadena.

(With 1 figure.)

Introduction.

Binnite, a well-crystallized variety of tennantite found in the Binnenthal, Wallis, Switzerland, belongs to the tetrahedrite group of minerals. X-ray studies of tetrahedrite have been reported by Palacios[1]), de Jong[2]), and Machatschki[3]). Our investigation confirms the results of Machatschki in most respects.

The Unit of Structure and Space-Group Symmetry.

The X-ray data used by us were obtained from oscillation and Laue photographs prepared from an excellent crystal from the Binnenthal kindly provided by Professor Charles Palache of Harvard University. The angles of reflection of planes reflecting in the equator on an oscillation photograph from (100) with [001] as axis of rotation, using molybdenum radiation filtered through zirconia, lead to $a_0 = 10.19 \pm 0.020$ Å (Table I). The less accurate value $a_0 = 10.25$ Å is given by the distance between layer lines. The cubic unit with $a_0 = 10.19$ Å accounts completely for all reflections observed on two completely analyzed Laue photographs (with the incident beam making angles of 1° and 7° with the direction [100]), and may hence be accepted with confidence as the true unit of structure.

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1) J. Palacios, An. Soc. Espan. Fis. Quim. **52**, 246. 1927.

2) W. F. de Jong, Dissertation, Delft, 1928. Our acquaintance with this work and that of Palacios is limited to the Strukturbericht abstract.

3) F. Machatschki, Norsk. Geol. Tidsskr. **10**, 23. 1928; Z. Krist. **68**, 204. 1928.

Table I. The determination of a_0 from oscillation data.

$(h\,k\,l)$	X-ray line1)	a_0	$(h\,k\,l)$	X-ray line1)	a_0
400	α_1	10.212 Å	800	α_2	10.160 Å
400	α_2	10.192 Å	10.2.0	α_2	10.229 Å
510	α_2	10.173 Å	12.0.0	α_2	10.213 Å
710	α_1	10.175 Å	16.0.0	α_1	10.202 Å
710	α_2	10.147 Å	16.0.0	α_2	10.189 Å
800	α_1	10.168 Å			

Average 10.187 Å

A symmetrical Laue photograph through (100) was found to show a four-fold axis and four planes of symmetry, requiring the space group to be isomorphous with one of the point groups T_d, O, and O_h. No odd-order reflections from planes with $h + k + l$ odd were observed on any oscillation or Laue photograph, showing the lattice to be the body-centered one, Γ_c''. Of the possible space groups T_d^3, T_d^6, O^5, O^8, O_h^9, and O_h^{10}, three are definitely eliminated by observed reflections. T_d^6 and O_h^{10} permit no reflections of the type (hhl) with $\frac{1}{2}(2h + l)$ odd; they are consequently eliminated by the appearance on Laue photographs of many first-order reflections from planes of this type, including (118), (1. 1. 12), (3. 3. 16), (338), etc. O^8 requires that $(h00)$ reflect only in the fourth, eighth, etc., orders, and is eliminated by the observation on an oscillation photograph of a very weak but unmistakable reflection in the sixth order, (600). Of the remaining space groups, T_d^3, O^5, and O_h^9, the first is shown to be correct by the tetrahedral face-development of the minerals of the tetrahedrite group.

The space group T_d^3 was found also by Machatschki, who further reported the value $a_0 = 10.189$ Å for tennantite from Redruth, Cornwall, and 10.205 Å for binnite. The lattice constants of antimony-rich tetrahedrites are considerably larger, ranging up to 10.55 Å.

The Chemical Formula of Minerals of the Tetrahedrite Group.

Using the reported values of the density and $a_0 = 10.19$ Å, the numbers of atoms in the unit of binnite according to Prior's analyses (the most recent and without doubt the most accurate that have been carried out on this substance) are given in Table II. These support the ideal formula Cu_3AsS_3 used by Machatschki rather than Cu_3AsS_4 suggested by de Jong. However, there is a notable excess of sulfur, amounting in the case of Analysis 75 to nearly two atoms. In default

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1) $MoK_{\alpha_1} = 0.7078$ Å; $MoK_{\alpha_2} = 0.7121$ Å.

Table II. Numbers of atoms in unit of binnite, according to Prior's analyses[1]).

Analysis No.	Density	Cu	Fe	Ag	$Cu + Fe + Ag$	As	S
75	4.62	23.18	0.59	0.51	24.28	7.50	25.43
76	4.598	20.43	1.94	1.30	23.67	(8.05)	24.69

of more reliable analyses of binnite, we have reconsidered the best analyses of the tetrahedrite minerals in general; namely, those resulting from the beautiful work of Kretschmer[2]). Because of the variability of density and lattice constant, we have calculated relative numbers of atoms on the basis $As + Sb = 1.00$. The symbol Cu in Table III represents $Cu + Ag$; Zn, $Zn + Fe$; and Sb, $As + Sb + Bi$. It is seen that the ratio $(Cu + Zn)/Sb$ lies very close to 3.00, the root-mean-square deviation being only 0.032 (excluding Analyses 8 and 15). However, the ratio S/Sb deviates pronouncedly from 3.00. The next possible value for this ratio, in view of the body-centered lattice, is $26/8 = 3.25$. The

Table III. Recalculation of Kretschmer's analyses of tetrahedrite minerals.

Origin	Cu	Zn	$Cu + Zn$	S
1. Horhausen	2.47	0.51	2.98	3.19
2. Hornachuelos . . .	2.52	.49	3.00	3.28
3. Huanchaca . . .	2.59	.43	3.02	3.25
4. Schemnitz	2.48	.52	3.00	3.25
5. Dillenburg	2.47	.51	2.98	3.20
6. Kapnik	2.58	.48	3.06	3.32
7. Siebenbürgen . . .	2.46	.55	3.01	3.34
*8. Müsen	2.13	.71	2.84	2.94
9. Kotterbach	2.60	.40	3.00	3.15
10. Brixlegg	2.56	.49	3.05	3.27
11. Algier	2.59	.39	2.98	3.20
12. Santiago	2.57	.46	3.03	3.29
13. Guanajuato . . .	2.58	.49	3.07	3.29
14. Kupferberg	2.82	.18	3.00	3.11
*15. Redruth	3.43	.13	3.56	3.39
* 8′. —	2.32	.68	3.00	3.20
* 15′. —	3.04	.00	3.04	3.00

* 8′ and 15′ are 8 and 15 as corrected by Kretschmer for $NiSb$ and Cu_3FeS_3, respectively.

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[1]) Quoted by Hintze, Handbuch der Mineralogie.

[2]) A. Kretschmer, Z. Krist. 48, 484. 1911.

observed figures approximate this value closely, the mean of all but 8 and 15 being 3.24, and the root-mean-square deviation from 3.25 being 0.066. We consequently feel that we are justified in adopting as the ideal formula for the tetrahedrite minerals the expression

$$(Cu_{10}\,Zn_2)Sb_4S_{13},$$

with $Cu = Cu' + Ag', Zn = Zn'' + Fe''$ and perhaps Cu'', $Sb = As''' + Sb''' + Bi'''$, two molecules of this composition being contained in the unit of structure. The parenthesis indicates that the *Cu* and *Zn* atoms are distributed among twelve equivalent positions.

Essentially this formula has been suggested before. Tschermak in 1894 wrote $Cu_{10}Zn_2Sb_4S_{13}$, and Kretschmer adopted the more general expression (Cu_xZn_y), $SbS_{3+y/2}$, with $x + y = 3$. Machatschki pointed out the existence of excess sulfur over that required by the formula Cu_3SbS_3, but preferred to retain this expression as the ideal formula, and to consider the excess sulfur as due to solid solutions of a type discussed later.

In view of the concordance of Kretschmer's analyses, we believe that the wide fluctuations shown by earlier analyses are to be attributed in the main to experimental error, and that actually the composition of the minerals of the tetrahedrite group does not depart greatly from that expressed by our ideal formula[1]).

The Atomic Arrangement.

Accepting our ideal formula, we must place $2\,(Cu,\ Fe)_{12}As_4S_{13}$ in positions provided by T_d^3. These positions, in Wyckoff's tabulation, are

2 a.	$000,\ \frac{1}{2}\frac{1}{2}\frac{1}{2}$.	12 a.	$u00$, etc.
6 e.	$0\frac{1}{2}0$, etc.	24 f.	$u0\frac{1}{2}$, etc.
8 a.	$uuu,\ u\bar{u}\bar{u}$, etc.	24 g.	$uuv,\ u\bar{u}\bar{v}$, etc.
12 h.	$\frac{1}{2}0\frac{1}{4},\ 0\frac{1}{4}\frac{1}{2}$, etc.	48.	xyz, etc.

Because of the large number of structures involving several parameters, a rigorous derivation of the atomic arrangement would be difficult. However, it was evident from the oscillation photographs that the

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1) A similar conclusion was reached from the consideration of selected chemical analyses by E. T. Wherry and W. F. Foshag (J. Wash. Acad. Sci., **11**, 1, 1921), who wrote ".... Tschermak's [formula] is here adopted; the more complex formulas of Prior and Spencer and of Kretschmer do not appear to be justified by the evidence". A. N. Winchell (Amer. Mineral., **11**, 181. 1926), on the other hand, has emphasized the deviations of the analyses from Tschermak's formula.

structure is closely related to that sphalerite, inasmuch as the strongest reflections which occur are those with $h + k + l = 0$ (mod 8) and with $h/2 = k/2 = l/2$ (mod 2). As pointed out by Machatschki, a structure of this type is the following:

$8\ As$ in $8\,a$ with $u_{As} \cong 0.250$;
$12\ Cu_{\mathrm{I}}$ in $12\,h$;
$12\ Cu_{\mathrm{II}}$ in $12\,a$ with $u_{Cu} \cong 0.250$;
$24\ S_{\mathrm{I}}$ in $24\,g$ with $u_S \cong 0.125$ and $v_S \cong 0.375$;
$2\ S_{\mathrm{II}}$ in $2\,a$.

On calculating intensities of reflection for these parameter values, it was found that the general agreement with observation for all except the very weak reflections was excellent, as is shown by the data in Table IV for useful reflections from 45° oscillation photographs from (100) with [001] as axis of oscillation. The observed relative intensities were estimated by the comparison of several photographs taken under identical conditions except for variation in the time of exposure. The calculated intensities are those given by the intensity formula

Table IV. Observed and calculated intensities of reflection on oscillation photograph from (100) with [001] as axis.

Equator

(200)	0.0[a]				
0.00[b]	0.00[c]				
(400)	25	(402)	0.0	(404)	50
21.0	23.5	0.01	0.00	62.5	56.8
(600)	0.2	(602)	0.6	(604)	0.0
0.00	0.17	0.11	0.39	0.00	0.00
(800)	30	(802)	0.3	(804)	4
33.8	28.4	0.01	0.17	5.9	4.5
(10.0.0)	0.0	(10.0.2)	0.5	(10.0.4)	0.0
0.1	0.03	0.09	0.36	0.01	0.09
(12.0.0)	1.0	(12.0.2)	0.0	(12.0.4)	6
1.3	1.1	0.00	0.09	8.4	5.6
(14.0.0)	0.0				
0.00	0.14				
(16.0.0)	1.5				
2.3	1.6				

a Observed intensity.
b Intensity calculated for ideal parameter values.
c Intensity calculated for final parameter values.

$$I = \frac{1 + \cos^2 2\vartheta}{2 \sin 2\vartheta}\, h\,\omega\, |F|^2 \cdot e^{-2B(\sin\vartheta/\lambda)^2}$$

in which ω is the Ott factor for varying time of reflection. Pauling-Sherman f_0-values for neutral atoms were used, and an estimated value of 1.00 was adopted for the coefficient B in the temperature factor. The factor h is required by the experimental method, involving reflection from the face of a small strongly-absorbing crystal bathed in the X-ray beam. Because of lack of knowledge of the effect of absorption for them, reflections from planes whose traces with the developed face (100) were not horizontal were not used in the parameter determination.

The observed strength of the reflections (602), (802), and (10.0.2) relative to (402), etc. can be accounted for only by keeping u_{As} close to 0.250 and decreasing u_{Cu} to about 0.225. The simultaneous determination of the two sulfur parameters cannot be made with much accuracy. However, inasmuch as the Cu_I atoms are surrounded tetrahedrally by four S_I atoms, each of which itself is surrounded by four metal atoms, the assumption may be made with considerable confidence that the $Cu — S$ distance is about the same as in chalcopyrite[1]), 2.32 ± 0.03 Å, and sulvanite[2]), 2.285 ± 0.014 Å. This limits v_S to values near 0.360. With this limitation, it was found that satisfactory agreement between calculated and observed intensities was obtained with the parameter values $u_{As} = 0.255$, $u_{Cu} = 0.225$, $u_S = 0.122$, and $v_S = 0.363$. The agreement is somewhat impaired by changing these values by as much as 0.005.

Description of the Structure.

The structure found for binnite is shown in Figure 1, the interatomic distances corresponding to the finally accepted parameter values being given in Table V. Each S_I atom is surrounded tetrahedrally by four other atoms, to which it is presumably attached by bonds which are largely covalent in character. The interatomic distances are in approximate

Table V. Interatomic distances in binnite.

Atom	Neighboring atoms	Interatomic distance[3])	Atom	Neighboring atoms	Interatomic distance[3])
As	$3\,S_I$	2.21 Å	S_I	$1\,As$	2.21 Å
Cu_I	$4\,S_I$	2.28 Å	S_I	$2\,Cu_I$	2.28 Å
Cu_{II}	$2\,S_I$	2.23 Å	S_I	$1\,Cu_{II}$	2.23 Å
Cu_{II}	$1\,S_{II}$	2.29 Å	S_{II}	$6\,Cu_{II}$	2.29 Å

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1) L. Pauling and L. O. Brockway, Z. Krist. 82, 188. 1932.

2) L. Pauling and R. Hultgren, Z. Krist. 84, 204. 1933.

3) All distances are accurate to about ± 0.05 Å.

agreement with this assumption, the sum of the normal covalent radii¹) for *As* and *S* being 2.25 Å, and of the tetrahedral radii²) for *Cu* and *S* 2.39 Å. The coordination number of Cu_{II} is only three, so that the observed decrease in $Cu_{II} = S_I$ distance from Cu_I (surrounded tetrahedrally by four sulfur atoms) is not unexpected. The atom S_{II} is surrounded by six Cu_{II} atoms at the corners of a regular octahedron, and, as would be anticipated, the $Cu_{II} - S_{II}$ distance is somewhat larger than the $Cu_{II} - S_I$ distance. Although rather rare, the coordination number six for sulfur is not unprecedented, being shown in the sulfides with the niccolite

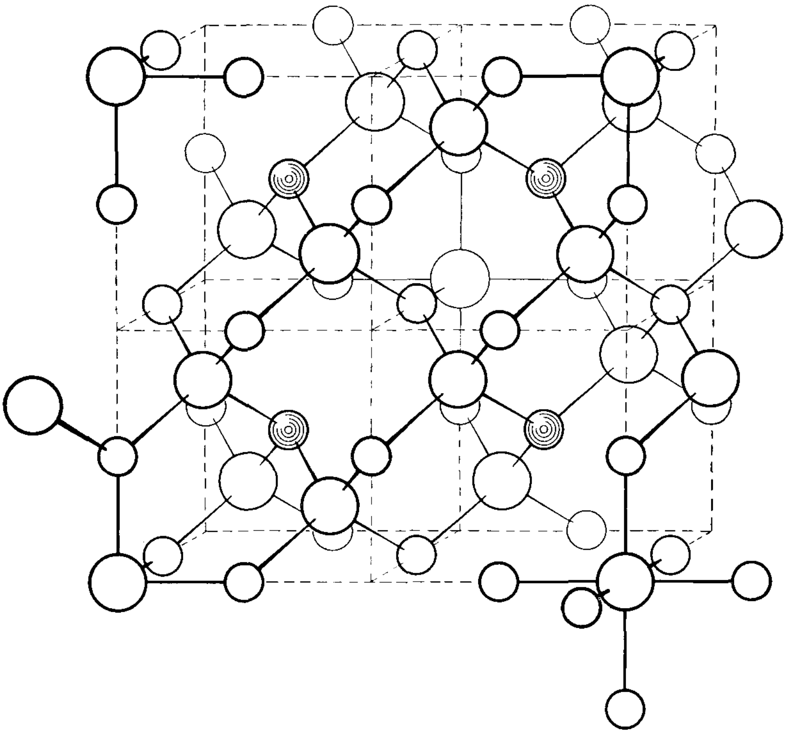

Fig. 1. Diagram showing the forward half of the unit cube of binnite. Large circles represent sulfur atoms, small open circles copper atoms, and small shaded circles arsenic atoms. Bonds between adjacent atoms are indicated. Note that there are two kinds of copper atoms and two kinds of sulfur atoms.

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1) L. Pauling, Pr. Nat. Acad. Sci. 18, 293. 1932.

2) L. Pauling and M. L. Huggins, Z. Krist. 87, 205. 1934.

structure, FeS, CoS, etc. (provided that the structures assigned them are correct).

The binnite structure may be described in terms of the sphalerite structure in the following way. In a large cube containing 32 ZnS, replace 8 Zn (at $\frac{1}{4}\,\frac{1}{4}\,\frac{1}{4}$, $\frac{1}{4}\,\frac{\bar{1}}{4}\,\frac{\bar{1}}{4}$, etc.) by As and the remaining 24 by Cu. Then remove 8 S (at $\frac{\bar{1}}{8}\,\frac{\bar{1}}{8}\,\frac{\bar{1}}{8}$, etc.), leaving As bonded to 3 S only, and introduce 2 S at 0 0 0 and $\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}$, the centers of the two tetrahedra formed by the eight sulfur atoms removed.

The structure assigned by Machatschki to tetrahedrite is essentially the same as the structure of binnite (neglecting the S_{II} atoms), his suggested parameter values being $u_{Sb} = \frac{5}{18} = 0.278$, $u_{Cu} = \frac{1}{4}$, $u_S = \frac{1}{8}$, $v_S = \frac{3}{8}$. Because of the large scattering power of Sb for X-rays, the value of u_{Sb} found by Machatschki must be very nearly correct, but small changes in the other parameters might well be made. It seems not unreasonable that u_{Cu}, u_S, and v_S have about the same values in tetrahedrite as in binnite, leading to about the same Cu — S interatomic distances. The change from $u_{As} = 0.255$ to $u_{Sb} = 0.278$ is, however, real, resulting from the increase in covalent radius from 1.21 Å for As^{III} to 1.41 Å for Sb^{III}. With these parameter values and with $a_0 = 10.30$ Å, the Sb—S distance is calculated to be 2.43 Å, in excellent agreement with the sum of the normal covalent radii, 2.45 Å.

In his first paper, Machatschki suggested that the sulfur atoms present in excess over the number required by his ideal formula, Cu_3SbS_3, occupy the positions 0 0 0 and $\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}$ at which we have located the S_{II} atoms. In his second paper, however, he considers the excess sulfur to occupy positions corresponding to the completed sphalerite arrangement ($\frac{\bar{1}}{8}\,\frac{\bar{1}}{8}\,\frac{\bar{1}}{8}$, etc.). There is little chance of deciding between these alternatives by X-ray data; however, our conviction that the ideal formula is $(Cu, Zn)_{12}Sb_4S_{13}$ requires the acceptance of the former.

We wish to thank Professor Palache for lending us an excellent crystal of binnite, and Dr. S. Weinbaum for carrying out many of the intensity calculations.

Summary.

Using data from Laue and oscillation photographs, it is shown that the unit of structure of binnite has $a_0 = 10.19 \pm 0.02$ Å, the space group being T_d^3. The unit contains 2 $(Cu, Fe)_{12}As_4S_{13}$, with the atomic arrangement

8 As in $8a$, $u_{As} = 0.255$;
12 Cu_{I} in $12h$;
12 Cu_{II} in $12a$, $u_{Cu} = 0.225$;
24 S_{I} in 24 g, $u_S = 0.122$, $v_S = 0.363$;
2 S_{II} in $2a$.

The parameter values are accurate to ± 0.005. In view of the work of Machatschki, it is probable that this structure is common to all members of the tetrahedrite group, except that on replacing As by Sb the corresponding parameter changes to $u_{Sb} = 0.278$.

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THE STRUCTURE OF THE CARBOXYL GROUP. II. THE CRYSTAL STRUCTURE OF BASIC BERYLLIUM ACETATE

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Communicated May 8, 1934

The crystal structure of basic beryllium acetate, $Be_4O(CH_3COO)_6$, has been studied by Bragg and Morgan,[1] who reported some spectrometric intensity measurements and showed the cubic unit of structure to have $a_0 = 15.72$ Å and to contain eight molecules, and by Morgan and Astbury,[2] who showed the space group to be T_h^4. In neither study was the atomic arrangement determined. We have found an atomic arrangement which accounts satisfactorily for the data of these authors and for additional intensity data obtained photographically, and which provides information regarding the structure of the acetate group.

The crystals used, which were kindly prepared for us by Dr. G. W. Wheland, were in the form of octahedra several millimeters in diameter. Laue and oscillation photographs were made and interpreted in the usual way. Layer-line separations on these led to the value $a_0 = 15.8 \pm 0.1$ Å for the edge of the unit, in agreement with the value reported by Bragg and Morgan. It was also found that a Laue photograph on (111) showed a three-fold axis but no symmetry planes, and that no reflections of the types $\{hkl\}$ with $h + k$ odd and $\{hk0\}$ with $^1/_2(h + k)$ odd occurred, verifying Morgan and Astbury's choice of T_h^4 as the space group.

The complexity of the possible atomic arrangements based on T_h^4 makes a rigorous structure determination impractical. However, the volatility of the substance and its solubility in non-ionizing solvents suggest that the crystal contains discrete molecules, which are required by the space group T_h^4 to have the point-group symmetry T. As suggested by the previous investigators, a reasonable type of structure for the molecule is that shown in figure 1. Each beryllium atom (or ion) is surrounded by four oxygen atoms at the corners of an approximately regular tetrahedron, as in beryllium oxide. The electrostatic valence rule is satisfied, assuming, each carboxyl oxygen to be held to carbon by a resonating single-double bond. (The symmetry of the crystal requires the two oxygen atoms to be equivalent.) This structure may be described in the following way, using Wyckoff's tabulation of the results of the theory of space groups:

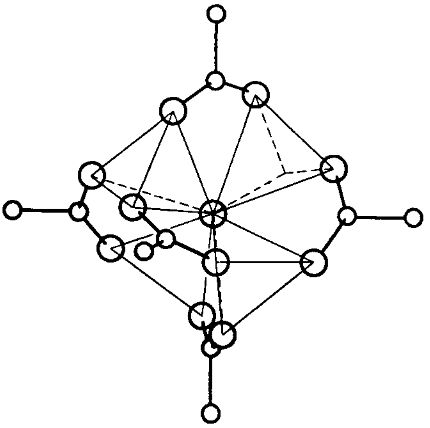

FIGURE 1

The arrangement of atoms in the molecule of $Be_4O(CH_3COO)_6$. Small circles represent carbon atoms, large circles oxygen atoms. The beryllium atoms occupy the centers of the four tetrahedra. One of the six acetate groups is not shown.

8 O_I in 8f: 000, etc.;
32 Be in 32b: uuu, etc.;
96 O_{II} in g: xyz, etc.;
48 C_I in 48c: $v00$, etc.;
48 C_{II} in 48c: $w00$, etc.

The six parameters cannot be rigorously evaluated by use of the x-ray data alone. We consequently resort to a treatment involving the elimination of some of them by invoking a few well-founded assumptions. The first assumption we make is that the distance between the two carbon atoms of an acetate group is the single-bond distance, 1.54 Å. This requires the relation $w - v = 0.098$ to hold between w and v. Second, we assume the Be–O distance to be 1.65 Å, as in BeO itself. This fixes the value of u as ± 0.0605, and in addition introduces a relation among the variables x, y and z, by means of which x can be determined for given values of y and z. Third, the carbon–oxygen distance in the carboxyl group is given the value 1.29 Å found for formic acid by electron diffraction.[3] These assumed values, according to previous experience, can hardly be in error by more than one or two per cent.

The problem in this way having been reduced to one involving only two parameters, which may be taken as the angle α between the carbon–oxygen bonds in the carboxyl group and the coördinate z determining the azimuthal orientation of the acetate groups, values of the intensity of reflection of x-rays from various planes were calculated according to the formula

$$I = \text{Constant} \cdot \frac{1 + \cos^2 2\vartheta}{2 \sin 2\vartheta} \cdot F^2 \cdot e^{-1.2/_{z}p'}$$

in which the structure factor F has its usual form

$$F_{hkl} = \sum_i f_i e^{2\pi i(hx_i + ky_i + lz_i)}.$$

Pauling-Sherman f-values[4] were used. The value 1.2 given for the exponent in the temperature factor was estimated from the angle at which a general rapid decrease in intensity of reflection sets in on oscillation photographs. Pronounced disagreement with the observed intensity values was found everywhere except in the region near $\alpha = 125°$ and $z = -0.04$, with $u = -0.0605$. No suitable range was found for the positive value of u. Calculated values of the intensity for various planes for $\alpha = 120°$, $125°$ and $130°$ and $0.03 \leqslant -z \leqslant 0.05$ are shown in figure 2. The intensity values observed by us and reported by Bragg and Morgan agree in the equality of $\{800\}$ and $\{444\}$ and the somewhat greater intensity of $\{555\}$. (Our intensity values are estimates made by visual comparison of photographs taken under identical conditions except for variation in the time of exposure.) It is seen from the figure that these relations require α to be nearly equal to 125° and z to -0.038. There are also in the figure intensity curves as a function of α for that value of z (-0.038, -0.038 and -0.042, respectively) for each value of α which causes the ratio $\{555\}/\{444\}$ to agree with observation. From this it is seen that the angle α is restricted by the observed equality of $\{800\}$ and $\{444\}$ to the value $124° \pm 3°$.

The correctness of the structure is supported by the general agreement between observed and calculated intensities shown in table 1. The observed values for very strong reflections are somewhat smaller than the calculated values; this we attribute to primary extinction, which seems to have been more significant for Bragg and Morgan's crystals than for ours. The remaining small discrepancies may be due to small errors in the *f*-values, the temperature factor or the parameters. Only for one form, {422}, do our observations show a pronounced deviation from the values of Bragg and Morgan. The calculated intensity for this reflection suggests that Bragg and Morgan's value is low.

TABLE 1

Comparison of Calculated and Observed Intensities of Reflection for $Be_4O(CH_3COO)_6$

{*hkl*}	I calculated	I observed PS	I observed BM	{*hkl*}	I calculated	I observed PS	I observed BM
111	520	400	300	311	22	30	35
222	140	140	110	331	80	65	55
333	1.2	0	Trace	422	105	130	55
444	27	30	35	620	10	15	20
555	36	40	45	442	0.8	0	
666	0	0		446	22	25	
777	2.4	2		662	3.3	4	
888	8.7	10	10	664	0.6	0	
400	400	300	220	511	0.0	0	Trace
800	27	30	35	533	8.7	10	
220	0.6	0	Trace				
440	55	55	55				

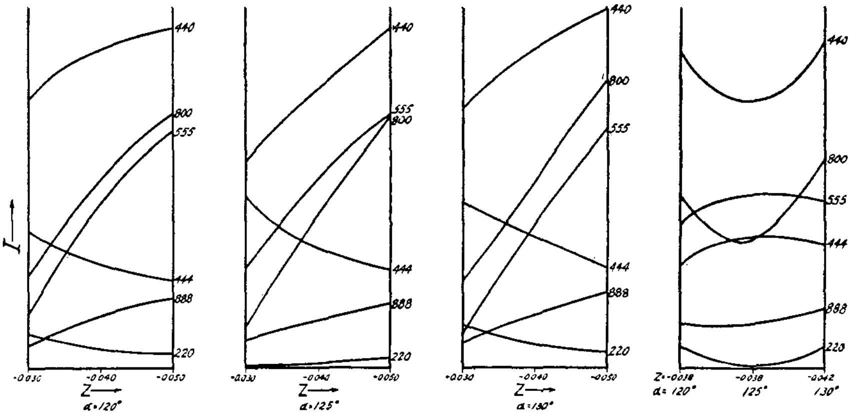

FIGURE 2

Calculated intensities for various reflections as functions of the parameters α and z.

The parameter values corresponding to the finally-chosen atomic arrangement are:

$$\begin{array}{llll} x = -0.163 & & u = -0.0605 \\ y = -0.064 & & v = 0.197 \\ z = -0.038 & & w = 0.295. \end{array}$$

The calculated intensity values are sensitive functions of these parameters, and an arbitrary variation of as much as 0.003 impairs the agreement with observed intensities (Fig. 2). The corresponding interatomic distances may hence be considered to be verified by experiment to within about 0.05 Å.

TABLE 2

INTERATOMIC DISTANCES IN $Be_4O(CH_3COO)_6$

ATOM	NEIGHBORS IN SAME ACETATE GROUP	NEIGHBORS IN SAME MOLECULE	NEIGHBORS IN OTHER MOLECULES
Carboxyl carbon, C_I	1 C_{II} at 1.54 Å	1 O_I at 3.10 Å	4 C_{II} at 4.08 Å
	2 O_{II} at 1.29	2 O_{II} at 3.36	4 C_I at 4.10
		2 O_{II} at 3.71	2 C_I at 4.38
			2 O_{II} at 3.52
			2 O_{II} at 4.04
Methyl carbon, C_{II}	1 C_I at 1.54 Å	2 O_{II} at 4.48 Å	4 C_{II} at 4.06 Å
	2 O_{II} at 2.39		4 C_I at 4.08
			2 O_{II} at 3.22
			2 O_{II} at 3.62
Central oxygen, O_I:		12 O_{II} at 2.80 Å	
		6 C_I at 3.10	
Carboxyl oxygen, O_{II}:	1 C_I at 1.29 Å	2 O_{II} at 2.55 Å	2 O_{II} at 3.87 Å
	1 O_{II} at 2.35	1 O_I at 2.80	2 O_{II} at 4.04
	1 C_{II} at 2.39	2 O_{II} at 3.87	1 C_I at 3.52
		2 O_{II} at 4.39	1 C_I at 4.04
		1 C_I at 3.36	1 C_{II} at 3.22
		1 C_I at 3.71	1 C_{II} at 3.62
		1 C_{II} at 4.48	

The structure may be described in the following way. It contains molecules as shown in figure 1, consisting of four BeO_4 tetrahedra with one common corner. The remaining corners are occupied by oxygen atoms of the acetate groups. The distance Be–O is 1.65 Å. The tetrahedra are slightly distorted, with three edges 2.80 Å and three 2.55 Å in length, the longer edges extending from the central oxygen atom. In the acetate group the angle α has the value 124° ± 3°, equal to the value 125° ± 5° found for formic acid; we may conclude that this value of the bond angle in the carboxyl group is probably retained in all aliphatic acids.

The arrangement of the centers of the molecules in the crystal is that corresponding to the diamond structure. Each molecule is surrounded tetrahedrally by four molecules. If we consider a molecule as roughly tetrahedral in shape with similar orientation to the tetrahedron formed by the four beryllium atoms, then the adjacent molecules are so oriented as to present tetrahedral faces to one another.

Interatomic distances for carbon and oxygen atoms in the crystal are given in table 2 (up to 4.5 Å). It is seen that the molecules pack snugly together, each methyl and carboxyl carbon and carboxyl oxygen atom having eight or twelve neighbors in adjacent molecules at distances between 3.22 and 4.10 Å.

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[1] W. H. Bragg and G. T. Morgan, *Proc. Roy. Soc.*, **A104**, 437 (1923).

[2] G. T. Morgan and W. T. Astbury, *Ibid.*, **A112**, 441 (1926).

[3] Linus Pauling and L. O. Brockway, these PROCEEDINGS, **20**, 336 (1934).

[4] Linus Pauling and J. Sherman, *Z. Krist.*, **81**, 1 (1932).

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The Structure of Alloys of Lead and Thallium*

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(*Received* 21 *May* 1951)

Alloys of lead and thallium have a structure based upon cubic closest packing from 0 to about 87·5 atomic percent thallium. The variation of the lattice constant with composition gives strong indication that ordered structures $PbTl_3$ and $PbTl_7$ exist. In the intermediate ranges, solid solutions of the types $Pb(Pb,Tl)_3$ and $Pb(Pb,Tl)Tl_6$ exist. Interpretation of interatomic distances indicates that thallium atoms present in low concentration in lead assume the same valence as lead, about 2·14, and that the valence of thallium increases with increase in the mole fraction of thallium present, having the same value, about 2·50, in $PbTl_3$ and $PbTl_7$ as in pure thallium. A theory of the structure of the alloys is presented which explains the observed phase diagram, and which in particular accounts for the existence of a maximum melting point at about 63 atomic percent thallium.

1. Introduction

The binary system lead–thallium shows an unusual type of phase diagram. Fig. 1, taken from Hansen (1936), represents in the main the results obtained by Kurnakow & Pushin (1907) and by Lewkonja (1907). The liquidus curve in the wide solid-solution region has a maximum at about 63 atomic percent thallium. The nature of this maximum has not previously been made clear.

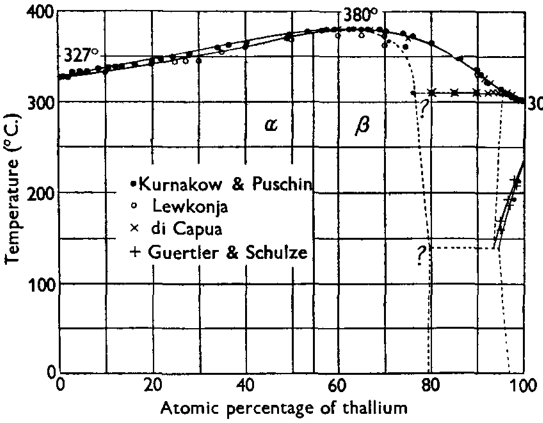

Fig. 1. The phase diagram of the alloy system lead–thallium taken from Hansen (1936).

The electric resistivity was measured by Kurnakow & Schemtschushny (1909) and by Guertler & Schulze (1923), and was found to vary smoothly, with no indication of the presence of a compound such as $PbTl_2$ or Pb_2Tl_3. McMillan & Pauling (1927) prepared X-ray powder photographs of alloys representing ten compositions. The only X-ray diffraction lines shown by the samples with from 0 to 80 atomic percent thallium were those corresponding to the cubic closest-packed arrangement $A1$, with the lattice constant decreasing from 4·948 kX. for pure lead to 4·858 kX. for 80 atomic percent thallium. Halla & Staufer (1928) reported results from a single crystal of an alloy containing 65 atomic percent thallium which substantiated those of McMillan & Pauling. Ölander (1934) noticed that the lattice constants reported by McMillan & Pauling did not vary linearly with the composition, and he determined the constants for eleven alloys, with greater precision. He was able to represent his values for a_0 by two straight lines intersecting at 54·6 atomic percent thallium, and therefore postulated that below 54·6 atomic percent thallium the alloys are present in a random solid solution, phase α, and above this composition in a partially ordered phase, phase β (Fig. 1). He suggested that the perfectly ordered arrangement of the β phase would conform to the formula $PbTl_7$.

The present investigation was carried out in order to test Ölander's suggestion and to obtain additional information about the nature of these alloys.

2. The preparation and X-ray photography of the alloys

Alloy samples weighing either 100 or 25 g. were prepared by melting weighed amounts of lead and thallium together. The c. p. granular test lead, free from silver, gold and bismuth (Fisher Scientific Company), was indicated by spectroscopic examination to contain approximately 0·005 % iron, 0·001 % thallium and 0·001 % copper. The thallium used was supplied by the Varlacoid Company. Spectroscopic examination showed the presence of approximately 0·01 % lead, 0·005 % iron, and 0·001 % copper.

The meltings occurred in Pyrex tubes under a vacuum of about 10^{-5} mm. Hg. The uniformity of the reguli with respect to composition was achieved by two measures: first, the alloys were kept in the molten state about 100° C. above their melting-points for more than 2 hr.; and secondly, effective agitation was provided by a magnetically driven stirring device.

Twenty-one samples were prepared and investigated.

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* Contribution No. 1565 from the Gates and Crellin Laboratories.

All but three of these samples were analyzed chemically and spectroscopically by the Smith-Emery Company of Los Angeles. The chemical analyses (Table 1) agreed with the synthetic compositions to within ±0·3 %. Duplicate 2 g. samples of each of sixteen of the alloys were analyzed and found to have the same composition, showing the alloys to be homogeneous.

Table 1. *Chemical analyses and lattice constants*

Sample	Atomic percent of thallium	Lattice constant a_0 (Å)
1	0	$4{\cdot}947_4 \pm 0{\cdot}001$
2	$4{\cdot}9 \pm 1{\cdot}0$	$4{\cdot}946_0 \pm 0{\cdot}001$
3	$11{\cdot}2 \pm 0{\cdot}5$	$4{\cdot}942_4 \pm 0{\cdot}001$
4	$21{\cdot}1 \pm 0{\cdot}5$	$4{\cdot}934_7 \pm 0{\cdot}001$
5	$30{\cdot}8 \pm 1{\cdot}0$	$4{\cdot}927_1 \pm 0{\cdot}001$
6	$40{\cdot}6 \pm 1{\cdot}0$	$4{\cdot}918_7 \pm 0{\cdot}001$
7	$50{\cdot}4 \pm 0{\cdot}5$	$4{\cdot}908_6 \pm 0{\cdot}001$
8	$53{\cdot}5 \pm 1{\cdot}0$	$4{\cdot}906_2 \pm 0{\cdot}001$
9	$55{\cdot}4 \pm 1{\cdot}0$	$4{\cdot}902_8 \pm 0{\cdot}001$
10	$61{\cdot}1 \pm 1{\cdot}0$	$4{\cdot}897_4 \pm 0{\cdot}001$
11	$64{\cdot}7 \pm 1{\cdot}0$	$4{\cdot}892_9 \pm 0{\cdot}001$
12	$67{\cdot}6 \pm 1{\cdot}0$	$4{\cdot}887_8 \pm 0{\cdot}001$
13	$70{\cdot}6 \pm 1{\cdot}0$	$4{\cdot}885_5 \pm 0{\cdot}001$
14	$75{\cdot}0 \pm 1{\cdot}0$	*A* $4{\cdot}879_5 \pm 0{\cdot}002$ *B* $4{\cdot}874_0 \pm 0{\cdot}002$
15	$77{\cdot}1 \pm 1{\cdot}0$	$4{\cdot}870_0 \pm 0{\cdot}002$
16	$80{\cdot}5 \pm 1{\cdot}0$	$4{\cdot}867_1 \pm 0{\cdot}002$
17	$83{\cdot}9 \pm 1{\cdot}0$	$4{\cdot}863_6 \pm 0{\cdot}002$
18	$87{\cdot}8 \pm 1{\cdot}0$	$4{\cdot}856_0 \pm 0{\cdot}002$
19	$93{\cdot}4 \pm 1{\cdot}0$	$4{\cdot}856_4 \pm 0{\cdot}002$
20	$96{\cdot}9 \pm 1{\cdot}0$	
21	100·0	

In an atmosphere of carbon dioxide, filings from the reguli were screened through a 200-mesh sieve and collected in thin-walled glass capillaries about ½ mm. in diameter. The capillaries were then evacuated and sealed, and the specimens were annealed at 280° C. for 40 hr. and allowed to cool at the rate of about 0·001° C./sec. (It was observed that specimens which were not annealed gave diffuse diffraction lines; the lines were made sharp by the process of annealing as described above.)

A series of powder photographs was taken in a Norelco camera 360 mm. in circumference which holds the film in the Straumanis arrangement and permits a maximum Bragg angle of 87·5°. The copper *K* radiation was filtered through 0·001 in. nickel foil. Eastman No-Screen X-ray film was used throughout. All photographs were taken at room temperature, 26 ± 2° C.

The diffraction patterns for the eighteen samples with between 0 and 87·8 atomic percent thallium correspond in positions and relative intensities of the lines to the *A* 1 arrangement. The photographs for 93·4 and 96·9 atomic percent thallium show this pattern, and in addition the lines of the room-temperature modification of thallium, which has the *A* 3 structure. The sample of pure thallium shows only the latter pattern.

For the alloys containing less than 70 atomic percent thallium the powder photographs showed the reflection 620. For the other alloys in the *A* 1 phase the photographs contained reflections only as far as 600 and 442. The presence of the reflection 620 at Bragg angles varying from 80·7 to 85·5° significantly improves the accuracy of the lattice constants derived from the former photographs.

For each photograph the measurements for the various lines were found to be satisfactorily represented by a straight line when plotted according to the method of Nelson & Riley (1945). This straight line was always drawn through the point representing the diffraction line observed at the maximum Bragg angle. The wavelengths 1·5405 Å for copper $K\alpha_1$, 1·5443 Å for copper $K\alpha_2$ and 1·5418 Å for the unresolved doublet were used. The values of a_0 obtained in this way are given in Table 1.

Two checks of the accuracy of the determinations of the lattice constants were made. Filings of samples 2 and 3 were placed in capillary tubes of two different diameters, and photographs were made and interpreted. For each sample the same lattice constant was obtained from the two photographs. For samples 11 and 14 filings were prepared from two different portions of the 25 g. sample, and powder photographs were prepared. In the case of specimen 11 the lattice constant determined from the two preparations was the same, whereas for specimen 14 values differing by 0·0055 Å were obtained. We believe that the latter variation is due to a small difference in composition, perhaps 0·5 %, in the two samples; the lattice constant is very sensitive to composition in this region.

3. Interpretation of the results

The values found for a_0 are shown in Fig. 2 as a function of composition. They are not linearly dependent upon the composition, but instead can be represented by two smooth curves, one covering the range 0–75 atomic percent thallium, and the other the range 75–87·5 atomic percent thallium. The lattice period of the *A* 1 phase is constant for the alloys with more than 87·5 atomic percent thallium, which indicates that the limit of solubility of thallium in lead is about 87·5 atomic percent. No evidence is provided by our investigation to support Ölander's suggestion of a discontinuity in slope of the lattice-constant curve at 54·6 atomic percent thallium. Our results are compared with those of Ölander and of McMillan & Pauling in Fig. 3. The values of a_0 reported by McMillan & Pauling agree with the new curve to within their estimated error of ± 0·1 %, as indicated by the span of the vertical lines. We think that it is likely that the disagreement between our curve and some of the values reported by Ölander is due to a somewhat larger error in his determination than that (± 0·02 %) suggested by him.

A reasonable interpretation can be given to the curve of Fig. 2, with its two discontinuities in slope: namely, that there exist ordered phases $PbTl_3$ and $PbTl_7$. Direct evidence from the intensities of X-ray reflections is not obtained for ordering in this case, because of the approximate equality in *f* values of lead and thallium. We can, however, discuss the probable structures of the ordered phases. The powder patterns given by these alloys show no splitting of lines. We estimate that the splitting corresponding to a deviation greater than 0·002 from unity in axial ratio could be detected; accordingly, it is very likely that no superstructure involving deviation from cubic symmetry is present. None of the photographs shows any lines requiring the assumption of a unit of structure larger than the four-atom unit. The near equality in scattering powers of lead and thallium would permit a cubic superstructure based on a larger unit to be present, in case that the atoms were at or very near the positions corresponding to the $A1$ arrangement. However, if the atoms were to be shifted appreciably from these positions (by as much as, say, 0·2 Å) observable diffraction lines requiring the larger unit would be expected.

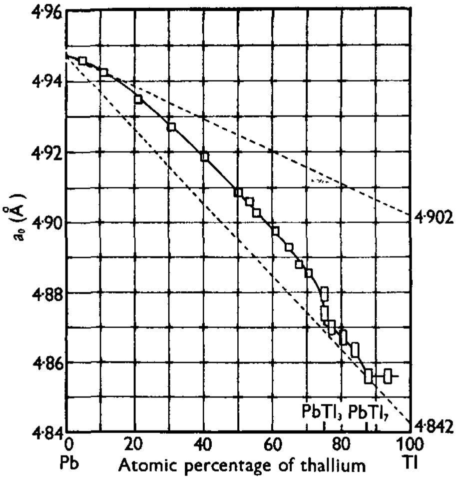

Fig. 2. The lattice-constant curve based on values given in Table 1. The edge lengths of squares and rectangles give the magnitude of uncertainties in a_0 and composition.

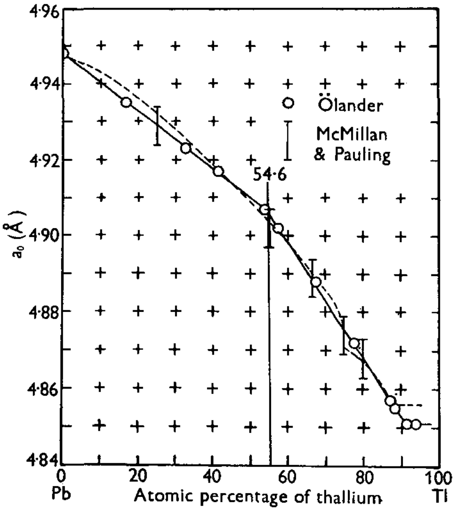

Fig. 3. The two-straight-line result as reported by Ölander. McMillan & Pauling's values are given for comparison. The new lattice-constant curve is also included.

Let us consider the types of superstructure compatible with the assumption that the atoms are completely ordered and occupy with cubic symmetry exactly the points of the $A1$ arrangement. The theory of space groups shows that for two elements, A and B, there exist only two structures compatible with this assumption. These are the structure AB_3 (Fig. 4) and AB_7 (Fig. 5). The structure of AB_3 is the $AuCu_3$ arrangement, with one atom A at 0, 0, 0 and three B at $\frac{1}{2}, \frac{1}{2}, 0$; $\frac{1}{2}, 0, \frac{1}{2}$; and $0, \frac{1}{2}, \frac{1}{2}$. The structure AB_7 is based on a face-centered lattice, the cubic unit containing 32 atoms in the positions indicated. In this structure the atoms B are not all crystallographically equivalent, but are of two types; the structure can in fact be achieved for three elements, A, B and C, and might be realized by a compound ABC_6, as indicated in Fig. 6.

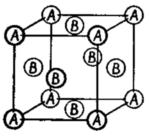

Fig. 4. The structure AB_3.

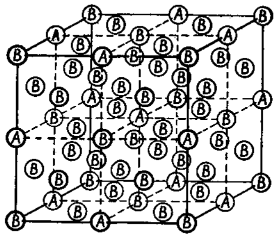

Fig. 5. The structure AB_7. $Z=4$.

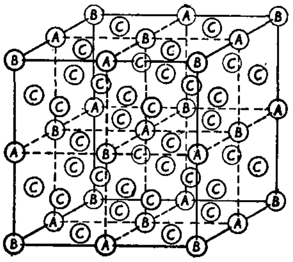

Fig. 6. The structure ABC_6. $Z=4$.

These are the only cubic arrangements provided by the theory of space groups in which every atom occupies an invariant position, and all of the atomic positions are those corresponding to the $A1$ arrangement. Very recently we have found that the cubic phase 'Pt_3Cu' is highly probably also based upon the cubic structure ABC_6 (Tang, 1951).

4. Interatomic distances in the alloys

According to our interpretation the lead–thallium alloys in the range 0–75 atomic percent thallium have the structure $Pb(Pb, Tl)_3$, and between 75 and 87·5 atomic percent thallium they have the structure $Pb(Pb, Tl)Tl_6$. The values of a_0 shown in Fig. 2 indicate that at 75 atomic percent thallium there is nearly complete order, corresponding to the compound $PbTl_3$.

It is possible to discuss the interatomic distances in relation to the valences of lead and thallium. From the system of metallic radii (Pauling, 1949) and the relation

$$D_n = D_1 - 0{\cdot}600 \log n$$

connecting interatomic distance D_n for bond number n with the interatomic distance for a single bond, D_1, which is equal to the sum of the single-bond radii of the two atoms, we calculate for lead in the pure element the valence 2·14 and for thallium in the pure element the valence 2·50, corresponding to lattice constant 4·842 Å for the $A\,1$ structure. It is interesting that a straight line drawn between the lattice constant for pure lead and that predicted for thallium with the $A\,1$ structure passes through the values of a_0 for the compounds $PbTl_3$ and $PbTl_7$, as shown in Fig. 2. At other compositions the observed values of a_0 are larger than those predicted from the linear relation. We conclude that in the intermediate ranges the strain introduced by isomorphous replacement of lead by thallium increases the lattice constants, perhaps by causing thallium to assume a slightly lower valence.

In connection with a discussion of alloys of aluminum and zinc (Pauling, 1949) it was pointed out that an element present in very small quantity in solid solution in another element would have a tendency to assume the valence of the second element. The upper straight line in Fig. 2 is drawn between the value of the lattice constant for pure lead and that calculated for thallium with valence 2·14, equal to that of lead in the state of the pure element. It is seen that it passes through the experimental values of a_0 for the alloys with 4·9 and 11·2 atomic percent thallium, thus supporting the suggestion that in these dilute alloys thallium has assumed the same valence as its solvent, lead.

5. An explanation of the maximum melting point of alloys in the lead-thallium system and related binary systems

We have found it possible to formulate a simple treatment of the lead–thallium alloys that accounts satisfactorily for the existence of a maximum in melting-point displaced from the composition $PbTl_3$ of the ordered structure, and that also accounts in a reasonably satisfactory way for the shapes of the liquidus and solidus curves throughout the range 0—75 atomic percent thallium (Fig. 1). The maximum in these curves occurs at a composition near that for a compound Pb_2Tl_3 or a compound $PbTl_2$. If either of these compounds existed, it would have to be considered as forming solid solutions with lead and with thallium. The data, however, give no evidence for the existence of such compounds.

A very simple treatment can be carried out by assuming that the liquid phase is a series of ideal solutions of lead and thallium, and that in the solid phase isomorphous replacement of thallium atoms in the $PbTl_3$ structure by lead atoms occurs in the way corresponding to the formation of an ideal solution. For the liquid phase the free energy would then be represented by the expression

$$F^0(l) = F^0_0(l) + ax - RT[x \ln x + (1-x)\ln(1-x)].$$

The term ax represents an assumed linear dependence of the free energy of the liquid solution on the mole fraction of thallium, x, and the last term in the expression is the free energy of mixing. For the solid phase in the range $0 \leqslant x \leqslant 0{\cdot}75$ we assume the free energy to be given by the expression

$$F^0(c) = F^0_0(c) + bx - RT[x \ln x + (\tfrac{3}{4}-x)\ln(\tfrac{3}{4}-x) - \tfrac{3}{4}\ln\tfrac{3}{4}].$$

Here the first term is the free energy of pure crystalline lead, the second term an assumed linear dependence on composition, and the third term the free energy of mixing lead and thallium in the atomic positions 0, ½, ½; ½, 0, ½; and ½, ½, 0 of the unit cube. Curves representing these expressions are shown in Fig. 7. The value of a has been put equal to 0 (this simplification does not affect the conclusions drawn below), and the value of b has been taken such as to cause the two curves to osculate at the composition $x = 0{\cdot}63$, as is indicated at the top of the diagram. At a somewhat decreased temperature, represented by the curves in the middle of the diagram of Fig. 7, the curves for liquid and solid intersect in such a way as to permit two common tangential lines to be drawn. Each of these lines, in the region between its points of tangency with the curves, represents a two-phase system, and the points of tangency give the compositions of liquidus and solidus corresponding to the temperature. The curve at the bottom of the diagram corresponds to the temperature

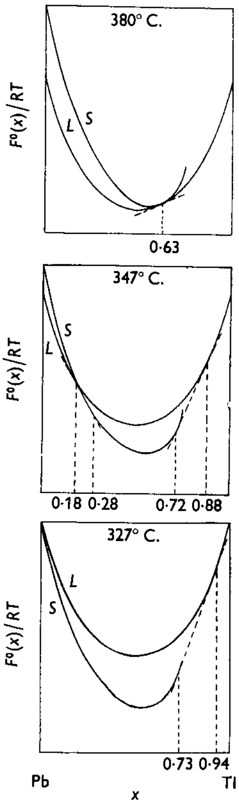

Fig. 7. The free-energy curves and the derivation of the liquidus and solidus curves.

of melting of pure lead; the points of tangency of the straight line at the right side of the diagram give the compositions of liquidus and solidus for the solid solutions of high thallium content.

The phase diagram constructed in this way, with the assumption that the difference in free energy of liquid lead and solid lead, $F^0_0(l) - F^0_0(c)$, is a linear function of the temperature, and that the other parameters remain unchanged, is shown as Fig. 8. It is seen that it is qualitatively similar to the phase diagram for the lead–thallium system in the range 0–75 atomic percent thallium.

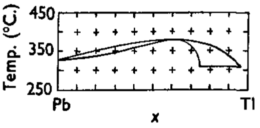

Fig. 8. The phase diagram derived from the free-energy curves in Fig. 7.

This simple theory is unsatisfactory, in that the rate of change of the difference in free energy of liquid and crystalline lead predicted by the Clausius–Clapeyron equation leads to a temperature scale for Fig. 8 four times as great as that in Fig. 1. This lack of agreement is eliminated if the assumption is made that the free energy of the crystalline phase depends in a more striking way on the characteristics of the ordered phase $PbTl_3$. In $PbTl_3$ each lead atom is surrounded by twelve thallium ligates, with the configuration corresponding to the cubic closest-packed arrangement, and each thallium atom is surrounded by eight thallium ligates and four lead ligates, the latter lying in an equatorial plane. It is not unreasonable to assume that the ordering is the result of a special stability of this configuration of eight thallium atoms and four lead atoms about each thallium atom. If we assume that a stabilizing contribution to the free energy of the crystalline phase is made by each thallium atom with this configuration, and that the thallium and lead atoms are distributed at random among the points $0, \frac{1}{2}, \frac{1}{2}$; $\frac{1}{2}, 0, \frac{1}{2}$ and $\frac{1}{2}, \frac{1}{2}, 0$, we conclude that a term cx^9 should be included in the free-energy expression for the crystal. A similar term might also be included in the free-energy expression for the liquid, but it is found to be so small in comparison with that in the crystal as to permit its neglect. We accordingly replace the expression in equation (2) by an expanded expression, obtained by adding the term cx^9 on the right side of this equation. When this is done, it is found that suitable values of b and c can be determined such as to make the maximum melting-point occur at $x = 0{\cdot}63$, as observed, with the temperature coefficient of $F^0_0(l) - F^0_0(c)$ equal to the value given by the Clausius–Clapeyron equation

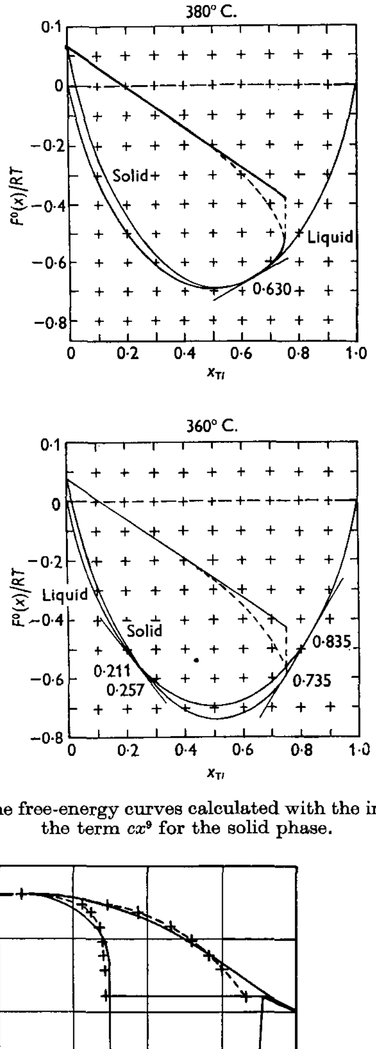

Fig. 9. The free-energy curves calculated with the inclusion of the term cx^9 for the solid phase.

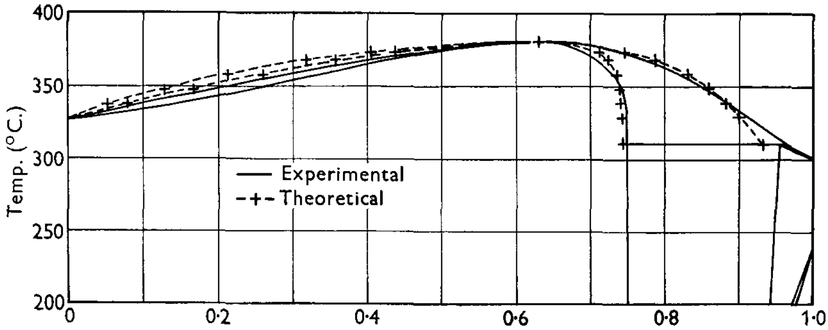

Fig. 10. The theoretical phase diagram derived from the free-energy curves in Fig. 9 is compared with the experimental one.

with the observed heat of fusion of lead, 1·3 kcal.mole^{-1}. Some free-energy curves calculated in this way are given in Fig. 9, and the corresponding phase diagram is represented in Fig. 10. The discrepancy in the lead-rich region between the theoretical liquidus and solidus curves and the experimental ones is probably due to the fact that the occupancy of the position 0, 0, 0 by lead atoms alone could not be retained at very small percentages of thallium; the dilute alloys may well have a random or nearly random replacement of lead atoms by thallium atoms in all positions.

There seem to be many binary metallic systems in which there are phases of this sort. In the sodium–lead system there are two such phases. One of them, based on the ideal structure Na_3Pb, extends from 27 to 30 atomic percent lead, with its maximum at about 28 atomic percent lead; and the other, corresponding to the ideal composition $NaPb_3$, extends from 68 to 72 atomic percent lead, with maximum at about 70 atomic percent. The intensities of X-ray reflection have verified that in the second of these phases sodium atoms occupy the positions 0, 0, 0, and the other three positions in the unit cell are occupied by lead atoms isomorphously replaced to some extent by sodium atoms (Zintl & Harder, 1931). These two phases are interesting in that the ranges of stability do not include the pure compounds Na_3Pb and $NaPb_3$.

It seems likely that there are many other phases of this sort. Among them is probably the γ phase of the mercury–thallium system, extending from 21 to 32 atomic percent thallium, and with maximum melting-point at 28 atomic percent thallium; this phase, which usually is described as having the ideal composition Hg_5Tl_2, presumably should be described as having the ideal composition Hg_3Tl.

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Interatomic Distances and Atomic Valences in NaZn_{13}*

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The crystal structure of NaZn_{13} and of several homologous compounds AB_{13} was reported by Ketelaar and by Zintl & Hauke to be based on space group O_h^6–$Fm3c$, with 8 Na in 8(*a*): $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$; ...; 8 $\mathrm{Zn_I}$ in 8(*b*): 0, 0, 0; ...; and 96 $\mathrm{Zn_{II}}$ in 96(*i*): 0, *y*, *z*; .... Approximate values were reported for the parameters a_0, *y*, and *z*; for NaZn_{13} Zintl & Hauke reported 12·27 Å, 0·178, and 0·122 for these three parameters. Each $\mathrm{Zn_I}$ is surrounded by twelve $\mathrm{Zn_{II}}$ at the vertices of a nearly regular icosahedron, and each Na by twenty-four $\mathrm{Zn_{II}}$ at the vertices of a snub cube. Our interest in the structure was largely concerned with the valences of the two different kinds of Zn atoms, it being presumptive that $\mathrm{Zn_I}$ has a larger valence than $\mathrm{Zn_{II}}$ because its icosahedral coordination requires it to be smaller than $\mathrm{Zn_{II}}$. Lines on new powder photographs of NaZn_{13} were measured and the intensities were estimated visually with as much precision as possible. Least-squares treatments were employed in order to obtain the best possible values for the three parameters; the values obtained are $a_0 = 12{\cdot}2836 \pm 0{\cdot}0003$ Å, $y = 0{\cdot}1806 \pm 0{\cdot}0003$, and $z = 0{\cdot}1192 \pm 0{\cdot}0003$. The uncertainties given are calculated standard deviations. Analysis of the interatomic distances yields a selfconsistent interpretation in which $\mathrm{Zn_I}$ is assumed to be quinquevalent and $\mathrm{Zn_{II}}$ quadrivalent, while Na may have a valence of unity or one as high as $1\frac{1}{4}$, the excess over unity being suggested by the interatomic distances and being, if real, presumably a consequence of electron transfer. A valence electron number of approximately 432 per unit cell is obtained, which is in good agreement with the value 428·48 predicted on the basis of a filled Brillouin polyhedron defined by the forms {444}, {640}, and {800}.

Introduction

Some years ago Ketelaar (1937) reported a tentative structure for NaZn_{13} and five other AB_{13} compounds (KZn_{13}, KCd_{13}, CaZn_{13}, SrZn_{13}, and BaZn_{13}). Zintl & Hauke (1937) reported the same structure for NaZn_{13} and two other compounds (KZn_{13} and KCd_{13}), and later (1938) for two more (RbCd_{13} and CsCd_{13}). The structure is based on a face-centered cubic lattice. The space group is O_h^6–$Fm3c$, with (e.g. for NaZn_{13}) eight Na in 8(*a*): $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$; ...; eight $\mathrm{Zn_I}$ in 8(*b*): 0, 0, 0; ...; and ninety-six $\mathrm{Zn_{II}}$ in 96(*i*): 0, *y*, *z*; .... The parameters obtained by these workers are summarized in Table 1.

Zintl & Hauke cited no limits of error, but Ketelaar cited an uncertainty of 0·005 Å for a_0 and an uncertainty of 0·003 in *y* and *z*. From comparisons among the intensities obtained for the five compounds that they investigated, Zintl & Hauke concluded that the *y* and *z* parameters are substantially the same for all five.

Table 1. *Parameters obtained in previous work on compounds of type* AB_{13}

Compound	Ketelaar			Zintl & Hauke		
	a_0*	*y*	*z*	a_0*	*y*	*z*
NaZn_{13}	12·255	—	—	12·27	0·178	0·122
KZn_{13}	12·335	—	—	12·36	—	—
KCd_{13}	13·785	0·183	0·117	13·77	—	—
CaZn_{13}	12·13	—	—	—	—	—
SrZn_{13}	12·215	—	—	—	—	—
BaZn_{13}	12·33	—	—	—	—	—
RbCd_{13}	—	—	—	13·88	—	—
CsCd_{13}	—	—	—	13·89	—	—

* Values for a_0 are apparently given in kX. units; Zintl & Hauke give $\lambda = 1{\cdot}539$ for Cu $K\alpha$, and 1·537 and 1·541 for the two components.

One of the features of this structure is that the $\mathrm{Zn_I}$ (or $\mathrm{Cd_I}$) at 0, 0, 0 is surrounded by twelve $\mathrm{Zn_{II}}$ at the vertices of a nearly regular icosahedron. The $\mathrm{Zn_I}$–$\mathrm{Zn_{II}}$ distance is accordingly substantially smaller than the average $\mathrm{Zn_{II}}$–$\mathrm{Zn_{II}}$ distance. If the icosahedron were regular the ratio of the radial distance to the edge distance would be 0·951. The observed radial distances (2·65 Å in NaZn_{13}, 2·99 Å in KCd_{13}) are in good agreement with the short distances in elementary zinc (2·660 Å) and cadmium (2·973 Å), to which have been assigned bond numbers of one-half (Pauling, 1947, 1949). This suggests that the atom at 0, 0, 0 forms twelve one-half bonds, and hence has a valence of six rather than the usual valence of 4·5 or 4.

The present investigation was undertaken in order

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Contribution No. 1656 from the Gates and Crellin Laboratories.

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to provide unit-cell and positional parameters and interatomic distances for $NaZn_{13}$ with sufficient precision for a satisfactory interpretation of this structure in terms of atomic valence and bond numbers.

Experimental method

Samples of $NaZn_{13}$ were prepared by heating zinc with a calculated excess of sodium in alundum extraction thimbles contained in a steel bomb sealed with copper gaskets. The bomb was filled with nitrogen or argon before being sealed, and was heated for several hours above the melting point of $NaZn_{13}$ (557° C.). The bomb was cooled and opened, and the excess of sodium was removed by extraction with anhydrous liquid ammonia. The materials were kept under dry paraffin oil until used. Samples of KCd_{13} and KZn_{13} were prepared in the same way.

Specimens for powder photography were prepared by grinding the materials in dry paraffin oil and drawing the resulting slurry into thin-walled pyrex capillary tubes about $\frac{1}{4}$ mm. in diameter. Powder photographs were taken with nickel-filtered Cu $K\alpha$ radiation in a Straumanis-type Philips powder camera of nominal radius 57·30 mm. This camera had been constructed with sufficient precision to preclude eccentricity errors, and indeed analysis of powder data obtained with this camera has shown that eccentricity errors are negligibly small. In the case of $NaZn_{13}$ each exposure was made with two superimposed Eastman No-Screen Dupli-tized X-ray films in the camera; two exposures were made, with exposure times of 2·50 and 9·25 hr. at 20 mA. The ratio of these exposure times is 3·7, which is equal to the assumed film factor for Cu $K\alpha$ radiation. This value of the film factor, which is the factor by which the intensity of the radiation is decreased on passing normally through a single film, was determined at the Eastman Kodak Company laboratories (H. E. Seemann, private communication). One heavily exposed film, two moderately and substantially identically exposed films, and one weakly exposed film were thus obtained, enabling a check to be made on the film factor, which was found to be 3·7 within experimental error.

The relative positions of the lines on the photographs were determined with use of a steel millimeter scale. The intensities of the lines on the $NaZn_{13}$ photographs were determined visually, by the multiple-film technique, with the use of no external standards.

Determination of the lattice constant

Reciprocal spacings ($1/d_{hkl} = q_{hkl} = (2\sin\theta)/\lambda$) were calculated from the positions of the powder lines, and the lines were indexed on the basis of a face-centered cubic lattice. Analysis of a few lines in the back-reflection region gave a preliminary value of 0·081409 Å^{-1} for $1/a_0$. A refinement of $1/a_0$ was carried out by the method of least squares (Whittaker & Robinson, 1937), with the introduction of an absorption parameter K in conjunction with the absorption function of Nelson & Riley (1945). The observational equations were of the form

$$(\sqrt{w_i})\frac{dq_i}{d(1/a_0)}\Delta(1/a_0)+(\sqrt{w_i})q_i\cdot\frac{1}{2}\left(\frac{\cos^2\theta_i}{\sin\theta_i}+\frac{\cos^2\theta_i}{\theta_i}\right)K = (\sqrt{w_i})(q_i^{\text{obs.}}-q_i^{\text{calc.}})\,, \qquad (1)$$

where $\Delta(1/a_0)$ and K are the parameters to be solved for, q_i is the reciprocal spacing of the ith line, and w_i is the weight assigned to the ith line. The coefficient of K contains, besides w_i, the absorption function of Nelson & Riley. The weight w_i was taken as

$$w_i = w_i'/\cos^2\theta_i\,, \qquad (2)$$

where w_i' is an auxiliary weight depending on the physical characteristics of the line and has been given arbitrary values ranging from 1 to 4. The derivative in equation (1) is

$$\frac{dq_i}{d(1/a_0)} = \sqrt{(h_i^2+k_i^2+l_i^2)}\,. \qquad (3)$$

The two normal equations were obtained in the usual way and solved for the two parameters. The results are

$$a_0 = 12{\cdot}2836 \pm 0{\cdot}0003\ \text{Å}\,,$$
$$K = 1{\cdot}35\times10^{-4} \pm 2{\cdot}34\times10^{-4}\,,$$

($\lambda = 1{\cdot}5418$ Å for unresolved Cu $K\alpha$; 1·54050 for α_1; 1·54434 for α_2) where the uncertainties are standard deviations as determined from the residuals and the coefficients of the normal equations (Whittaker & Robinson, 1937). The absorption parameter K is positive, as it should be, but the value given is evidently not significant. The precision of the lattice-parameter determination corresponds to one part in forty thousand. This precision is higher than needed for our purpose, and is not especially significant, as the ambient temperature during photography is not precisely known, the photograph having been taken at room temperature (about 25° C.). The high precision that is obtainable with this experimental and computational technique justifies accurate knowledge of the temperature at which the exposure is made.

In Table 2 there are given data pertinent to the lattice-parameter determination, as well as intensity data used in the determination of atomic positional parameters.

Determination of atomic positional parameters

The parameters reported by Zintl & Hauke were taken as the starting point of the parameter determination. Using these parameters, structure factors were calculated for all of the planes in the sphere of reflection. The atomic form factors of James & Brindley (1935) were used. (Subsequent calculations made with two

Table 2. *Reciprocal spacings and intensity data for* $NaZn_{13}$

hkl	w'	$q_{\text{obs.}}$	Δq ($\times 10^4$)	w''	$F_{\text{calc.}}$	$G^2_{\text{calc.}}$ ($\times 10^{-2}$)	$G^2_{\text{obs.}}$ ($\times 10^{-2}$)	ΔG^2 ($\times 10^{-2}$)
200	—	—	—	4	66·5	259	236	−23
220	—	—	—	4	−30·2	104	104	0
222	—	—	—	—	2·1	0	< 7	—
400	—	—	—	4	18·4	18	18	0
420	—	—	—	4	−39·6	335	307	−28
422	—	—	—	4	90·3	1703	1502	−201
440	—	—	—	4	−60·8	370	357	−13
531	—	—	—	4	−124·2	6074	5388	−686
600 442	—	—	—	4	165·5 87·4	2834	2243	−591
620	—	—	—	4	43·3	361	356	− 5
622	—	—	—	4	27·8	144	140	− 4
444	—	—	—	4	74·0	332	341	9
640	—	—	—	4	−43·3	335	330	− 5
642	—	—	—	4	28·9	293	260	−33
731	—	—	—	4	15·7	84	119	35
800	—	—	—	4	111·0	513	556	43
820 644	—	—	—	4	−36·9 −39·4	474	597	123
822 660	—	—	—	4	−31·0 63·5	474	560	86
751	—	—	—	4	34·8	378	351	−27
662	—	—	—	—	13·6	30	< 56	—
840	—	—	—	—	11·6	20	< 60	—
753	—	—	—	4	−83·8	2106	2153	47
842	—	—	—	1	39·0	452	350	−102
664	—	—	—	4	−50·1	365	369	4
931	—	—	—	4	65·5	1232	1282	50
844	—	—	—	4	93·8	1227	1192	−35
10,0,0 860	—	—	—	4	135·4 73·5	1359	1412	53
10,2,0 862	—	—	—	4	21·8 44·1	584	571	−13
951	—	—	—	4	60·5	956	1122	166
10,2,2 666	—	—	—	—	− 6·4 −28·7	41	<107	—
953 10,4,0 864	—	—	—	1	−96·9 −18·8 45·5	2909	2293	−616
10,4,2	—	—	—	4	24·0	140	79	−61
880	—	—	—	4	−37·1	79	120	41
11,3,1 971	—	—	—	2	−78·2 11·5	1428	1282	−146
10,4,4 882	—	—	—	2	− 4·6 −95·6	1037	1132	95
10,6,0 866	—	—	—	4	75·4 79·0	1325	1302	−23
973 10,6,2	—	—	—	1	—34·4 18·6	332	314	−18
12,0,0 884	—	—	—	4	60·8 13·0	116	110	− 6
11,5,1	—	—	—	4	−14·9	46	110	64
12,2,0	—	—	—	—	− 0·9	0	< 95	—
12,2,2 10,6,4	—	—	—	4	58·4 −10·4	368	355	−13
11,5,3 975	1	1·0139	3·6	4	−26·8 −14·8	184	185	1

Table 2 (*cont.*)

hkl	w'	$q_{\text{obs.}}$	Δq ($\times 10^4$)	w''	$F_{\text{calc.}}$	$G^2_{\text{calc.}}$ ($\times 10^{-2}$)	$G^2_{\text{obs.}}$ ($\times 10^{-2}$)	ΔG^2 ($\times 10^{-2}$)
12,4,0	1	1·0297	−0·6	4	−39·5	151	158	7
12,4,2 10,8,0 886	2	1·0424	−1·5	4	39·2 33·1 18·9	427	450	23
10,8,2	—	—	—	—	− 7·1	10	< 91	—
11,7,1	—	—	—	—	−21·7	86	<103	—
10,6,6	—	—	—	—	13·3	16	<102	—
12,4,4	—	—	—	—	10·3	9	< 87	—
13,3,1 11,7,3	4	1·0891	−0·9	6	−30·2 61·5	818	861	43
12,6,0 10,8,4	—	—	—	—	− 9·6 21·4	87	<114	—
12,6,2	—	—	—	—	18·0	55	< 95	—
888	2	1·1282	1·6	6	−142·8	549	510	−39
13,5,1 11,7,5	3	1·1369	0·8	3	66·8 19·3	768	721	−47
14,0,0 12,6,4	1	1·1400	2·7	1	−18·2 −51·1	417	428	11
14,2,0 10,10,0 10,8,6	4	1·1514	1·0	6	−34·1 68·6 57·1	774	742	−32
13,5,3 11,9,1	2	1·1598	−1·1	4	15·0 −34·2	211	202	− 9
14,2,2 10,10,2	—	—	—	—	21·6 5·4	37	< 91	—
12,8,0	2	1·1744	3·0	4	47·0	163	196	33
11,9,3	3	1·1824	−1·4	2	86·0	1073	1002	−71
14,4,0 12,8,2	1	1·1851	−2·4	1	−36·2 47·2	417	436	19
14,4,2 12,6,6 10,10,4	4	1·1964	−0·7	6	75·3 −44·0 2·6	940	852	−88
13,7,1	—	—	—	—	−18·5	48	< 65	—
12,8,4	4	1·2184	−0·3	6	69·7	655	587	−68
13,7,3 11,9,5	2	1·2269	3·4	3	20·8 28·6	164	203	39
14,4,4 10,8,8	3	1·2293	0·4	1	81·5 −41·9	552	525	−27
14,6,0	—	—	—	—	−11·0	8	< 48	—
15,3,1	—	—	—	—	6·5	4	< 44	—
14,6,2 10,10,6	2	1·2507	0·6	0	16·6 30·2	92	72	−20
13,7,5	2	1·2689	−1·5	0	−55·6	375	234	−141
12,10,0 12,8,6	3	1·2716	−0·6	0	14·3 51·1	328	253	−75
14,6,4 12,10,2	3	1·2821	0·6	0	19·0 25·9	122	99	−23
15,5,1 13,9,1 11,9,7	3	1·2897	−0·8	0	34·9 −57·6 − 3·3	526	229	−297

electrons subtracted from the form factor for zinc at all angles to take account of the tight binding of K-shell electrons with Cu $K\alpha$ radiation changed significantly only the scale and temperature parameters.) The structure factors were calculated on the basis of one-eighth of a unit cell. Structure-factor derivatives were also calculated, and a least-squares treatment was carried out, giving $y = 0{\cdot}1797$, $z = 0{\cdot}1193$. However, an error was made in the application of the temperature factor, which resulted in incorrect weights; therefore the structure factors and their derivatives were recalculated on the basis of these parameters and a second least-squares treatment was carried out as described below.

Since many of the powder lines are incapable of resolution into their component reflections, a least-squares refinement with respect to the structure factors themselves is inappropriate. The refinement was therefore carried out with respect to quantities G^2, defined as follows:

$$G_i^2\,(\text{calc.}) = t_i^2 \sum_j m_j (F_j^{\text{calc.}})^2\,, \tag{4}$$

$$G_i^2\,(\text{obs.}) = I_i^{\text{obs.}}/kLP\,, \tag{5}$$

$$\Delta G_i^2 = G_i^2\,(\text{obs.}) - G_i^2\,(\text{calc.})\,, \tag{6}$$

where

$$t_i = \exp\left[-B\,(\sin\theta_i/\lambda)^2\right] \tag{7}$$

is the temperature factor, m_j is the multiplicity of the jth form present in the line, L and P are the Lorentz and polarization factors, and k is a scale factor. The observational equations were of the form

$$(\sqrt{w_i})\,\frac{\partial G_i^2\,(\text{calc.})}{\partial y}\,\Delta y + (\sqrt{w_i})\,\frac{\partial G_i^2\,(\text{calc.})}{\partial z}\,\Delta z = (\sqrt{w_i})\,\Delta G_i^2 \tag{8}$$

for each observed line i, where w_i is the weight of the measurement of intensity for line i and is defined as follows:

$$\left.\begin{aligned} w_i &= \frac{w_i''}{(G^2\,(\text{obs.}))^2}\,, \quad G_i^2\,(\text{obs.}) \geq 4G^2_{\text{min.}} \\ w_i &= \frac{w_i''}{4G_i^2\,(\text{obs.})\,G^2_{\text{min.}}}\,, \quad 4G^2_{\text{min.}} \geq G_i^2\,(\text{obs.}) \geq G^2_{\text{min.}} \end{aligned}\right\} \tag{9}$$

where $G^2_{\text{min.}}$ is the value of I/kLP for the weakest observable line in the neighborhood of the line in question and w'', like w', is an auxiliary weight depending as objectively as possible on physical characteristics of the line which affect the ease of estimating its intensity. For a normal line a value of 4 was assigned to w''. A line which was well resolved into its two components was given a w'' not of 8, but rather of 6 in consideration of the increased difficulty of estimating each component. Values of 1 or 2 were assigned to poorly resolved lines. The least-squares procedure and the procedure of assigning weights are similar to those of Hughes (1941), except that in the weighting procedure of Hughes equations (9) would contain the number 16 rather than the number 4.

The temperature-factor parameter B and the scale factor k were determined by a least-squares procedure, with observational equations set up in logarithmic form and with weights obtained from those in equation (9) by multiplying by $(G_i^2\,(\text{obs.}))^2$. Since a semi-logarithmic plot of $G_i^2\,(\text{obs.})/G_i^2\,(\text{calc.})$ against B showed a pronounced deviation from linearity for the last five lines, these lines were omitted from the subsequent treatments. They were much broader than the others, and apparently their intensities were underestimated. The temperature-factor parameter B was found by this treatment to have the value 1·47 Å^2.

Fifty-two observational equations were set up and reduced in the usual way to two normal equations, which were solved for Δy and Δz. The resulting final values of the positional parameters y and z are

$$\begin{aligned} y &= 0{\cdot}18063 \pm 0{\cdot}00025\,, \\ z &= 0{\cdot}11924 \pm 0{\cdot}00028\,. \end{aligned}$$

The uncertainties are standard deviations, calculated in the appropriate manner (Whittaker & Robinson, 1937).

The values of $G_i^2\,(\text{calc.})$, calculated with the final parameters, are given in Table 2, where they are compared with $G_i^2\,(\text{obs.})$. Considering that the intensities were estimated visually from photographs, the agreement is excellent. The conventional reliability factor R, as applied here to the G^2 rather than to structure factors, i.e.

$$R = \frac{\sum_i |\Delta G_i^2|}{\sum_i G_i^2\,(\text{obs.})}\,, \tag{10}$$

calculated for all observable lines except the last five, has a value of 0·108. This corresponds to a value of about 0·05 in the structure factors; the value of R calculated from the structure factors for the twenty-nine non-degenerate lines was found to be 0·050. The excellence of agreement is presumably due to two main causes: (1) the atoms in the crystals are nearly all of the same kind, so that form-factor errors can be largely compensated for by adjusting the temperature factor; and (2) the visual estimation of the integrated intensity of a line is probably capable of greater precision than the visual estimation of the integrated intensity of a spot obtained on a single-crystal photograph. In single-crystal work, with visual estimation of intensities, R as calculated from the structure factors is seldom less than 0·10 or 0·12.

The distances between adjacent atoms are given in Table 3. The functional dependence of the distance on the two parameters was taken properly into account in calculating the standard deviations of these distances.

Table 3. *Bond distances in* $NaZn_{13}$

Bond to atom	Number of bonds	D (Å)	σ (Å)
A. Bonds involving Zn_{I} $(0, 0, 0)$			
Zn_{II} $(0, y, z)$	12	2·659	0·003
B. Bonds involving Zn_{II} $(0, y, z)$			
Zn_{II} $(0, z, \frac{1}{2}-y)$	2	2·571	0·004
Zn_{I} $(0, 0, 0)$	1	2·659	0·003
Zn_{II} $(z, \frac{1}{2}-y, 0)$	2	2·682	0·006
Zn_{II} $(z, 0, y)$	4	2·764	0·003
Zn_{II} $(0, y, \bar{z})$	1	2·929	0·007
Na $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$	2	3·569	0·002
C. Bonds involving Na $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$			
Zn_{II} $(0, y, z)$	24	3·569	0·002

Discussion of the structure

Part of the structure, showing the environments of the Na and Zn_{I} atoms, is shown in Fig. 1, and the environment of a $\mathrm{Zn_{II}}$ atom is shown in Fig. 3. The Na and $\mathrm{Zn_{I}}$ atoms, taken by themselves, are in the cesium chloride arrangement. They are surrounded by $\mathrm{Zn_{II}}$ atoms, which form nearly regular snub cubes around the Na atoms and nearly regular icosahedra around the $\mathrm{Zn_{I}}$ atoms. Each icosahedron is surrounded cubically by, and shares triangular faces with, eight snub cubes, four of which (tetrahedrally arranged about the icosahedron) are right-handed and four (in the opposite tetrahedron) are left-handed. Each snub cube shares triangular faces with eight icosahedra, which are all identical but which alternate in orientation. Between each pair of adjacent icosahedra there is a tetrahedron of $\mathrm{Zn_{II}}$ atoms, which shares an edge with each of the two icosahedra. Each right-handed snub cube is surrounded octahedrally by six left-handed snub cubes, with which it shares square faces.

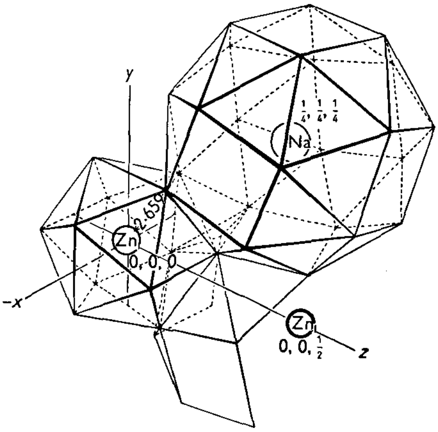

Fig. 1. Drawing of part of the $\mathrm{NaZn_{13}}$ structure, showing the environment of atoms $\mathrm{Zn_{I}}$ and Na, and showing the $\mathrm{Zn_{I}}$–$\mathrm{Zn_{II}}$ distance.

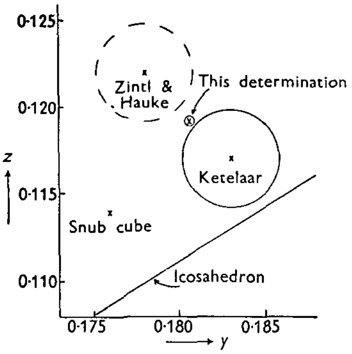

Fig. 2. Parameter plot for $\mathrm{NaZn_{13}}$, showing the line corresponding to a regular icosahedron, the point corresponding to a 'regular' snub cube, and the parameters actually obtained in the previous and present investigations.

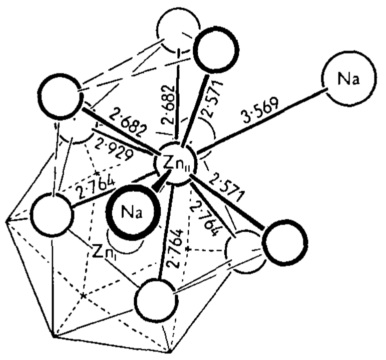

Fig. 3. The environment of $\mathrm{Zn_{II}}$, with interatomic distances. For the $\mathrm{Zn_{I}}$–$\mathrm{Zn_{II}}$ distance, see Fig. 1.

For a regular icosahedron y and z are constrained by the relation

$$y = \tfrac{1}{2}(1+\sqrt{5})z = 1{\cdot}618z\,. \qquad (11)$$

A regular snub cube (i.e. one with all edges equal) requires the unique values

$$y = 0{\cdot}1761,\ z = 0{\cdot}1141\,, \qquad (12)$$

obtained by solution of the equations

$$z = \frac{\frac{1}{4}-y}{1-2y} = y-2y^2\,, \qquad (13)$$

which are incompatible with the condition (11) for a regular icosahedron. Hence there exists no set of parameters y and z for which both the icosahedron and the snub cube are regular. For general values of y and z each icosahedron has edges of two different lengths, six of which, of one length, are bisected by twofold axes of the structure, while the remaining twenty-four, of the other length, bound the eight triangular faces which are shared with snub cubes; each snub cube has edges of three different lengths, twenty-four of one length bounding the six square faces, twenty-four of another length bounding the eight triangular faces shared with the icosahedra, and twelve of the third length.

In Fig. 2 conditions (11) and (12) are plotted on a parameter map together with the parameter values reported for $\mathrm{NaZn_{13}}$ by Zintl & Hauke, those reported for $\mathrm{KCd_{13}}$ by Ketelaar, and those determined for $\mathrm{NaZn_{13}}$ in the present investigation. The uncertainties are indicated by the radii of circles drawn around the points determined by the parameter values; since Zintl & Hauke reported no uncertainty value, the uncertainty reported by Ketelaar (0·003) was assumed. It is seen that the parameter values obtained in the present work lie between those of Zintl & Hauke and those of Ketelaar, and that they differ considerably from the values required either by a regular icosahedron or by a regular snub cube.

With the parameters found in the present investigation, the distance from $\mathrm{Zn_{I}}$ to each of the twelve $\mathrm{Zn_{II}}$ around it is 2·659 Å. This value is very close to the value 2·660 Å found for the six shorter ligates around a given zinc atom in the elementary metal. It has been assumed (Pauling, 1949) that these six ligates represent half-bonds, and that the six longer ligates (2·907 Å) represent one-sixth bonds, the valence of zinc in the element thus being 4·0. It would therefore seem reasonable to assume that in $NaZn_{13}$ the Zn_I–Zn_{II} bonds are half-bonds and that accordingly the valence of Zn_I is 6·0. The single-bond radius that has been assumed for sexivalent zinc, however, is 1·176 Å, which is considerably shorter than the value assumed for quadrivalent zinc, 1·229 Å, in consequence of a larger amount of *d* character of the bond orbitals. This shorter radius is not consistent with the bond number one-half, which is necessary for a valence of six for Zn_I. It is instead found by trial that the interatomic distances are compatible with the valence 5 for Zn_I and 4 for Zn_{II}. The values for the single-bond radius for zinc atoms with valence 5 and 4 are 1·202 and 1·229 Å, respectively (Pauling, 1949). Values of the bond numbers *n* calculated from the observed interatomic distances by means of the equation

$$R(n) = R(1) - 0{\cdot}600 \log n \qquad (14)$$

are 0·649 for the Zn_{II}–Zn_{II} bonds with length 2·571 Å (2), 0·424 for 2·682 Å (2), 0·309 for 2·764 Å (4), and 0·164 for 2·929 Å (1), and also 0·417 for the Zn_I–Zn_{II} bonds, which have length 2·659 Å, and 0·053 for the Zn_{II}–Na bonds, with length 3·569 Å. The twelve bonds with bond numbers 0·417 lead to the valence 5·00 for Zn_I, exactly the value assumed. The sum of the bond numbers for the twelve bonds formed by the Zn_{II} atom is 4·07, satisfactorily close to the assumed value 4·00. The valence obtained for sodium, 24 × 0·053. is 1·27. The excess over unity may be only apparent, and indicate a small compression of the bonds, or it may be real, and due to electron transfer (Pauling, 1950).

Hence, the interatomic distances indicate that the Zn_{II} atoms are quadrivalent and the Zn_I atoms are quinquevalent (corresponding to equal resonance between the quadrivalent electron configuration and the sexivalent configuration). The increase in single-bond radius from Zn_I to Zn_{II} combines with the decrease in bond number from the Zn_I–Zn_{II} bonds to the Zn_{II}–Zn_{II} bonds that mark the edges of the icosahedron to produce the characteristic 5% difference in length between the radius and the edges of the regular icosahedron.

The brittleness of these intermetallic compounds suggests an electronic structure involving a filled Brillouin zone. It was pointed out by Ketelaar (1937) that the strongest reflection, that of form 531, corresponds to a Brillouin polyhedron for which the inscribed sphere has a volume of 217 electrons per unit cube, which agrees well with the value 216 calculated on the assumption that the sodium atom is univalent and the zinc atoms are bivalent; that is, calculated in the usual Hume-Rothery way. It has also been shown (Pauling & Ewing, 1948) that the number of valence electrons per unit cell obtained by summing the new metallic valences often agrees strikingly well with the number of electrons required to fill completely a Brillouin polyhedron corresponding to some set of forms with large structure factors; good agreement was found for the γ alloys, β manganese, α manganese, and other structures.

For $NaZn_{13}$ the polyhedron 531 corresponds to electron number 238·2. When truncated by 600 and 442, which are also strongly reflecting forms, the electron number becomes 224·38, slightly larger than the volume of the inscribed sphere and the electron number given by the ordinary valences for $NaZn_{13}$, 216, but in good agreement with that for $CaZn_{13}$, 224. The next form giving very strong reflections is 800. It is truncated by several other forms that reflect strongly, of which 444 is the most important. The polyhedron formed by 800, 444, and 640 has an electron number of 428·48. The only other moderately strongly reflecting form in this region is 642, which has, however, only a very slightly truncating action, which would reduce the electron number to 428·02. Both of these polyhedra are satisfactory, in that the ratio of maximum radius to minimum radius is close to unity, being only 1·17; the polyhedron accordingly does not deviate greatly from sphericity. The value 428 for the electron number given by the Brillouin polyhedron is close to that corresponding to the valences reported above; the sum of the valences, assuming 5 for Zn_I, 4 for Zn_{II}, and 1 for Na, is 432. Exact filling of the zone would be obtained by taking the valence of Zn_{II} as 3·94, instead of 4·00.

Potassium compounds

Measurements of our powder photographs of KZn_{13} and KCd_{13} gave $a_0 = 12{\cdot}360$ Å for the former and $a_0 = 13{\cdot}803$ Å for the latter, in both cases without least-squares refinement, and with a standard deviation of about 0·005 Å. These values are in good agreement with those previously reported by Zintl & Hauke and by Ketelaar. The lattice constant for KZn_{13} is only 0·6% larger than that for $NaZn_{13}$, while that for KCd_{13} is about 12% larger than those for the two zinc compounds. The ratio of the lattice constants for KCd_{13} and KZn_{13} is in fact 1·117, which is very close to the ratio, 1·119, of the atomic radii of cadmium and zinc for coordination 12. Hence it appears that if the *y* and *z* parameters for KCd_{13} and KZn_{13} are the same as for $NaZn_{13}$, as is probably true to a close approximation, the situation regarding bonding and valency is essentially the same for the cadmium atoms in KCd_{13} and for the zinc atoms in KZn_{13} as it is for the zinc atoms in $NaZn_{13}$.

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The Crystal Structure of the Metallic Phase Mg_{32} (Al, Zn)$_{49}$*

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A complete determination of the crystal structure of the ternary phase (λ or T phase) in the magnesium–aluminum–zinc system with composition approximately $Mg_3Zn_3Al_2$ has been carried out with use of intensity data from single-crystal Weissenberg photographs. The refinement of the structural parameters was carried out by use of Fourier projections, followed by application of the method of least squares. The unit of structure, based on the body-centered cubic lattice, has $a_0 = 14{\cdot}16$ Å, as previously reported by Laves, Löhberg & Witte. The space group is T_h^5, with 162 atoms per unit cube. The structure shows the correct formula to be $Mg_{32}(Al, Zn)_{49}$; there is some disorder in occupancy of positions by aluminum and zinc atoms. The icosahedron and truncated tetrahedron are prominent coordination polyhedra in this structure.

Introduction

Phase diagram studies of the magnesium–aluminum–zinc system have shown that there exists a ternary phase, which has been given the name λ phase or T phase (Egar, 1913; Köster & Wolf, 1936; Köster & Dullenkopf, 1936; Riederer, 1936; Fink & Willey, 1937; Little, Raynor & Hume-Rothery, 1943). The approximate composition $Mg_3Zn_3Al_2$ was assigned to the phase, which extends over a wide range of values of the Zn/Al ratio. The atomic percentage of magnesium is nearly constant for the alloys, as would be expected from the fact that the metallic radius of magnesium is about 15% greater than those of aluminum and zinc.

Laves, Löhberg & Witte (1935) made an X-ray

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study of the phase, and reported that the structure is based on a body-centered cubic lattice with $a_0 = 14{\cdot}16 \pm 0{\cdot}03$ Å, the calculated number of atoms per unit cell being 161. They also found that the ternary phase with approximate composition Mg_4CuAl_6 described by Vogel (1919) has almost certainly the same structure; the value of a_0 for this phase was found to be $14{\cdot}25 \pm 0{\cdot}03$ Å, with 161 atoms per unit cube. Strawbridge, Hume-Rothery & Little (1947) reported the existence of a quaternary magnesium–aluminum–zinc–copper phase, including these two ternary regions. We have made an X-ray study of a representative crystal, containing magnesium, zinc, and aluminum, which has led to a complete structure determination. Brief accounts of the structure have been published (Bergman, Waugh & Pauling, 1952; Pauling, 1955). In the present paper the results of a refinement of the parameter values are communicated, together with a detailed discussion of the structure.

Experimental methods

Crystals of the phase were made by melting the pure metals in proportions corresponding to the composition $Mg_3Zn_3Al_2$ in a sealed quartz tube, mixing the melt by vigorous shaking, and then allowing it to solidify by slow cooling (about 10° C. per hour). The appearance of the quartz tube after the pellet had been removed indicated that there had been some reaction between the quartz and the melt; chemical analysis showed, however, that the crystals of the metallic phase did not contain more than 0·1 atomic % of silicon. A complete analysis gave the following result:

Mg, 22·1%; Zn, 60·8%; Al, 17·0%; Si, < 0·1% .

This composition is very nearly the composition $Mg_3Zn_3Al_2$.

Laue photographs of isolated single crystals about 0·1 mm. in diameter were found to have Laue symmetry T_h. Rotation and Weissenberg photographs verified the value of a_0 quoted by Laves *et al.* (1935). Visual estimates of intensities of reflections for planes *hk*0 were obtained from Weissenberg photographs (copper $K\alpha$ radiation) with use of the multiple-film techniques of Lange, Robertson & Woodward (1939) and Robertson (1943). Estimates of intensities of some general reflections *hkl* were also made. Powder photographs did not indicate the presence of a second phase.

Determination of the structure

No systematic extinctions were found in addition to those characteristic of body-centering. The only space groups with Laue symmetry T_h allowed by this observation are T_h^5, T^3, and T^5. No non-systematic absences were recorded.

A structure based upon space group T_h^5 has been derived by use of the stochastic method. The assumption was made that, in this crystal, as in a number of other metallic crystals containing atoms with metallic radii differing by about 15%—for example, those with composition A_2B_{11}:Mg_2Zn_{11} and $Mg_2Cu_6Al_5$ (Samson, 1949) and Na_2Cd_{11} (Pauling & Ewing)—the structure is based upon the ligation around many of the atoms of twelve atoms at the corners of an approximately regular icosahedron. It is characteristic of the icosahedron that groups of four contiguous atoms occur only at corners of a tetrahedron; every triangle formed by three contiguous atoms in the icosahedron has a fourth atom lying approximately above its center. Accordingly, a structure involving icosahedral packing may be built up by placing atoms out from the centers of the triangular faces of an inner poly-

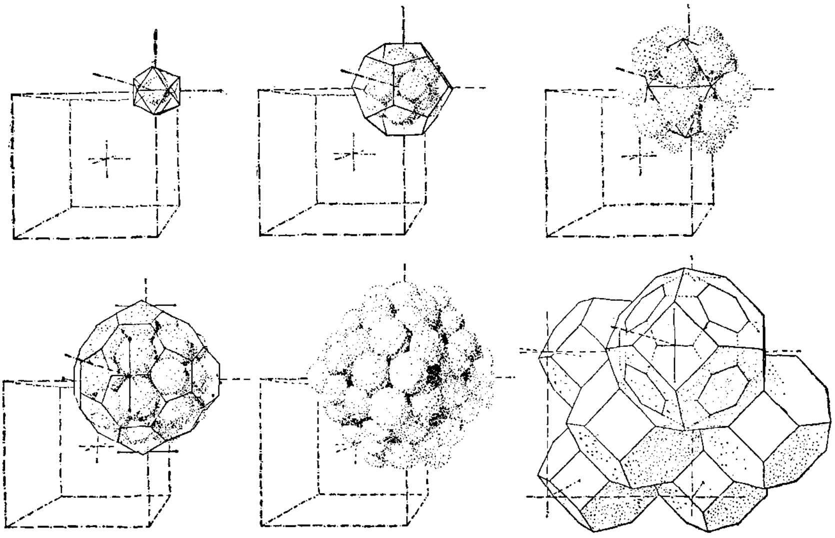

Fig. 1. The successive shells of atoms about the point (0, 0, 0) and the sharing of the outermost atoms between neighboring groups.

hedron. The metrical nature of the icosahedron is such that the distances from the atom at the center of an icosahedron to its twelve ligands is 5% smaller than the distances between these ligands; accordingly, the retention of icosahedral packing through successive ligation spheres requires a continued steady increase in average size of the atoms in these spheres. This increase in size can be achieved, for four spheres, by the use of the smaller atoms, zinc and aluminum, in the inner spheres, and the introduction of the larger magnesium atoms in the outer spheres.

The application of these arguments in the derivation of the structure for the phase $Mg_{32}(Zn, Al)_{49}$ proceeds as follows. In the first two drawings (upper left) of Fig. 1 there is shown a central atom with an icosahedral sphere of twelve atoms surrounding it. As shown in the next two drawings, twenty atoms may then be placed out from the centers of the twenty triangular faces of the icosahedron, forming a pentagonal dodecahedron, and twelve more out from the centers of the pentagonal faces of the dodecahedron. These thirty-two atoms constitute the third sphere of the aggregate; they lie at the corners of a rhombic triacontahedron. Sixty atoms, at the corners of a truncated icosahedron, may then be placed out from the centers of the sixty triangular half-rhombs of the triacontahedron, and by introducing twelve more atoms, as shown in the fifth and sixth drawings of Fig. 1, an outer sphere of seventy-two atoms lying on the faces of a cubooctahedron is obtained. Because of the property of cubooctahedra of packing together in a body-centered lattice, these complexes can be packed together in this way by sharing all of the seventy-two atoms of the outer shell with similar complexes. The resulting structure has seventy-two atoms, each of which serves as the outer shell of two adjacent complexes, and two inner groups of forty-five atoms each, about the positions 0, 0, 0 and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, giving a total of 162 atoms in the unit cube.

In this structure, 98 of the atoms have ligancy twelve (icosahedral coordination) and of the remaining 64 atoms 40 have ligancy sixteen, 12 have ligancy fifteen and 12 have ligancy fourteen. It is reasonable to assume the 98 icosahedral atoms to be either zinc or aluminum, and the others to be magnesium atoms. This assignment corresponds to the composition $Mg_{32}(Al, Zn)_{49}$, which is in reasonable agreement with $Mg_3Zn_3Al_2$.

Approximate atomic coordinates were obtained by assuming the effective metallic radius of magnesium to be about 1·60 Å and the radii of aluminum and zinc to be about 1·40 Å. The corresponding calculated structure factors were in fairly good agreement with those obtained from the observed intensities. The preliminary atomic coordinates are given in Table 1.

A set of improved atomic parameters was obtained from three successive Fourier projections on the *xy* plane, the first based on 34, the second on 56, and the third on 98 of the 126 observed *hk*0 reflections. From the heights of the peaks it was concluded that all or nearly all of the atoms in the position *B* are zinc atoms and that those in positions *C* and *F* are about 50% zinc atoms and 50% aluminum atoms. The peaks corresponding to the atoms in positions *A* were smaller than could be expected even for aluminum and were too small to appear on the third Fourier projection shown in Fig. 2.

Table 1. *Preliminary and final structural parameters*

Type of atom	Position		Positional parameters		Kind of atom
			Preliminary	Final	
A	2: (*a*)		—	—	(80%) Al or ≈ 30% Zn
B	24: (*g*)	*y* =	0·11	0·0908	81% Zn
		z =	0·16	0·1501	19% Al
C	24: (*g*)	*y* =	0·19	0·1748	57% Zn
		z =	0·32	0·3007	43% Al
D	16: (*f*)	*x* =	0·19	0·1836	Mg
E	24: (*g*)	*y* =	0·32	0·2942	Mg
		z =	0·13	0·1194	
F	48: (*h*)	*x* =	0·16	0·1680	64% Zn
		y =	0·18	0·1860	36% Al
		z =	0·41	0·4031	
G	12: (*e*)	*x* =	0·40	0·4002	Mg
H	12: (*e*)	*x* =	0·20	0·1797	Mg

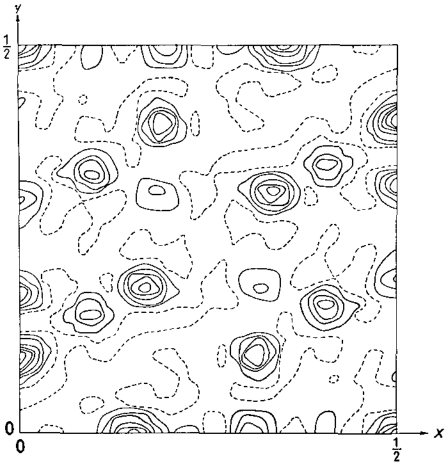

Fig. 2. The third Fourier projection on the *xy* plane. Contours at equal, arbitrary intervals.

The parameters were then further refined by four successive least-squares procedures, as described by Hughes (1941). Only *hk*0 data were used. The form factor for zinc was taken to be 2·4 times the average of the form factors for magnesium and aluminum. The values of the form factor for zinc used in making the average was corrected for the anomalous dispersion expected for copper *Kα* radiation. The customary Lorentz, polarization, temperature, and absorption factors were used. A preliminary combined scale, temperature, and absorption factor was evaluated graph-

Table 2. *Calculated and observed structure factors*

hkl	F_c	F_o	*hkl*	F_c	F_o	*hkl*	F_c	F_o	*hkl*	F_c	F_o
000	3143	—	910	−40	41	7,11,0	260	250	2,16,0	−96	120
110	185	125	390	110	78	11,7,0	−20	92	16,2,0	50	45
200	−60	22	930	67	62	3,13,0	38	52	8,14,0	53	56
220	−78	86	770	80	55	13,3,0	−39	87	14,8,0	85	37
130	−34	94	10,0,0	562	490	6,12,0	73	89	4,16,0	−37	33
310	181	180	680	−150	190	12,6,0	156	170	16,4,0	−11	36
400	−140	170	860	36	38	5,13,0	−46	43	7,15,0	−44	66
330	−98	115	2,10,0	−175	180	13,5,0	−69	65	15,7,0	−32	35
240	−104	120	10,2,0	−12	49	14,0,0	−66	43	12,12,0	91	93
420	74	75	590	−378	300	10,10,0	64	68	11,13,0	−33	54
150	−36	33	950	−352	300	2,14,0	21	55	13,11,0	111	135
510	−108	110	4,10,0	87	150	14,2,0	107	73	1,17,0	−1	19
440	−82	67	10,4,0	−199	210	9,11,0	−52	51	17,1,0	29	19
350	−682	550	11,1,0	−84	170	11,9,0	−124	140	6,16,0	97	45
530	−369	320	1,11,0	75	125	8,12,0	56	58	16,6,0	−105	125
600	800	590	880	54	49	12,8,0	−183	180	10,14,0	−29	27
260	28	27	3,11,0	−73	63	4,14,0	−27	70	14,10,0	18	75
620	24	37	11,3,0	−120	120	14,4,0	60	62	3,17,0	−97	93
170	43	61	790	83	70	7,13,0	47	47	17,3,0	−35	34
710	408	380	970	−117	97	13,7,0	22	48	9,15,0	−52	81
550	178	68	6,10,0	509	510	1,15,0	16	46	15,9,0	−53	48
460	−355	350	10,6,0	111	91	15,1,0	−10	46	5,17,0	70	28
640	128	135	12,0,0	416	360	6,14,0	−80	130	17,5,0	27	28
370	−156	165	5,11,0	133	69	14,6,0	−27	47	8,16,0	−28	20
730	8	95	11,5,0	−40	125	3,15,0	−156	180	16,8,0	1	20
800	−119	110	2,12,0	78	66	15,3,0	−44	47			
280	−51	48	12,2,0	−178	145	11,11,0	−44	83	435	539	*vs*
820	101	45	4,12,0	−53	84	10,12,0	157	155	666	−464	*vs*
660	22	46	12,4,0	−96	95	12,10,0	81	81	453	380	*vs*
570	−84	66	990	74	60	5,15,0	−123	140	1,12,1	−21	Abs.
750	20	46	8,10,0	−90	80	15,5,0	−49	53	341	5	Abs.
480	−1	57	10,8,0	−11	42	9,13,0	28	40	2,16,2	9	Abs.
840	94	85	1,13,0	24	46	13,9,0	51	63	233	24	Abs.
190	−33	63	13,1,0	203	200	16,0,0	71	68	455	18	Abs.
									11,5,6	3	Abs.

ically by plotting log (I_o/F_c^2) against $\sin^2\theta$. The two parameters determining this factor were introduced in the least-squares refinement together with the twelve positional parameters and the four compositional parameters, these four parameters expressing the fraction of zinc atoms in the positions A, B, C, and F. The F_o values with weights proportional to F_o^{-2} were taken as observational quantities, and the normal equations were solved by application of the method described by Crout (1941). All the reflections were used in the final refinement; there were no accidentally absent reflections.

The reliability factor R was 0·276 after the first refinement and 0·211 after the fourth refinement. The parameters from the third and fourth refinements differed very little from one another. The final values are given in Table 1. As large systematic errors were introduced in the refinement process by the unavoidable use of very poor atomic form factors, the probable errors in the parameters as obtained in the refinement were considered to be of questionable significance. For this reason they are not given in the table. The average error was, however, estimated to be 0·001 for the positional parameters and 5% for the compositional parameters. The scattering power of the two atoms of type A was given by the least-squares refinement as only 0·8 times that of aluminum (the fraction zinc in positions A was −14%). The significance of this result is discussed below. Atoms of type B are indicated to be about 80% zinc and 20% aluminum, and those of types C and D about 60% zinc and 40% aluminum.

The observed and calculated values of F for prism planes are given in Table 2.

Discussion of the structure

In this structure there are two predominant coordination polyhedra: all of the 98 zinc and aluminum atoms in the unit cell have icosahedral coordination, and 40 of the 64 magnesium atoms have a coordination polyhedron with sixteen corners and twenty-eight triangular faces, which was first observed for the magnesium atoms in the Friauf phase $MgCu_2$ (Friauf, 1927). Twelve of the remaining twenty-four magnesium atoms (H) have ligancy 15, the coordination polyhedron being bounded by twenty-six triangular faces, and the other twelve (G) have ligancy fourteen, the polyhedron being bounded by twenty-four triangular faces. All four of the polyhedra are shown in Fig. 3 in the sequence in which they were discussed above.

Interatomic distances are given in Table 3. There are some very short (Zn, Al)–(Zn, Al) distances in the structure: A–B = 2·484 and B–C = 2·442 Å. These

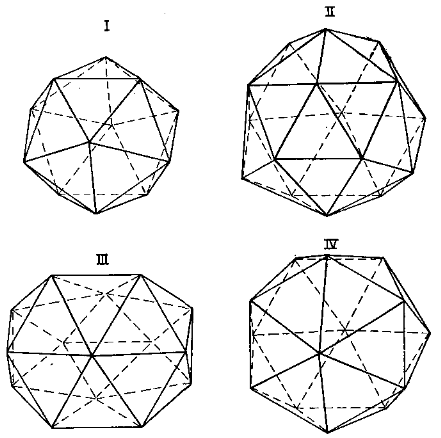

Fig. 3. The four different coordination polyhedra in the Mg_{32}(Al, Zn)$_{49}$ structure.

Table 3. *Interatomic distances*

(All values in Ångström units)

A–B	12	2·484	*F–C*	1	2·791
			F–C	1	2·624
B–A	1	2·484	*F–D*	1	3·116
B–B	4	2·622	*F–D*	1	3·055
B–B	1	2·571	*F–E*	1	3·132
B–C	1	2·442	*F–E*	1	3·123
B–D	2	3·274	*F–F*	2	2·621
B–E	1	2·908	*F–F*	1	2·747
B–E	2	2·945	*F–G*	1	3·005
	12		*F–H*	1	3·344
			F–H	1	2·974
C–B	1	2·442		12	
C–D	2	3·326			
C–E	1	3·074	*G–C*	2	3·016
C–E	2	2·992	*G–E*	4	3·652
C–F	2	2·791	*G–F*	4	3·005
C–F	2	2·624	*G–G*	1	2·832
C–G	1	3·016	*G–H*	2	2·911
C–H	1	3·494	*G–H*	1	3·122
	12			14	
D–B	3	3·274	*H–C*	2	3·494
D–C	3	3·326	*H–E*	2	2·927
D–D	1	3·257	*H–F*	4	3·344
D–E	3	3·168	*H–F*	4	2·974
D–F	3	3·116	*H–G*	2	2·911
D–F	3	3·055	*H–G*	1	3·122
	16			15	
E–B	1	2·908			
E–B	2	2·945			
E–C	1	3·074			
E–C	2	2·992			
E–D	2	3·168			
E–E	1	3·381			
E–F	2	3·132			
E–F	2	3·123			
E–G	2	3·652			
E–H	1	2·927			
	16				

short distances appear less remarkable in view of the fact that some evidence was obtained for only partial occupancy of the positions *A*. Both the last Fourier projection and the last least-squares refinement provided such evidence. In case of partial occupancy the *A–B* distance can be expected to be shortened considerably. If the assumption of partial occupancy is not correct it is likely that these bonds are under compressional strain, and that the bond numbers obtained by application of the equation $R_n = R_1 - 0{\cdot}300 \log_{10} n$ are larger than the true values. Moreover, it is likely that some transfer of valence electrons from the zinc atoms to atoms of magnesium and aluminum has taken place (Pauling, 1950). Values of effective valences of seven of the eight crystallographically different kinds of atoms have been calculated by use of assumed radii for magnesium and zinc/aluminum atoms. The value 1·214 Å for the single bond radius may be used for the zinc/aluminum atoms *B*, *C*, and *F*, and the value 1·335 Å for magnesium, which may be assumed to have accepted one half an electron, increasing its valency to 2·5. The values of the valences obtained in this way are 4·87 for *B*, 2·17 for *C*, and 2·80 for *F* (these being zinc/aluminum atoms); and 1·95 for *D*, 2·44 for *E*, 2·35 for *G*, and 2·56 for *H* (these being magnesium atoms). Because of uncertainties in the argument, these values of the valences of the different kinds of atoms are not very reliable. The value of the effective valence of the atoms *A* was not calculated because of the definite possibility of partial occupancy. In case of partial occupancy a correction of the valence of atoms *B* as calculated above should be made.

The nature of the structure found for this phase, with strong indication that there are thirty-two magnesium atoms per lattice point, suggests that the quaternary phase should be assigned the general formula Mg_{32}(Al, Zn, Cu)$_{49}$.

Attempts to relate the stability of this phase to the filling of a Brillouin zone were not successful: no well-defined zone could be found.

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*A TRIRETICULATE CRYSTAL STRUCTURE: TRIHYDROGEN COBALTICYANIDE AND TRISILVER COBALTICYANIDE**

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Many reticulate (framework) crystal structures are known, in which the atoms are attached to one another by essentially covalent bonds to form a three-dimensional framework. A simple example is diamond; a more complex example is Prussian blue, $KFeFe(CN)_6 \cdot H_2O$, in which iron atoms at the lattice points of a simple cubic lattice are joined together by cyanide groups extending along the edges of the cubes, with the potassium ions and water molecules occupying alternate positions in the centers of the cubes.[1] Cuprous oxide, Cu_2O, and argentous oxide, Ag_2O, have a bireticulate structure. Each copper or silver atom forms covalent bonds, at 180° with one another, to two oxygen atoms, and each oxygen atom is bonded to four copper or silver atoms that surround it tetrahedrally, to form a tetrahedral framework like that of diamond; there are, however, two interpenetrating frameworks, not bonded to one another, each of which occupies the interstices of the other. We have now found that trihydrogen cobalticyanide (trihydrogen cobalt(III) hexacyanide, $H_3Co(CN)_6$) and trisilver cobalticyanide (trisilver cobalt(III) hexacyanide, $Ag_3Co(CN)_6$) have a structure in which the atoms are bonded together to form three interpenetrating frameworks.

Crystals of these two substances have been described by Ludi, Güdel, and Dvorak[2] as hexagonal with $a = 6.431 \pm 0.004$ Å and $c = 5.695 \pm 0.004$ Å for the acid and $a = 7.030 \pm 0.009$ Å and $c = 7.127 \pm 0.004$ Å for the silver salt. The hexagonal unit of structure of each contains one formula. The authors report the spacings and observed intensities for 25 X-ray powder diffraction lines for each substance. They suggest a structure in which there are octahedral cobalticyanide groups at each point of the hexagonal lattice, with each group bonded to the group directly above and below it along the hexagonal axis by hydrogen bonds between the nitrogen atoms or by silver atoms midway between the nitrogen atoms. These structures, which were not supported by a comparison of calculated and observed intensities of the X-ray diffraction maxima, are, however, stereochemically unreasonable. Because of the large amount of triple-bond character of the carbon-nitrogen bond in cyanides, as shown by the carbon-nitrogen distance 1.15 Å, a single bond formed by the nitrogen atom would be expected to make an angle of 180° with the carbon-nitrogen axis, as in the Prussian-blue structure. With the hydrogen atoms and silver atoms located in the positions assigned to them by Ludi *et al.*, the corresponding angle is 100° for trihydrogen cobalticyanide and 120° for the silver salt. In addition, the nitrogen-hydrogen-nitrogen distance corresponding to their structure (given by them as 3.23 Å) is much larger than would be expected by comparison with tetrahydrogen ferrocyanide,[3] in which the corresponding distances have the values 2.68 and 2.88 Å.

TABLE 1. *Observed and calculated structure factors for* $Ag_3Co(CN)_6$.

$HK\cdot L$	$\lvert F\rvert$ obs.	$\lvert F\rvert$ calc.	$HK\cdot L$	$\lvert F\rvert$ obs.	$\lvert F\rvert$ calc.
001	96	98	300	Abs.	5
100	(<60)*	10	113	124	111†
101	70	71	301	(72)	51
002	(98)	106	203	106	77
110	(40)	35	004	(190)	125
111	65	76†	302	Abs.	34
102	(34)	21	220	(110)	96
200	116	135	104	Abs.	21
201	89	96	221	(83)	83†
112	(<33)	8†	310	Abs.	16
003	(148)	105	213	74	55
202	113	128	311	(43)	49
210	Abs.	24	222	124	123
103	(63)	45	204	126	110
211	56	49†	400	(90)	115

* Values of $|F|$ obs. in parentheses are obtained from reported powder-line intensities <1, 1, or 2, and are accordingly less reliable than the others, with reported intensities 3, 4, . . ., 10.

† Values marked with a dagger are the root-mean-square values for $HK\cdot L$ and $HK\cdot\bar{L}$.

We have found that the observed X-ray intensities for trisilver cobalticyanide are incompatible with the structure suggested by Ludi *et al.*, and correspond instead to a structure in which each cobalticyanide group is connected through covalently bonded silver atoms to cobalticyanide groups that are related to it by translation by the amount $a + c$, rather than by c.

Derivation of the Structure.—The observed intensities reported by Ludi *et al.* for the silver salt have been converted to F-values by dividing by the multiplicity of the form or pair of forms and the Lorentz and polarization factors (Table 1). With these F-values we have calculated the section $z = 0$ of the Patterson function. Maxima are found at the positions $^1/_2\,0$, $0\,^1/_2$, and $^1/_2\,^1/_2$. These maxima represent the silver-silver vectors, and require that silver atoms lie at or near the positions $^1/_2\,0\,z$, $0\,^1/_2\,z$, $^1/_2\,^1/_2\,z$. The section $z = {}^1/_2$ of the Patterson function also shows pronounced maxima at $^1/_2\,0$, $0\,^1/_2$, and $^1/_2\,^1/_2$, with no maximum in the neighborhood of $^1/_6\,^1/_3$. These maxima are to be attributed to the silver-cobalt vectors, and they require that the cobalt atom lie at the position 0 0 0, if z for the silver atoms is assigned the value $^1/_2$. Thus the Patterson section for $z = {}^1/_2$ eliminates the structure proposed by Ludi *et al.*

With the location of cobalt and silver atoms within the unit of structure found in this way, a reasonable structure for the crystal can be based on the space group $D_{3d}{}^1$-$C\bar{3}m$, as follows: Co,$(a)000$; 3Ag,$(g)\,^1/_2\,0\,^1/_2, 0\,^1/_2\,^1/_2, ^1/_2\,^1/_2\,^1/_2$; 6C,$(k)x0z$, $0xz, \bar{x}\bar{x}z, \bar{x}0z$, $0\bar{x}z, xxz$; 6N, the same set of positions with different values of the parameters x and z.

Because the observed intensities are not very accurate, we have made use of structural arguments to evaluate x and z for the carbon atoms and nitrogen atoms. In the crystal $K_3Co(CN)_6$, the hexacyanide group has the configuration of a regular octahedron, with the distances cobalt-carbon and cobalt-nitrogen equal to 1.89 ± 0.02 Å and 3.04 ± 0.02 Å, respectively.[4] The same values are found[3] for the iron-carbon and iron-nitrogen distances in $H_4Fe(CN)_6$. On the basis of arguments presented below, we have given the hexacyanide group a small prolate de-

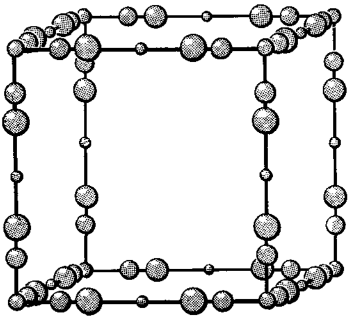

FIG. 1.

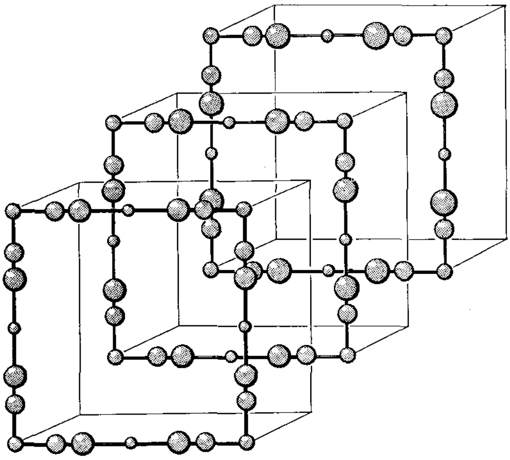

FIG. 2.

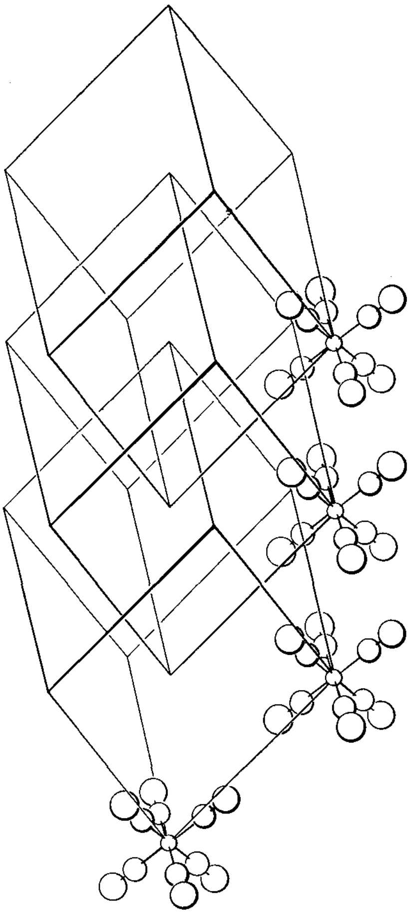

FIG. 3.

FIG. 1.—A simple cubic framework of trisilver cobalticyanide. The circles, in increasing size, represent silver, cobalt, carbon, and nitrogen, respectively.

FIG. 2.—Representation of three mutually interpenetrating cubic frameworks of trisilver cobalticyanide, each displaced to another by translation by one third along the body diagonal of the unit cube.

FIG. 3.—The structure of trisilver cobalticyanide. There are three mutually interpenetrating rhombohedral frameworks, distorted from the cubic frameworks of Fig. 2 in such a way as to achieve increased density and closer approximation to the optimal packing of the bulky cobalticyanide groups.

formation along the hexagonal axis, such that six of the NC-Co-CN angles have the value 88.5° and the other six the value 91.5°. The parameters for trisilver cobalticyanide are then $x_C = 0.216$, $z_C = 0.157$, $x_N = 0.348$, $z_N = 0.253$. The F-values calculated for these parameters with use of the atomic f-values given in the International Tables for the Determination of Crystal Structures are presented in Table 1. The agreement with the experimental values is satisfactory, to within the reliability of these values. The intensities of the powder lines were reported by Ludi *et al.* as $<1, 1, 2, \cdots, 10$. Uncertainties ± 0.5 in the reported intensities correspond to uncertainties in F ranging from 29 per cent for intensity 1 to 3 per cent for intensity 10. A small trend in the curve of average reported intensities with angle of diffraction has been corrected for by multiplying the structure factors by $0.70 + (\sin \theta)/2$.

Discussion of the Structure.—The structure found for trisilver cobalticyanide, shown in Figure 3, may be conveniently described by reference to the simpler structures shown in Figures 1 and 2. The simple cubic framework shown in Figure 1 is an ideal structure for a regular cobalticyanide octahedron, with the linear arrangement of the bonds at the silver atom and the bond angle 180° for nitrogen. With the bond lengths Co—C = 1.89 Å, C—N = 1.15 Å, and N—Ag = 2.06 Å, the edge of the unit cube has the value 10.2 Å, which is just that observed for Prussian blue. The structure of Prussian blue is obtained from that shown in Figure 1 by introducing three ferrocyanide groups, at $0\ ^1/_2\ ^1/_2$, $^1/_2\ 0\ ^1/_2$, and $^1/_2\ ^1/_2\ 0$, in addition to replacing the cobalticyanide group 0 0 0 by a ferrocyanide group. The iron atoms that replace the silver atoms, as well as the fourth iron atom, at $^1/_2\ ^1/_2\ ^1/_2$, have octahedral ligancy to six surrounding nitrogen atoms, so that the structure is a complete simple cubic framework with bonds along all edges of small cubes, 5.1 Å on edge. The centers of the eight small cubes in the 10.2-Å cube of Prussian blue are alternately occupied by potassium ions and water molecules. The volume of the Prussian blue crystal is 18.95 Å^3 per framework atom.

The very open framework of trisilver cobalticyanide shown in Figure 1 might be stabilized by introducing very large neutral molecules into the cubes, or by duplicating or triplicating the framework. The structure shown in Figure 2 represents three interpenetrating frameworks, the second and third being obtained from the first by translation by one third and two thirds of the distance, respectively, along one of the body diagonals of the cube. This structure has a volume of 22.1 Å^3 per atom, The packing is poor, in that each cobalticyanide group, which is roughly spherical in shape, would have two neighboring groups, above and below along the threefold axis, at 5.89 Å, and six others, in the equatorial plane, at 8.33 Å. The symmetry of the structure is no longer cubic, but is that of the space group $D_{3d}{}^1$-$\bar{3}m$. The crowding of the cobalticyanide groups in the direction of the threefold axis can be relieved by a prolate deformation of the unit of structure along the axis, as shown in Figure 3, which represents the actual structure of the substance. The edge of the rhombohedron is decreased from 10.20 to 10.01 Å by a bend of 22.5° from a straight angle at the nitrogen atoms. The principal diagonal of the rhombohedron is $3c = 21.05$ Å, which is 19 per cent greater than that for the undistorted cube. The distortion decreases the volume of the rhombohedron from 22.1 Å^3 per atom to 19.06 Å^3, nearly the same as for Prussian blue (18.95 Å^3). Each cobalticyanide group is surrounded by eight groups at nearly the same distance (two at c = 7.127 Å and six at a = 7.030 Å), as well as by the six (at 10.01 Å) to which it is bonded by the silver atoms.

Each silver atom is bonded to two nitrogen atoms at the distance 2.06 Å. With the single-bond radius of nitrogen taken at 0.70 Å, this bond length leads to 1.36 Å for the single-bond radius of bicovalent silver, in good agreement with the value for Ag_2O (Ag—O = 2.04 Å, radius of bicovalent silver atom 1.38 Å) and in $AgCl_2^-$ ion in $Cs_2AgAuCl_6$(Ag—Cl = 2.36 Å, radius of bicovalent silver atom 1.37 Å).

The structure of $H_3Co(CN)_6$ may be assumed to be the same as that of the silver salt, with hydrogen bonds replacing the N—Ag—N bonds between the cobalticyanide groups. If the cobalticyanide group in the acid is assumed to have the same prolate deformation as for the silver salt (N—Co—N bond angles 88.5° and 91.5°), and the same bond lengths, the parameters have the values x_C = 0.237, z_C = 0.197, x_N = 0.381, and z_N = 0.316. The angle Co—N···N is then 17.5° less than a straight angle, and the N—H···N hydrogen-bond length is found to be 2.60 Å. This is the shortest hydrogen bond between nitrogen atoms that has been found. A short hydrogen bond may be expected for such a strong acid as trihydrogen cobalticyanide. The N—H···N hydrogen-bond lengths in tetrahydrogen ferrocyanide[3] are 2.68 Å and 2.88 Å. These hydrogen bonds are expected to be somewhat weaker than those in trihydrogen cobalticyanide because one nitrogen atom acts as proton acceptor for two protons in the ferrocyanide, whereas each nitrogen atom serves as proton donor or proton acceptor for only one hydrogen bond in the cobalticyanide.

There is the possibility that these short hydrogen bonds in trihydrogen cobalticyanide are symmetrical. This possibility is, however, unlikely, because the N—H···N distance, 2.60 Å, is 0.22 Å larger than would be expected for symmetrical hydrogen bonds. The N—H single-bond length, 1.01 Å in ammonia, would be increased by 0.18 Å for a half-bond, leading to 2.38 Å as the expected nitrogen–nitrogen distance for a symmetrical hydrogen bond. There is the possibility that the energy curve for the proton has such a flat double minimum that the proton does not stay closer to one of the two nitrogen atoms than to the other, but resonates between the two positions. There is, however, also the possibility that one position is stabilized by proton-proton interactions in the crystal, and that the crystal should show strong ferroelectric properties along the hexagonal axis. The N—H···N directions make an angle of 36° with the hexagonal axis of the crystal.

Summary.—The crystals trisilver cobalticyanide and trihydrogen cobalticyanide have been shown to have a trireticulate structure, with nearly regular cobalticyanide octahedra connected by nitrogen-silver-nitrogen bonds or by hydrogen bonds between the nitrogen atoms.

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CRYSTALLOGRAPHY AND CHEMICAL BONDING OF SULFIDE MINERALS

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ABSTRACT

The sulfur atom in sulfide minerals may have an argononic structure, with the sum of the covalent bonds and unshared pairs equal to 4 (with use of four sp^3 orbitals), or a transargononic structure, with this sum greater than 4 (with use also of one or more $3d$ orbitals). Conclusions about the nature of the bonds and the structure of the sulfur atom can be drawn from the experimentally determined ligancies, bond lengths, and bond angles. A detailed discussion of realgar, orpiment, cinnabar, molybdenite, proustite, pyrargyrite, pyrostilpnite, sphalerite, wurtzite, greenockite, metacinnabarite, galena, baumhauerite, gratonite, binnite, covellite, sulvanite, mackinawite, pyrite, and marcasite leads to the conclusion that the principal structures of sulfur in these minerals are argononic with covalence 2, 3, or 4, and transargononic with covalence 4, 5, or 6. In some cases the structure is an argononic-transargononic hybrid. Fractional bonds (ligancy greater than covalence) are found in some minerals, such as galena.

INTRODUCTION

The principles determining the structure of the sulfide minerals have not as yet been formulated in a comprehensive way. The bonds between the sulfur atoms and the surrounding atoms in these minerals are covalent bonds, usually with only a rather small amount of ionic character. The metallic properties of many of the sulfide minerals, such as luster and electronic conductivity, show that the bonds resonate among alternative positions, and that some of the atoms have a metallic orbital, as in metals (Pauling, 1938, 1948a,b). The observed values of ligancy, bond lengths, and bond angles of sulfur show that the sulfur atom has transargononic structures in some minerals.

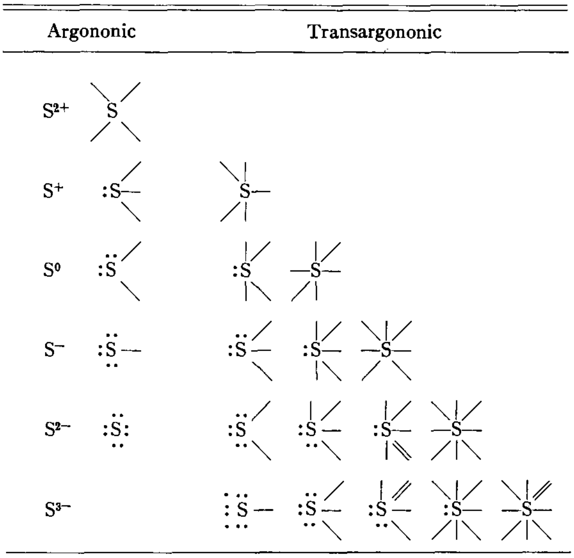
The discussion of chemical bonding of the sulfide minerals in the following pages is for the most part based on the general principles described in my book *The Nature of the Chemical Bond* (Pauling, 1960).

TYPES OF SULFUR ATOMS

It is convenient to base the discussion on the 20 types of sulfur atoms shown in Table 1. The horizontal rows correspond to different formal charges of the sulfur atom, from 2+ to 3−. (The formal charge is calculated by assigning all unshared electrons and one electron for each covalent bond to the atom.) The five argononic structures involve use of the $3s$ orbital and the three $3p$ orbitals for covalent-bond formation or occupancy by unshared electron pairs. (I use the word argononic to mean having the same number of electron pairs, shared or unshared, as in an argonon atom; that is, a noble-gas atom, and transargononic to mean having a larger number (Pauling, 1964).) The 15 transargononic structures make use also of one or more of the five $3d$ orbitals.

The properties of some sulfide minerals can be discussed in a reasonably satisfactory way by assigning one or another of the structures of Table I to the sulfur atoms. For some minerals the ligancy of the sulfur atom is equal to its covalence, and for others it is greater, the bonds then having fractional bond numbers. It is often necessary to assign a hybrid structure to the sulfur atoms. I shall assume that the covalent bonds indicated in Table I always have the normal amount of covalent character, as given by the difference in electronegativity of the metal atom and the sulfur atom.

TABLE I. ELECTRONIC STRUCTURES OF SULFUR ATOMS



THE COVALENT RADIUS OF SULFUR

I shall use the value 1.030 Å for the normal single-bond covalent radius of sulfur, instead of the value 1.04 Å that has been accepted for a long time (Goldschmidt, 1926; Pauling and Huggins, 1934). This value is half the sulfur-sulfur distance 2.060±0.003 Å in the S_8 molecule in orthorhombic sulfur, as determined by Caron and Donohue (1965). The value S—S = 2.048±0.006 Å has been reported by van de Grampel and Vos (1969) in $S_6(NH)_2$. The value 1.030 Å may be used for sulfur with other argononic structures. A somewhat larger value, about 1.07 to 1.10 Å, is indicated for transargononic sulfur.

INTERATOMIC DISTANCES

The length of a single covalent bond A—S may be taken as

$$D(1) = R_{\mathrm{A}} + R_{\mathrm{S}} - 0.060\ \mathrm{A}\ (x_{\mathrm{A}} - x_{\mathrm{S}}) \qquad (1)$$

in which x_{A} is the electronegativity of A and x_{S} is that of sulfur (Schomaker and Stevenson, 1941; Pauling, 1960, p 228). For formal charge zero the customary values of x are used (2.5 for S°). For S^{+} the value 2.7 is estimated, and for S^{2+}, with 25 percent s character to the bond orbitals, the value 3.2. Because of the contribution of the $3d$ orbitals, which have a smaller value of the ionization energy than $3p$, a smaller value of x is expected for transargononic sulfur.

For other elements the same dependence of electronegativity will be assumed; that is, a change by 0.2 z for electric charge z, increase by 0.3 for sp^3 bond orbitals (relative to p bonds), and an equal decrease for d character in transargononic bonds.

To within the reliability of the Schomaker-Stevenson correction, the value of Δx may be taken as that for the atoms with resultant charges $\pm 1/2$, in case that the formal charges are ± 1. For larger formal charges the electronegativity of each atom may be taken as corresponding to the resultant charge when each bond except the one under consideration has the amount of ionic character that for all bonds would reduce the charge to ± 1.

For example, for quadricovalent Cu^{3-} (sp^3 bonds) the charge on the copper atom becomes -1 for 50 percent ionic character of the four bonds. This amount of ionic character for three bonds leads to $\mathrm{Cu}^{1.5-}$, for which $x = 1.9 - (1.5 \times 0.2) = 1.6$.

Bond Length and Bond Number

Metals and alloys can be treated as involving covalent bonds that resonate among alternative positions (Pauling, 1938). Extra orbitals (metallic orbitals), usually 0.7 per atom, are needed for the unsynchronized resonance that gives rise to metallic properties (Pauling, 1948a,b). The value of an interatomic distance (bond length) corresponding to a fractional bond number n is given by the equation (Pauling, 1947)

$$D(n) = D(1) - 0.600 \log n \qquad (2)$$

$D(1)$ is the sum of the single-bond radii of the two atoms plus the correction for the difference in electronegativity. I assume that this equation holds for the sulfide minerals, and also that a metallic orbital is needed for metallic properties.

The Electroneutrality Principle

The electroneutrality principle (Pauling, 1960, p. 172) states that for stable structures the electric charge on each atom is close to zero. The charge is calculated by correcting the formal charges of the atoms by the charges transferred to the atoms by the partial ionic character of the bonds, as given by equation 3 (Pauling, 1960, p. 98):

$$\text{Ionic character } i = 1 - \exp\left[-(x_{\mathrm{A}} - x_{\mathrm{B}})^2/4\right] \qquad (3)$$

In applying this equation to a multicovalent atom, it should be used for each stage of formal charge, with the corresponding values of the electronegativity. The use of the electroneutrality principle is illustrated in several of the following discussions of sulfide structures.

Minerals Containing Bicovalent Argononic Sulfur

The normal valence (normal covalence) of sulfur, corresponding to its position in the periodic table, is 2. The electronic structure of the normal bicovalent sulfur atom is the argononic structure $:\ddot{\mathrm{S}}\!<$ with bond orbitals about 93 percent $3p$ and 7 percent $3s$, bond angle between 92° and 108°. Orthorhombic sulfur, realgar, orpiment, and cinnabar may serve as examples of minerals containing this sort of sulfur atom.

The bond angle in orthorhombic sulfur equals 108.0° ±0.1°.

In realgar there are molecules $\mathrm{As_4S_4}$. Each sulfur atom is bonded to two arsenic atoms, at 2.243 Å (average of eight nonequivalent values, from 2.19 Å to 2.28 Å; Ito, Morimoto and Sadanaga, 1952). The As—S bond length in the $\mathrm{As_4S_4}$ gas molecule is 2.23 ± 0.02 Å (Lu and Donohue, 1944). The average values of the As—S— As bond angle are 101.5° for realgar and 100° for $\mathrm{As_4S_4(g)}$.

Orpiment, $\mathrm{As_2S_3}$, has a layer structure in which each sulfur atom is bonded to two arsenic atoms and each arsenic atom to three sulfur atoms. The average bond length and average bond angle in orpiment and in $\mathrm{As_4S_6(g)}$ have nearly the same values as for realgar and $\mathrm{As_4S_4(g)}$; the bond lengths are $2.25 + 0.02$ Å in both orpiment and $\mathrm{As_4S_6(g)}$.

The observed bond angles and bond lengths in realgar and orpiment support the assignment of normal-valence structures to them. The single-bond covalent radius of arsenic is taken to be 1.25 Å, from the observed bond length 2.50 Å in As(c). (The value 2.49 Å is reported for the As—As bonds in realgar.) The expected value for the normal As—S bond length is $1.25 \pm 1.03 = 2.28$ Å minus the correction for the difference in electronegativity of arsenic and sulfur. This correction, the Schomaker-Stevenson correction (Equation 1), is $-\Delta x \times 0.060$ Å for a bond between sulfur and a more electronegative atom not of the first row in the periodic table (Pauling, 1960, p. 229). The quantity Δx is the difference in electronegativity of sulfur ($x = 2.5$) and the atom to which it is bonded ($x = 2.0$ for arsenic). With this correction, -0.030 Å, the expected value for the As—S bond length is 2.25 Å, in agreement with the realgar-orpiment value.

In realgar the short non-bonding contact distances are 3.3 Å for sulfur-sulfur, 3.6 Å for sulfur-arsenic, and 3.5 Å for arsenic-arsenic. They are accordingly about 1.2 Å greater than the corresponding single-bond lengths, as found in other crystals.

In cinnabar, HgS, the sulfur atom has a normal-valence structure, in which it forms two bonds with mercury atoms. The Hg—S—Hg bond angle is 105°. The mercury atom may be described as forming two oppositely directed bonds with use of two sp hybrid bond orbitals; the value of the S—Hg—S angle is 172°. The bond length, 2.36 Å, leads, with $R = 1.03$ Å for sulfur and the Δx correction ($x = 1.9$ for mercury), to the value 1.36 Å for the mercury single-bond radius. This value may be compared with that of the metallic single-bond radius of mercury, 1.386 Å, which however, corresponds to metallic valence 4.56 (Pauling, 1960, p. 403).

MINERALS CONTAINING TERCOVALENT ARGONONIC SULFUR

The symbol $[:\ddot{\mathrm{S}}\substack{\diagup\\ -\\ \diagdown}]^{+}$ represents tercovalent argononic sulfur. Like $:\ddot{\mathrm{S}}\substack{\diagup\\ \diagdown}$, it is argononic in that, counting shared as well as unshared electron pairs, it has four pairs in its outer shell, giving it the electron number of argon. A tercovalent argononic sulfur atom resembles a normal (neutral) tercovalent phosphorus atom. The bond orbitals of $:\ddot{\mathrm{S}}\substack{\diagup\\ -\\ \diagdown}^{+}$ are similar to those of $:\ddot{\mathrm{S}}\substack{\diagup\\ \diagdown}$.

Molybdenite, $\mathrm{MoS_2}$, has a layer structure in which each sulfur atom has three molybdenum atom neighbors at 2.417 Å. If we assume that the bonds are single covalent bonds, with tercovalent argononic sulfur, the molybdenum atom is given the formal charge -2, which might seem to be incompatible with the electroneutrality principle. It is found, however, as shown below, that the amount of ionic character of the bonds is great enough to make the structure acceptable.

To calculate the amounts of ionic character we use the electronegativity values 1.8 for Mo^0, 1.4 for Mo^{2-}, 2.7 for S^+, 2.5 for S^0, and so on. To simplify the calculation we may assume a value of the average charge of the molybdenum atom, and use the corresponding average value of x, in calculating the ratios of S^+, S^0, S^-, and S^{2-}. Trial shows $\mathrm{Mo}^{0.75-}$, with $x = 1.65$, to be consistent with the amounts of partial ionic character and the number of structures (1 for each tercovalent S^+ and zerocovalent S^{2-}, 3 each for bicovalent S^0 and unicovalent S^-). The values of partial ionic character of the bonds of S^+, S^0, and S^- are 24, 17, and 10 percent, respectively, and the contributions of S^+, S^0, S^-, and S^{2-} to the structure are 47, 44, 9, and 0.3 percent, respectively, leading to the average charge $+0.37$ on sulfur and -0.74 on molybdenum. A similar calculation with use of an average value of x for sulfur, 2.57 (corresponding to average charge $+0.37$), leads to the contributions 18, 45, 30, 7 percent for Mo^{2-}, Mo^-, Mo^0, and Mo^+, respectively, average charge -0.74 for molybdenum. The agreement indicates that the approximate calculations involve little error. With the Schomaker-Stevenson correction of -0.042 Å in the bond length and the radius 1.030 Å for sulfur, the observed Mo—S distance 2.417 Å leads to 1.43 Å for the single-bond covalent radius of sexicovalent Mo^{2-}. The increase over the metallic radius 1.296 Å of neutral molybdenum (metallic valence 6) is reasonable as the effect of the unshared electron pair in the valence shell of Mo^{2-}.

Molybdenite was the first substance found to contain a trigonal prism as ligation polyhedron for ligancy 6, instead of the more common octahedron (Dickinson and Pauling, 1923). An acceptable explanation of the stability of the molybdenite structure, rather than the cadmium iodide structure, which is a closely similar layer structure but with octahedral ligation about the metal atom, has been advanced (Pauling, 1960, p. 175). The molybdenum bond orbitals are *dsp* hybrids. The best *dsp* bond orbitals correspond to the values 73.15° and 133.62° for the unstrained bond angles. These values are much closer to the observed values for the angles S—Mo—S in molybdenite, 82° and 136°, than to those for the cadmium iodide structure, 90° and 180°.

Proustite, $\mathrm{Ag_3AsS_3}$, is another good example of a mineral containing $:\ddot{\mathrm{S}}\substack{\diagup\\ -\\ \diagdown}^{+}$. It consists of two interpenetrating frameworks. Each sulfur atom is bonded to 1 As and 2 Ag, the bond angles having values close to 90° (83° for Ag—S—Ag, 100° and 107° for As—S—Ag). The observed As—S bond length has the expected value, 2.25 Å (as in enargite); Harker (1936) found 2.25 Å, and Engel and Nowacki (1966) found 2.254 Å.

The Ag-S bond length is 2.44 Å. This value is also found in pyrargyrite and pyrostilpnite, both of which have the formula $\mathrm{Ag_3SbS_3}$ and contain bicovalent silver and tercovalent argononic sulfur. It leads to 1.45 Å for R for bicovalent silver with formal charge -1, which may be compared with the values 1.396 Å and 1.528 Å for silver with metallic valence 3 and 1, respectively (Pauling, 1960, p. 420).

QUADRICOVALENT ARGONONIC SULFUR

Huggins (1922) was the first investigator to assign structures to sphalerite, wurtzite, chalcopyrite, pyrite, marcasite, arsenopyrite, and other sulfide minerals in which each sulfur atom forms four tetrahedrally directed covalent bonds with surrounding atoms. These structures would be described as involving quadricovalent argononic S^{2+}.

For sphalerite and wurtzite, for example, the discussion of partial ionic character as described above for molydenite leads to the resultant average charges $+0.67$ for sulfur and -0.67 for zinc. The distribution of the sulfur atoms is calculated to be 12% S^{2+} (quadricovalent), 50 percent S^+, 32 percent S^0, 6 percent S^-, 0.2% S^{2-}. The observed bond length 2.34 Å with the sulfur radius 1.03 Å and the Schomaker-Stevenson correction 0.05 Å leads to $R_i = 1.36$ Å for zinc (quadricovalent Zn^{2-}). The increase by 0.05 Å over the value 1.309 Å for sp^3 bonds of Zn^0 is reasonable as the result of screening of the nucleus by the extra electrons.

The Cd-S distance 2.53 Å in greenockite and the Hg-S distance 2.54 Å in metacinnabar similarly lead to the values $R = 1.55$ Å for Cd^{2-} and 1.55 Å for Hg^{2-}, 0.06 Å larger than the sp^3 radii of the neutral atoms, 1.485 Å and 1.490 Å, respectively (Pauling, 1960, p. 420).

The above results for ZnS, CdS, and HgS indicate that an additional electron in a transition-metal atom increases its radius by 0.03 Å.

SULFIDE MINERALS CONTAINING RESONATING BONDS

Galena, PbS, has the sodium chloride structure, with ligancy 6 for each atom. The Pb-S distance is 2.968 Å. A possible structure is that based on the normal sulfur atom (bicovalent argononic sulfur), with the two single bonds resonating among the six positions, giving $n=1/3$. Another reasonable structure is that based on the tercovalent argononic atoms $:\mathrm{Pb}\begin{smallmatrix}\diagup\\ -\\ \diagdown\end{smallmatrix}^{-}$ and $:\mathrm{S}\begin{smallmatrix}\diagup\\ -\\ \diagdown\end{smallmatrix}^{+}$, with three bonds resonating among the six positions. This structure makes use of all of the outer orbitals of the lead atom and the sulfur atom, and with its greater number of bonds may be expected to correspond to a lower energy value than the structure with bicovalent atoms, which, in fact, represents its partial ionic character.

Treatment of the tercovalent structure as given above for molybdenite leads to 51 percent S^+ (Pb^-), 42 percent S^0 (Pb^0), 7 percent S^- (Pb^+), and 0.2 percent S^{2-} (Pb^{2+}), average charges +0.43 for S, − 0.43 for Pb. The observed Pb−S distance with the bond-number correction 0.181 Å, Schomaker-Stevenson term − 0.042 Å, and sulfur radius 1.030 Å gives 1.80 Å for the single-bond radius of lead in this crystal. This value is 0.26 Å larger than the p-bond radius of neutral bicovalent lead. Of this amount, 0.03 Å can be attributed to the screening effect of the extra electron in Pb^- and 0.20 Å to the repulsion of the outer unshared pairs of both lead and sulfur for the surrounding atoms.

THE LEAD SULFARSENITES AND RELATED MINERALS

It is likely that the lead and sulfur atoms in most of the lead sulfarsenites and related minerals have the tercovalent argonic structures $:\mathrm{Pb}\begin{smallmatrix}\diagup\\ -\\ \diagdown\end{smallmatrix}^{-}$ and $:\mathrm{S}\begin{smallmatrix}\diagup\\ -\\ \diagdown\end{smallmatrix}^{+}$, as in galena. Nowacki (1969) has published a valuable summary of results of structural studies of the so-called sulfosalt minerals, in relation to a system of classification of the structures that he has developed. Many structures of sulfide minerals have been determined by him and his coworkers.

In the sulfarsenite minerals arsenic has ligancy 3, with S—As—S bond angles usually between 95° and 105°, as expected for tercovalent arsenic, $:\mathrm{As}\begin{smallmatrix}\diagup\\ -\\ \diagdown\end{smallmatrix}$. In binnite, $Cu_{12}As_4S_{18}$, for example (Pauling and Neumann, 1934; Wuensch, Takeuchi, and Nowacki, 1966), the S—As—S bond angle is 98.4° and the As—S bond length is 2.246 Å, in agreement with the argononic structure. Lead is usually found with ligancy 6, 7, 8, or 9. In baumhauerite, $Pb_{11.6}As_{15.7}Ag_{0.6}S_{36}$ (Engel and Nowacki, 1969), there are 12 kinds of lead atoms, eight of which are surrounded by nine sulfur atoms, which lie approximately at the corners of a trigonal prism and out from the centers of its rectangular faces. The Pb—S distances for these atoms range from 2.73 Å to 3.70 Å, with averages about 3.2 Å.

I think that the average bond length has little significance. A more significant quantity, which might be generally adopted, is the *valence-average bond length.* Let us consider Engel and Nowacki's lead atom Pb(12), with 9S at 2.91, 3.00, 3.01, 3.02, 3.22, 3.28, 3.32, 3.47 and 3.53. The average of these values is 3.20 Å. The valence-average bond length is calculated by use of equation 2; it is the bond length for the assumed ligancy that corresponds to the same valence for lead and equal Pb—S distances. For the Pb(12) atom its value is 3.121 Å, and for the others it is 3.095, 3.084, 3.120, 3.107, 3.121, 3.124 and 3.116. The average for all eight is 3.111±0.013 Å, which is 0.14 Å greater than for galena. The expected increase from ligancy 6 to ligancy 9, for the same covalence of lead (3), is 0.60 log 1.5=0.11 Å. Hence the bond lengths in baumhauerite agree with those in galena to within 0.03 Å.

As another example I take gratonite, $Pb_9As_4S_{15}$, in which there are two kinds of lead atoms, each with ligancy 7 (Ribar and Nowacki, 1969). For the two kinds of lead atoms the averages of the seven Pb—S bond lengths are 3.03 Å and 3.09 Å, differing by 0.06 Å, whereas the valence-average bond lengths are 3.000 Å and 2.996 Å, in excellent agreement with one another. The expected value, calculated from the value 2.968 Å for galena by subtracting the term 0.600 log 6/7 for change in ligancy of lead from 6 to 7, without change in valence, is 3.008 Å.

In gratonite, as in galena, baumhauerite, and other minerals with ligancy 5 or more for sulfur and 6 or more for lead, the valence-average bond lengths agree with the values calculated from the single-bond value 2.79 Å by applying the bond-number correction of equation 2, with the covalence of lead taken to be 3.

TRANSARGONONIC SULFUR

A transargononic structure for sulfur, with six bonds formed by sp^3d^2 hybrid orbitals, was suggested for sulfur in the octahedral molecule SF_6 long ago, and also for one of the sulfur atoms, with ligancy 6, in binnite (Pauling and Neuman, 1934). Some transargononic structures of metal sulfides have been proposed recently by Franzen (1966).

In $F_5S—SF_5$ the S—S distance is 2.21 Å, which indicates the value 1.105 Å for the single-bond covalent radius of transargononic sulfur. Support for this value is provided by the reported S—S bond lengths 2.209±0.002 Å in potassium pyrosulfite, $K_2S_2O_5$, and 2.16±0.02 Å in sodium dithionate dihydrate, $Na_2S_2O_6 \cdot 2H_2O$, and potassium dithionate, $K_2S_2O_6$. The sulfur-oxygen double bonds in these complexes make the sulfur atoms transargononic. Values from 2.10 to 2.14 Å, average 2.13 Å, are reported also for the argononic-transargononic $—S—SO_3^-$ bond length in $Na_2S_4O_6 \cdot 2H_2O$, $BaS_4O_6 \cdot 2H_2O$, $BaS_5O_6 \cdot 2H_2O$, $BaS_5O_6 \cdot H_2O \cdot (CH_3)_2CO$, $BeSeS_4O_6 \cdot 2H_2O$, $BaTeS_4O_6 \cdot 2H_2O$, and $(NH_4)_2TeS_4O_6$. This average corresponds to 2.10 Å for transargononic sulfur.

If we assume that the increase of R over the value 1.030 Å is proportional to the amount of d character of the bond orbitals, we obtain the values 1.10 Å for sp^3d^2 bonds, 1.07 Å for sp^3d bonds, and 1.08 Å for p^3d bonds ($:\mathrm{S}\begin{smallmatrix}\diagup\!\diagup\\ -\\ \diagdown\!\diagdown\end{smallmatrix}^{+}$).

SEXICOVALENT TRANSARGONONIC SULFER

In binnite, $Cu_{12}As_4S_{13}$, one of the 13 sulfur atoms is ligated to six copper atoms, which lie at the corners of an octahedron about it (Pauling and Neuman, 1934). The other sulfur atoms have tetrahedral ligation, and are presumably argononic (as in sphalerite, chalcopyrite, and other tetrahedral sulfides). These six copper atoms have ligancy 3; the bonds from them to the transargononic sulfur atom have length 2.29 Å, which is 0.06 Å greater than that of the bonds from them to the tetrahedral sulfur atoms. Hence the single-bond radius for sexicovalent transargononic sulfur in bonding to metal atoms is 1.09 Å, 0.06 Å greater than for argononic sulfur, in agreement with the value from S_2F_{10} and the polythionic acid ions.

Quinquecovalent Transargononic Sulfur

In covellite, $CuCu_2SS_2$, the disulfide sulfur atoms have a tetrahedral quadricovalent argononic structure, with S—S = 2.09 Å and S—Cu(I) = 2.30 Å. The sulfide sulfur atom has ligancy 5, with the bonds directed toward the corners of a trigonal bipyramid, as expected for S^+ with dsp^3 bonds (analogous to P in PCl_5).

The values of R for Cu(I) with sp^3 bonds and Cu(II) with dsp bonds are 1.352 Å and 1.185 Å, respectively (Pauling, 1960, p. 420), and those for quadricovalent S^{2+} and quinquecovalent S^+ are 1.030 Å and 1.075 Å. The respective values of x for use in the Schomaker-Stevenson correction term are 1.6, 1.8, 2.95 and 2.6. The calculated and observed bond lengths are Cu(I)—S_2 = 2.36 (2.34 observed), Cu(I)—S = 2.31 (2.30), and Cu(II)—S = 2.20 (2.19 Å), in excellent agreement.

Quadricovalent Transargononic Sulfur

The configurations expected for quadricovalent transargononic sulfur, with nonresonating bonds, $:\mathrm{S}\begin{smallmatrix}\diagup\!\diagup\\ \diagdown\!\diagdown\end{smallmatrix}$, are those in which the bonds are directed toward four of the five corners of a trigonal bipyramid or a tetragonal pyramid, with the unshared pair occupying a larger solid angle than a shared pair.

Ever since its discovery (Pauling and Hultgren, 1933; also Trojer, 1966), the structure of sulvanite, Cu_3VS_4, has constituted a puzzle. The sulfur atoms form four bonds, directed to one side of the atom; three to copper, at 2.29 Å, and one to vanadium, at 2.21 Å. The angles Cu—S—Cu and V—S—Cu have the values 110° and 72°, respectively. I have pointed out (1965) that there are weak bonds between copper and vanadium atoms in this crystal, as an explanation of its unusual structure, and that the bond lengths calculated for argononic sulfur (Cu—S = 2.37 Å, V—S = 2.27 Å) are larger than those observed. This discrepancy is eliminated by assigning the quadricovalent transargononic structure to the sulfur atom, with R = 1.08 Å. The V—Cu bonds have bond number 1/3 (from equation 2), leading to covalence 6 for V(V^-, R = 1.186 Å) and 4 2/3 for Cu(R = 1.192 Å), and to calculated bond lengths Cu—S = 2.24 Å, V—S = 1.21 Å. The observed values indicate some contribution also of the argononic structure. For a crystal of this sort, for which two alternative structures have about the same stability, a hybrid structure that gives nearly zero charge to the atoms is to be expected. The structure based on tercovalent S^+ leads, with consideration of the ionic character of the bonds, to the charge +0.4 on the sulfur atom, and that based on quadricovalent transargononic S^0 to −0.4; accordingly, the two structures may be expected to make about equal contributions.

Structures in which the sulfur atom is tetraligated and one-sided (bonds in one hemisphere, leaving room for the unshared electron pair of $:\mathrm{S}\begin{smallmatrix}\diagup\!\diagup\\ \diagdown\!\diagdown\end{smallmatrix}^{+}$) have been reported for only a few sulfide minerals. One example, in addition to sulvanite, is mackinawite, FeS (Berner, 1962). The tetragonal mineral has been assigned the B10 (anti-PbO) structure, in which there are layers SFeS, iron having tetrahedral ligation to sulfur and sulfur having square pyramidal ligation, appropriate to transargononic quadricovalent S^0. As for sulvanite, we may expect about equal contributions of this structure and the structure based on tercovalent argononic S^+. The calculated values of the Fe—S bond length for the two structures (R for iron 1.170 Å; Fe also forms four Fe-Fe bonds with length 2.60 Å, bond number 0.37) are 2.21 Å and 2.22 Å; the reported bond length is 2.23 Å.

Structures for many sulfides that do not occur as minerals have been reported in which sulfur forms four bonds directed to one side, leaving room for the unshared pair of the sulfur atom. There is little doubt that these sulfides, too, have transargononic structures, as suggested by Franzen (1966).

Pyrite and Marcasite

From among the many other sulfide minerals that might be discussed I select pyrite and marcasite.

The structure of pyrite, including a rough determination of the sulfur parameter, was first described by W. L. Bragg (1914), in the paper in which the structures of hauerite, sphalerite, fluorite, calcite, rhodochrosite, chalybite, and soda niter were also reported. The sulfur parameter was then accurately determined, by the comparison of the relative intensities of reflections *hkl* and *khl* on symmetric Laue photographs, by Ewald and Friedrich (1914). Their parameter value leads to the bond lengths S—S = 2.10 ± 0.01 Å and Fe—S = 2.27 ± 0.01 Å. Later investigators have reported approximately the same values. The iron atom has ligancy 6, and each sulfur atom has ligancy 4 (one S and 3 Fe). Marcasite has an orthorhombic structure in which the ligancies are the same as in pyrite.

Huggins (1922) assigned argononic structures to pyrite and marcasite (sexicovalent Fe^{4-} and quadricovalent S^{2+}). It is evident, however, that this assignment has to be revised, as has been pointed out long ago by Buerger (1937).

I take this opportunity to extend a belated apology to Professor M. J. Buerger, in which Dr. Maurice L. Huggins also joins. Long ago (Pauling and Huggins, 1934) we attempted to extend and refine a set of covalent radii that had been formulated by Huggins (1926). We were led to accept 2.08 Å for the S—S single-bond length, and in a table we listed the value 2.25 Å reported by Buerger (1931) for marcasite with the comment "Parameters probably inaccurate." Professor Buerger, to whom we are all indebted for his structure determinations of many sulfide minerals as well as other important contributions to mineralogy, was more skeptical about simple theoretical arguments than we were; he carried out a second careful investigation of marcasite, with very nearly the same result: he found S—S = 2.210 Å. I agree that this value shows clearly that the sulfur atom does not have an argononic structure in marcasite.

The increase in the S—S bond length over the argononic value 2.06 Å indicates a transargononic structure. A structure based on quadricovalent transargononic S^0 and sexicovalent Fe^0 is reasonable, in that the iron atom in metallic iron is sexicovalent and neutral. The radius 1.08 Å that we have assigned to quadricovalent S^0 is a little smaller than that indicated by the S—S bond length in marcasite. It is likely, as has been suggested for other crystals (Pauling and Soldate, 1948), that the amount of *d* character of the sulfur bond orbitals is different for the S—S bond and the S—Fe bonds.

For both pyrite and marcasite a hybrid structure is to be assigned, with more argononic character for pyrite and more transargononic character for marcasite. This difference in hybrid character is correlated with the larger amount of room for the unshared electron pair of transargononic sulfur in marcasite. Bond lengths greater than the argononic values are also found for As—S, Sb—S, As—As, and other complexes in minerals with the marcasite structure, showing that in these minerals the electronegative atoms have some transargononic character.

Conclusion

The foregoing discussion of the structures of some sulfide minerals, especially the observed bond lengths and bond angles, leads to the conclusion that the sulfur atom may have either an argononic or a transargononic structure with formal charge 0, +1, or (argononic only) +2, sometimes with resonance between two structures. Ligancy 2 and bond angle 100° to 110° indicate bicovalent argononic S^0, and ligancy 3 and angles 100° to 110° indicate tercovalent argononic S^+. Ligancy 4 indicates argononic S^{2+} if the bonds are tetrahedrally directed, and transargononic S^0 if they are one-sided (leaving room for the unshared electron pair). Quinquecovalent S^+ (trigonal bipyramid) and sexicovalent S^0 (octahedron, trigonal prism) are also found. In some minerals the bond lengths resonate among alternative positions, as in metals, leading to bond numbers less than 1, and to bond lengths greater than expected for single covalent bonds. A positive formal charge for sulfur is stabilized by the back transfer of negative charge corresponding to the partial ionic character of the bonds to the metal atoms, which have smaller electronegativity than the sulfur atom. For argononic sulfur the chemical formula of the mineral corresponds to the normal valences (As_2S_3, Cu_3AsS_3, PbS, etc.), whereas for transargononic sulfur it may show deviations ($Cu_{12}As_4S_{13}$, etc.).

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Chapter 7

MOLECULES IN THE GAS PHASE AND ELECTRON DIFFRACTION

Contents

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[Contribution from Gates Chemical Laboratory, California Institute of Technology, No. 507]

The Radial Distribution Method of Interpretation of Electron Diffraction Photographs of Gas Molecules

By Linus Pauling and L. O. Brockway

Introduction

The only method of interpretation of electron diffraction photographs of gas molecules which has been used to any great extent is the so-called *visual method*, involving the correlation of apparent maxima and minima on the photographs with maxima and minima on simplified theoretical curves calculated for various models of the molecule under consideration. This method of interpretation, originally developed by Wierl,[1] has been thoroughly tested by Pauling and Brockway[2] who have shown it to yield values of interatomic distances accurate to within about 1% (estimated probable error). The main disadvantage of the method is that it does not involve a straightforward process of determining the structure of a molecule from the analysis of experimental results, but consists instead in the testing (and rejection or acceptance) of any structures which may be formulated, a tedious calculation being required for each structure.

We have developed a new method of interpretation of the photographs which does not suffer from this disadvantage. This *radial distribution method*, which is closely related to the method of interpretation of x-ray diffraction data developed by Zernike and Prins[3] for the study of the structure of liquids and applied by Warren and Gingrich[4] to crystals, consists in the calculation (from

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(1) R. Wierl, *Ann. Physik*, **8**, 521 (1931); **13**, 453 (1932).

(2) L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

(3) F. Zernike and J. A. Prins, *Z. Physik*, **41**, 184 (1927); see also P. Debye and H. Menke, *Ergeb. Tech. Röntgenkunde*, Akad. Verlagsges., Leipzig, Vol. II, 1931.

(4) B. E. Warren and N. S. Gingrich, *Phys. Rev.*, **46**, 368 (1934).

data provided by the electron diffraction photograph) of a distribution function for scattering power, representing the product of the scattering powers in volume elements the distance l apart as a function of l. Since the scattering power of an atom for fast electrons is large only in the neighborhood of the nucleus, a maximum in this distribution function indicates that the internuclear distance for two atoms in the molecule is given by the corresponding value of l. The radial distribution method thus leads directly to values of the internuclear distances and hence to the structure of the molecule.

Because of the difficulty of obtaining satisfactory photometer records of electron diffraction photographs of gas molecules, we have adapted and extended the visual method to the calculation of radial distribution curves, by making use of the values of $(4\pi \sin \vartheta/2)/\lambda$ obtained by the measurement of ring diameters (as in the usual visual method) in conjunction with visually estimated intensities of the rings, as described below. Various tests of the method indicate that the important interatomic distances can be determined in this way to within 1 or 2% (probable error).

The radial distribution method, while thus not completely independent of the usual visual method, is sufficiently different from it to lead in some cases to somewhat different values for interatomic distances. We feel that these values carry some weight, and we have accordingly discussed by the new method a number of molecules whose structures as determined by the usual visual method have been reported in earlier publications, and have then combined the results of the two methods in presenting a revised set of values of interatomic distances for these molecules.

The radial distribution method is especially satisfying in that it leads directly to the values of the principal interatomic distances, and so immediately rules out all structures for the molecule except those compatible with these values. Moreover, the method can be applied unchanged to those molecules for which the investigator is unable to formulate a reasonable structure (such as S_2Cl_2, in which the rotation about the S–S bond may be restricted to some extent, leading to difficultly predictable variation in the Cl–Cl distance), yielding a distribution curve which reveals the information provided by the photograph regarding the structure of the molecule.

We are greatly indebted to Dr. S. Weinbaum, Dr. J. Sherman, and Mr. J. Y. Beach for assistance in the preparation of this paper.

Description of the Method

The intensity of the coherent electron scattering at the angle ϑ by gas molecules is usually represented by the expression

$$I(\vartheta) = K \sum_i \sum_j \psi_i \psi_j \frac{\sin x_{ij}}{x_{ij}} \qquad (1)$$

in which K is a constant, and

$$x_{ij} = \frac{4\pi \sin \vartheta/2}{\lambda}\, l_{ij} \qquad (2)$$

with l_{ij} the distance between atoms i and j in the molecule, λ the wave length of the electrons, and ψ_i the scattering function for the ith atom. A more general expression is

$$s^4 I(s) = K' \int_0^\infty l^2\, D(l)\, \frac{\sin sl}{sl}\, dl \qquad (3)$$

in which we have introduced the new angle variable

$$s = (4\pi \sin \vartheta/2)/\lambda \qquad (4)$$

and have replaced the double sum by an integral, writing in place of the product of atomic scattering powers $\psi_i\psi_j$ the function $l^2\, D(l)/s^4$, representing, aside from the factor $1/s^4$ (the scattering factor for electrons by a unit charge), the product of scattering powers in all volume elements the distance l apart. This expression is a Fourier integral for $s^5 I(s)$, the coefficients of the Fourier terms being $lD(l)$. On inverting the Fourier integral we obtain the following expression for $D(l)$ in terms of $I(s)$

$$D(l) = K'' \int_0^\infty s^6\, I(s)\, \frac{\sin sl}{sl}\, ds \qquad (5)$$

Instead of attempting to apply the expression in this form, we simplify it radically in a way suggested by the appearance of the electron diffraction photographs, which to the eye show a succession of rings; namely, by replacing the integral by a finite sum of terms, including one term for each ring. We accordingly write, ignoring the constant K''

$$D\,(l) = \sum_{k=1}^{n} I_k \frac{\sin s_k l}{s_k l} \qquad (6)$$

in which

$$s_k = (4\pi \sin \vartheta_k/2)/\lambda$$

ϑ_k being the scattering angle for the kth ring as measured in the usual way,[2] and I_k an estimated value[5] for the integrated intensity of the kth ring

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(5) It is our experience that the intensities as estimated visually (the change from ring to ring being small, as seen in the tables) are satisfactory, despite neglect of the factor s^6. This may be due in part to the comparison by the eye of each ring with the adjacent background, which falls off in intensity approximately with $1/s^4$.

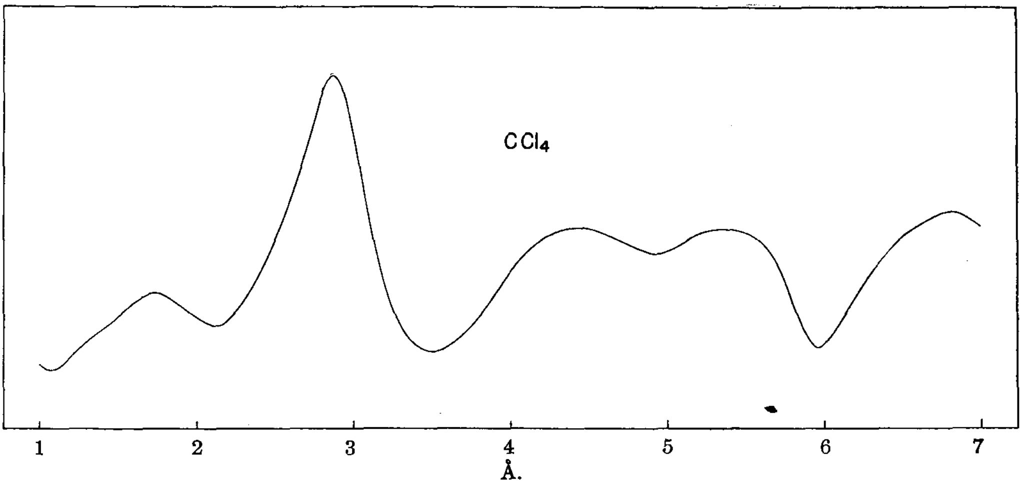

Fig. 1.—Radial distribution function for carbon tetrachloride. The part of the curve beyond 4 Å. is without significance.

(the factor s^6 being included in I_k). This simplification, which at first seems extreme, is seen on analysis not to be unreasonable; each section of the integral, corresponding to the range of angles between successive apparent minima, is replaced by a single Fourier term, whose frequency is in the middle of the frequencies for the range replaced, the coefficient of the single term being an integrated coefficient over the range. For values of l in the region of importance (corresponding to interatomic distances in the molecule) this simplification will not change the form of $D(l)$ very much; at smaller and larger values of l, however, it will introduce false maxima, instead of falling asymptotically to zero.

It is seen that the calculation of a radial distribution curve is closely similar to the calculation of a simplified theoretical intensity curve for the usual visual method, the summation being over the rings seen on the photograph instead of over the interatomic distances in the assumed model; but whereas in the usual treatment the calculation may need to be repeated for many models, a single curve only is required for the new method.

In the usual treatment the apparent intensities of the rings play only a minor part, in that some use is made of them in the decision among models by qualitative comparison of photograph and curves. Numerical values of estimated intensities are needed for the new method; it is found empirically, however, that the positions of the principal maxima are not very sensitive to changes in the estimated intensities, as long as the rings are kept in correct qualitative relation to one another. It is sometimes necessary to introduce a term in the series to represent a shelf on one side of a ring, or some similar feature of the photograph.[6]

In the calculations reported in this paper the curves were evaluated at intervals of 0.1 Å. except in the neighborhood of the principal maxima, where smaller intervals (usually 0.02 Å.) were used. The values of $(\sin sl)/sl$ were obtained from tables prepared by Dr. P. C. Cross with the aid of Sherman's $(\sin x)/x$ tables.[7]

Tests of the Method

Carbon Tetrachloride.—By the usual visual method and by other methods involving microphotometer records, we have assigned[8] to the carbon tetrachloride molecule the value 1.760 ± 0.005 Å. for the C–Cl distance, a value supported by other recent work.[9] The radial distribution function for this molecule calculated by Equation 6, using the ten terms for which data are given in Table I, is shown in Fig. 1.

It is seen that the six Cl–Cl terms are shown by a very sharp peak, the four C–Cl terms appearing

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[6] Dr. Simon Bauer has suggested that it may sometimes be convenient to introduce terms corresponding to the apparent minima between rings, using negative coefficients.

[7] J. Sherman, *Z. Krist.*, **85**, 404 (1933). The tables prepared by Dr. Cross give values of $(\sin sl)/sl$ for $0.80 \leqslant s \leqslant 4.00$ at intervals of 0.01, for values of l up to 40, and $4.02 \leqslant s \leqslant 8.00$ at intervals of 0.02, for values of l up to 20, the intervals for l being 0.2.

[8] L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

[9] V. E. Cosslett and H. de Laszlo [*Nature*, **134**, 63 (1934)] report 1.754 ± 0.02 Å. and V. E. Cosslett [*Trans. Faraday Soc.*, **30**, 981 (1934)] reports 1.74 ± 0.02 Å. C. Degard, J. Pierard and W. van der Grinten give the values 1.75 ± 0.02 Å. (electron diffraction) and 1.74 ± 0.02 Å. (x-ray diffraction) in a letter to *Nature*, **136**, 142 (1935).

TABLE I

CARBON TETRACHLORIDE

k	I_k	s_k
1	20	2.93
2	30	4.91
3	15	7.13
4	10	9.23
5	10	11.34
6	5	13.54
7	4	15.79
8	2	17.82
9	1	19.98
10	1	22.34

as a small peak at a smaller value of *l*; in addition some broad peaks occur at larger values of *l*. The complete Fourier integral representing the radial distribution would, of course, fall asymptotically to zero *after* the Cl–Cl maximum. Because of the crudity of our approximation to the integral by a series of ten terms we can expect our function to continue to vary appreciably in this region, the maxima there having no significance.

The *l* value given by the small C–Cl peak, about 1.74 Å., is unreliable, inasmuch as it is rather sensitive to change in the number of rings considered. That given by the Cl–Cl hump, however, is reliable. It is Cl–Cl = 2.856 Å., which corresponds to C–Cl = 1.749 Å., in good agreement with the earlier value, the deviation being in the direction of the values of Cosslett and de Laszlo.

The effect of including successive rings is shown in Fig. 2, the first curve including only one term (ring 1), the second two (rings 1 and 2), and so on. It is seen that the principal peak assumes its position and shape very quickly, the Cl–Cl distance being given to within 2% (2.81 Å.) by two terms alone, and quickly rising to a constant value (2.85 Å. for five terms, 2.86 Å. for six and more terms). The small C–Cl peak, on the other hand, fluctuates considerably, the *l* value varying between 1.72 and 1.78 Å. for curves 5 to 10.

Bromine and Chlorine.—Accurate values of the internuclear distances in the molecules Br_2 and Cl_2 are known from band spectral studies, namely, Br–Br = 2.281 Å. and Cl–Cl = 1.988 Å. The visual method led to results (2.289 Å. and 2.009 Å., respectively) in satisfactory agreement with these.[8] Radial distribution curves for these substances are shown in Fig. 3, the data used being given in Tables II and III. For bromine, with seven rings, three different estimates of intensities lead to the same Br–Br distance, 2.270 Å., less than 0.5% from the band spectral value. The Cl–Cl distance, given by the curve, 1.995 Å., is still closer to that found from band spectra. The agreement for these two molecules indicates that there is no large error inherent in the radial distribution method.

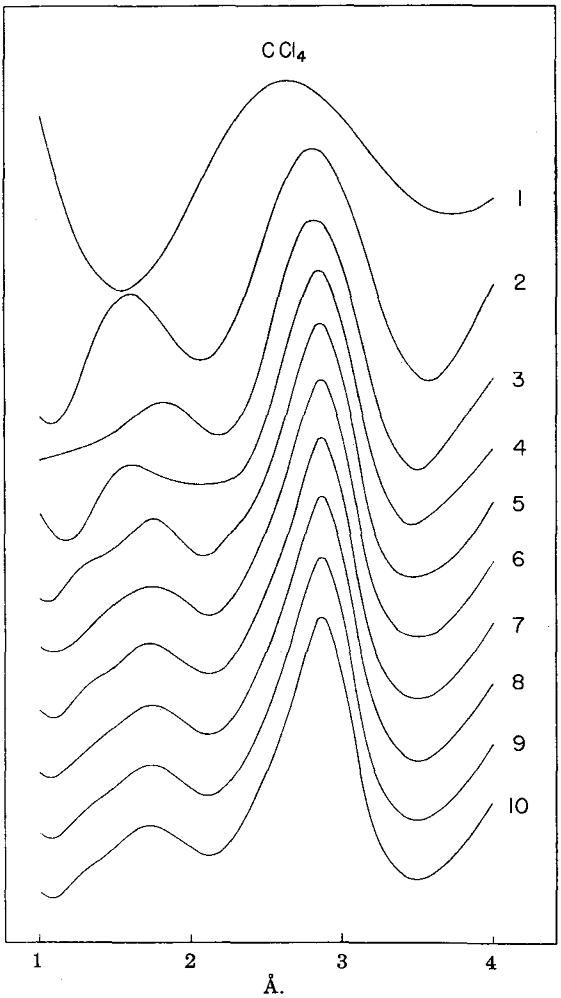

Fig. 2.—Radial distribution curves for carbon tetrachloride, calculated with one term (1), two terms (2) and so on.

Benzene.—A careful study of photographs of benzene both by the visual method and by the analysis of microphotometer records[8] has led to the value C–C = 1.390 ± 0.005 Å. for the edge of the plane hexagon formed by the carbon atoms, in agreement with the values 1.39 ± 0.03 Å. and 1.40 ± 0.03 Å. reported by Wierl.[1] The accuracy of this determination and the fact that the various carbon–carbon distances are geometrically related

TABLE II

BROMINE

	I_k			
k	A	B	C	s_k
1	6	32	16	3.50
2	5	16	12	6.17
3	4	8	8	8.90
4	3	4	4	11.67
5	2	2	2	14.44
6	1	1	1	17.19

TABLE III

CHLORINE

k	I_k	s_k
1	10	3.94
2	5	6.99
3	2	10.08
4	1	13.30

TABLE IV

BENZENE

k	I_k	s_k
1	50	3.35
2	160	5.805
3	20	9.55
4	5	11.50
5	15	13.83
6	3	16.23
7	8	18.66

make benzene a suitable substance for testing the new method.

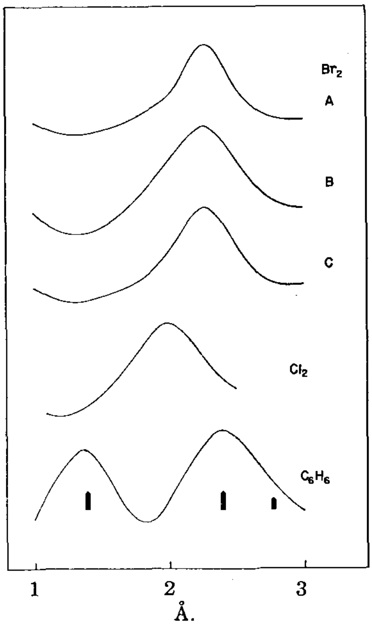

Fig. 3.—Radial distribution curves for bromine, chlorine and benzene.

The radial distribution curve calculated with the inclusion of seven terms, for which data are given in Table IV (the fourth and sixth terms corresponding to apparent shelves rather than well-defined rings), is shown in Fig. 3.

Only the two principal distances, corresponding to the six ortho C–C interactions and the six meta C–C interactions, are represented by maxima, the three para C–C interactions (which should yield a hump about one-half as pronounced as the others at the position indicated by the smallest arrow) and the various C–H interactions not being indicated on the curve. This is in agreement with our experience in general with the radial distribution method, which usually can be relied on (in the form in which we are using it) to provide information regarding only the two or three most important interactions, the peaks for which must also be separated by at least about 0.5 Å. in order to be resolved.

The two maxima occur at the distances 1.381 and 2.390 Å., their ratio being 1:1.731. The close approximation of this ratio to the value $1:\sqrt{3}$ required by the hexagonal configuration of the molecule provides an interesting check on the method.

The value 1.381 Å. is 0.009 Å. less than that found in the earlier treatment. We believe that in this case the earlier treatment, involving the analysis of microphotometer records as well as the application of the usual visual method, is the more reliable, and we prefer not to change from the value 1.390 ± 0.005 Å. Indeed, we think that the usual visual method is itself somewhat more reliable than the radial distribution method in the case of benzene, inasmuch as the photographs show some precisely measurable features (very sharp fourth minimum and fourth maximum) as well as some rather diffuse rings which can be measured only with less precision; in the usual visual method great weight can be given to the results calculated from the precisely measured features, whereas in the radial distribution method the weighting is determined by the intensities of the rings, the result being dependent on the diffuse as well as the sharp ones.

Tetrahedral Molecules.—The tetrahedral molecules MX_4 permit an interesting test of the radial distribution method in that the ratio of the two distances X–X and M–X should be $2\sqrt{2}/\sqrt{3} = 1.633$. We have seen that in carbon tetrachloride this ratio is given by the curve to within about 1%. The compounds CF_4, SiF_4,

$SiCl_4$, $GeCl_4$ and $SnCl_4$ provide better tests, inasmuch as the two maxima arise from more nearly equal interactions. The curves for these five molecules, calculated for the constants[10] given in Table V, are shown in Fig. 4. It is seen that each curve shows two well-defined peaks, that for X–X being stronger than that for M–X in CF_4 and $SiCl_4$, and weaker in the other three. The lack of symmetry of the peaks (particularly pronounced for $GeCl_4$) could presumably be remedied by changing the estimated values of I_k; though such a procedure might be justified, we have not adopted it, retaining instead the original estimates in every case.

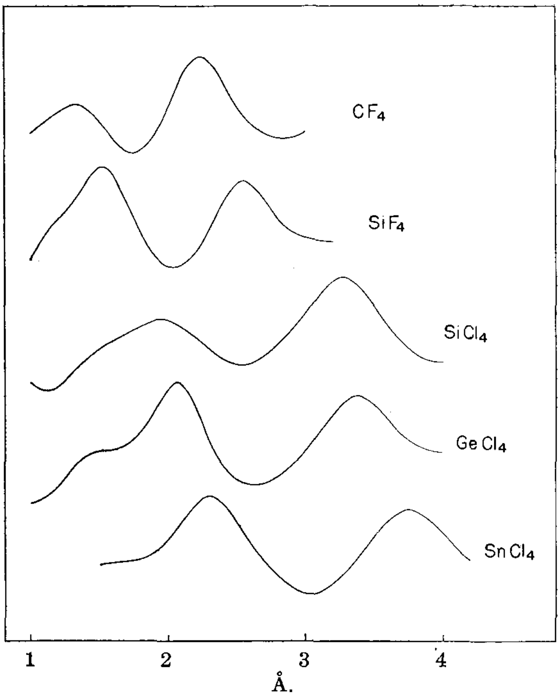

Fig. 4.—Radial distribution curves for carbon and silicon tetrafluorides and silicon, germanium and tin tetrachloride.

The values of l for the X–X and M–X peaks are given in Table VI, together with their ratios. It is seen that the ratio is in every case slightly higher than the correct value 1.633. The deviations of 0.3 to 2.7% provide some indication as to the reliability of the method; there seems to be some tendency for the maxima of the two peaks to be displaced away from one another.

TABLE V

TETRAHALIDES

	CF₄		SiF₄		SiCl₄		GeCl₄		SnCl₄	
k	I_k	s_k	I_k	s_k	I_k	s_k	I_k	s_k	I_k	s_k
1	10	3.56	40	5.41	15	2.55	3	2.29	60	3.67
2	25	6.18	20	8.27	40	4.25	30	4.09	60	5.62
3	10	9.28	5	9.97	15	6.29	20	6.27	20	6.70
4	3	12.06	10	13.02	5	8.04	8	7.22	16	8.78
5	3	14.49	3	17.27	8	9.90	15	9.75	8	11.67
6			1	21.34	1	11.89	6	12.75	4	14.23
7					3	13.85	3	15.46	2	16.79
8					1	15.93	2	18.51		

TABLE VI

DISTANCES IN TETRAHALIDE MOLECULES

Compound	CF₄	SiF₄	CCl₄	SiCl₄	GeCl₄	SnCl₄
X–X, Å.	2.235	2.555	2.870	3.274	3.385	3.760
M–X, Å.	1.335	1.527	1.74	1.963	2.070	2.295
Ratio	1.674	1.673	1.649	1.668	1.635	1.638

Carbon Disulfide and Carbon Oxysulfide.—Radial distribution curves for carbon disulfide and carbon oxysulfide (treated by the usual method by Cross and Brockway[11]) are shown in Fig. 5. For carbon disulfide the maxima of the two peaks occur at 1.60 and 3.07 Å. In this symmetrical linear molecule the C–S distance is just one-half the S–S distance; the values found deviate from this ratio by 4%. Similarly in carbon oxysulfide the sum of two interatomic distances equals the third. The values C–S = 1.60 Å. and O–S = 2.70 Å. given by the two maxima differ by 1.10 Å. The C–O distance is not given by the curve (being indicated only by a hump at the point indicated by the arrow); there is little doubt that the value 1.16 ± 0.02 Å. found by Cross and Brockway is

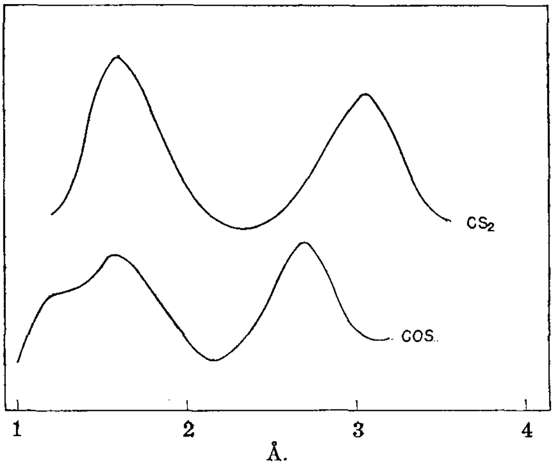

Fig. 5.—Radial distribution curves for carbon disulfide and carbon oxysulfide.

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[10] The s_k values are in the main taken from (a) L. O. Brockway and F. T. Wall, THIS JOURNAL, **56**, 2373 (1934), and (b) L. O. Brockway, *ibid.*, **57**, 958 (1935), with values for shelves (not given in these papers) obtained by measurement of the original photographs.

[11] P. C. Cross and L. O. Brockway, *J. Chem. Phys.*, **3**, December (1935).

reliable, however, showing that there is an error of about 3% in the values given by the maxima. It is interesting to note that the two peaks for these curves are displaced toward one another, rather than away from one another as for the tetrahalides.

The comparison with the interatomic distance values reported by Cross and Brockway, C–S = 1.54 ± 0.03 Å. and S–S = 3.08 ± 0.06 Å. in CS_2, C–O = 1.16 ± 0.02 Å., C–S = 1.56 ± 0.03 Å., and O–S = 2.72 ± 0.05 Å. in COS, indicates that of the two peaks of these radial distribution curves the outer one is somewhat more reliable than the inner one.

TABLE VII

CARBON DISULFIDE AND CARBONYL SULFIDE

Ring	CS_2 *I*	CS_2 *s*	COS *I*	COS *s*
1	50	4.713	15	5.23
2	12	6.312	10	7.67
3	16	8.698	4	9.82
4	4	10.63	6	12.20
5	8	12.65	2	14.04
6	2	14.58	3	16.65
7	4	16.81		
8	1	18.7		
9	2	21.0		

Discussion of the Method

From the examples given we see that the radial distribution method in the simplified form which we have developed for the treatment of electron diffraction photographs of gas molecules is reasonably reliable and accurate, usually providing values of the two or three most important interatomic distances in the molecule (that is, those which contribute most to the diffraction pattern) with an accuracy of 1 or 2%. Probably the principal advantage of the method is that its application is straightforward; no previous information or hypothesis regarding the structure of the molecule (or, in fact, regarding even the chemical composition of the scattering gas) is needed. The information provided by a radial distribution curve usually eliminates all models of the molecule under consideration except those defined by a narrow range of values of the structural parameters; these models can then be considered in detail by the usual method, this consideration usually leading to a further restriction in the parameter values. The calculation of a radial distribution curve is thus the logical first step in the analysis of an electron diffraction photograph. Examples showing the use of these curves are included in the following paper.

We recommend that in general values of interatomic distances given by the two methods be averaged, with about equal weights unless it is felt that in a special case one method is more satisfactory than the other. The usual visual method is superior to the radial distribution method under circumstances such as the following: (1) when there are geometrical relations among interatomic distances (CS_2, C_3O_2, benzene, etc.); (2) when the photographs show some especially precisely measurable features, such as some very sharp rings (benzene); (3) when knowledge regarding certain structural parameters is available and it is desired to vary only the others; (4) when the molecule contains two or more important interatomic distances with values so close to one another that the corresponding peaks are not resolved on the radial distribution curves. On the other hand, the radial distribution method is superior in cases such as the following: (1) when the molecule contains rotating groups or some other structural feature making the detailed formulation of a model difficult (S_2Cl_2, etc.); (2) when the decision as to the model depends on quantitative intensity estimates and small changes in ring diameters (ClO_2, SO_2, etc.).

Revised Values of Structural Parameters of Molecules

On calculating radial distribution curves for molecules for which structures have been previously reported from this Laboratory on the basis of the usual method of interpretation, we have in some cases obtained interatomic distance values agreeing exactly with the earlier values and in some cases values which deviate by a small amount (rarely more than 3%). For a few molecules the new method has provided information (bond angles in ClO_2 and SO_2) not before available. We feel that it is worth while to present a table of revised values of structural parameters for these molecules, giving weight to the results of both methods. The revision includes most of the substances which have been studied in this Laboratory; some (methyl azide, diacetylene, carbon suboxide, dioxane, etc.) are omitted because of the small number of rings shown on the photographs or the unsuitability of the radial distribution method (for reasons such as those mentioned above).

Benzene.—We recommend no change in the value C–C = 1.390 ± 0.005 Å. in benzene.

Tetrahalides.—Values of M–X and (X–X)/1.633 given by the maxima on the radial distribution curves (Figs. 1 and 4) for six tetrahalides are shown in the second and third columns of Table XI, with the values obtained by the usual visual method[10a] in the fourth column. In averaging these we have assigned weights to the two radial distribution peaks as indicated by their prominence, and have given the two distinct methods about equal weight. It is seen that in no case is the change made greater than 1%.

Trihalides of Phosphorus and Arsenic.—Radial distribution curves for PF_3, AsF_3, PCl_3 and $AsCl_3$, calculated with the data given in Table VIII, are shown in Fig. 6. Each curve shows two peaks, corresponding to M–X and X–X; values for their maxima (except for X–X in AsF_3, this peak being so broad as to make its maximum unreliable) are given in Table XII, together with the values obtained by the usual visual method in an earlier investigation.[10a] The weighted averages for M–X, X–X and the X–M–X angle are given in the last three columns.

TABLE VIII

TRIHALIDE MOLECULES

	PF_3		AsF_3		PCl_3		$AsCl_3$	
Ring	*I*	*s*	*I*	*s*	*I*	*s*	*I*	*s*
1	4	5.74	10	4.73	5	2.76	2	2.33
2	2	8.82	5	8.09	15	4.54	20	3.944
3	1	13.45	2	11.77	10	6.66	10	6.234
4			1	15.26	1	8.75	3	9.55
5					4	10.38	2	12.13
6					3	12.58		

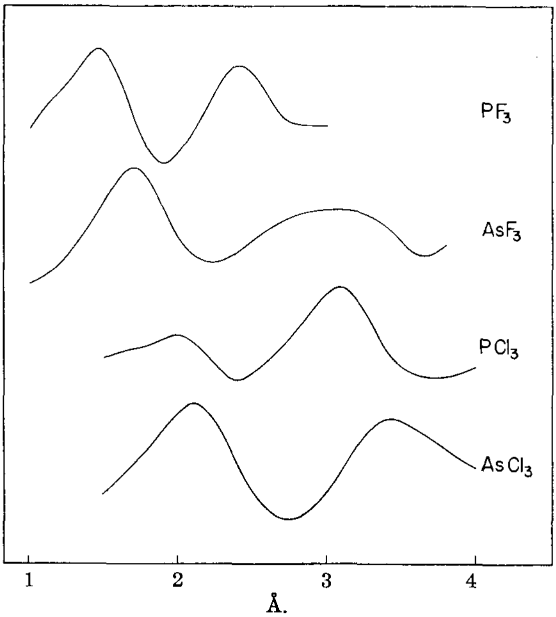

Fig. 6.—Radial distribution curves for triflourides and trichlorides of phosphorus and arsenic.

Methylene Chloride and Chloroform.—Curves for CH_3Cl, CH_2Cl_2 and $CHCl_3$ (Table IX) are shown in Fig. 7. The maximum for methyl chloride lies at 1.80 Å.; we do not consider this value sufficiently reliable to warrant a change from the value C–Cl = 1.77 ± 0.02 Å. previously reported.[12] The M–X and X–X values given by the maxima for methylene chloride and chloroform (Table XII) are in excellent agreement with those found by the usual method.

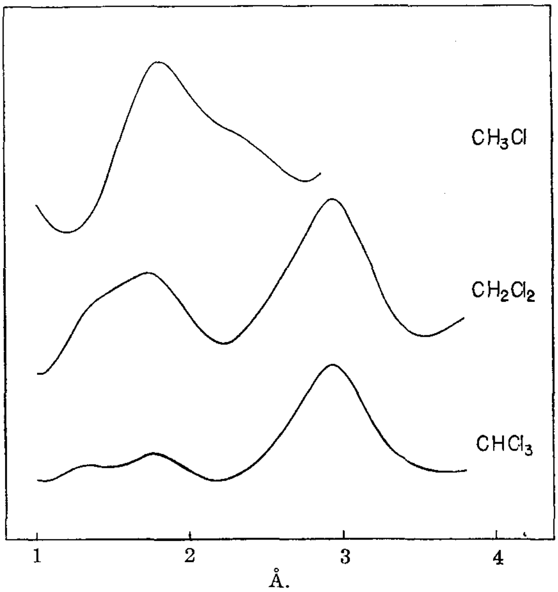

Fig. 7.—Radial distribution curves for methyl chloride, methylene chloride and chloroform.

TABLE IX

	CH_3Cl		CH_2Cl_2		$CHCl_3$	
Ring	*I*	*s*	*I*	*s*	*I*	*s*
1	15	4.07	15	2.81	25	2.74
2	8	8.12	40	4.81	40	4.78
3	3	11.24	15	7.00	20	6.99
4	1	14.49	8	8.84	10	9.04
5			10	11.01	15	11.16
6			3	13.28	3	13.32
7			5	15.41	3	15.32
8			1	17.94	1	17.47

Chlorine Monoxide, Dimethyl Ether, Chlorine Dioxide and Sulfur Dioxide.—The radial distribution curves for Cl_2O, $(CH_3)_2O$, ClO_2 and SO_2 (Fig. 8) show two peaks, the positions of the

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(12) Sutton and Brockway, THIS JOURNAL, **57**, 473 (1935).

maxima being recorded in Table XII. For chlorine monoxide we have averaged the results of the two methods with equal weights (the agreement being less satisfactory than usual). In the case of dimethyl ether smaller weight is given to the results of the radial distribution method because of the lack of symmetry of the first peak, which may cause the maximum to be displaced. It is interesting to note that the radial distribution method provides values of the angles in ClO_2 and SO_2, whereas the usual method of interpretation failed in this respect, presumably because the qualitative comparisons must be supplemented by quantitative considerations in order to obtain this information.

TABLE X

	ClO_2		$(CH_3)_2O$		ClO_2		SO_2	
Ring	*I*	*s*	*I*	*s*	*I*	*s*	*I*	*s*
1	5	2.801	10	6.024	5	4.98	10	5.625
2	15	4.835	4	9.744	2	9.25	6	9.66
3	3	7.328	2	13.63	1	13.68	2	13.76
4	1	9.14	1	17.78			1	18.15
5	1	11.45						

TABLE XI

M–X DISTANCES IN TETRAHALIDE MOLECULES

	Radial distribution M–X	X–X/1.633	Visual method	Final values of M–X
CF_4	1.335 Å.	1.369 Å.	1.360 Å.	1.36 ± 0.02 Å.
SiF_4	1.527	1.565	1.544	1.54 ± 0.02
CCl_4	(1.74)	1.749	1.760	1.755 ± 0.005
$SiCl_4$	1.963	2.005	2.016	2.00 ± 0.02
$GeCl_4$	2.070	2.073	2.103	2.08 ± 0.02
$SnCl_4$	2.295	2.303	2.289	2.30 ± 0.02

Summary

It is shown by empirical tests that the radial distribution function given by a sum of Fourier terms corresponding to the rings observed on an electron diffraction photograph of gas molecules (using visually measured ring diameters and estimated intensities) provides values of the important interatomic distances accurate to one or two per cent. (probable error). The substances used in the tests include carbon tetrachloride and other tetrahalides, bromine, chlorine, benzene, carbon disulfide and carbon oxysulfide.

TABLE XII

INTERATOMIC DISTANCES IN MOLECULES MX_2 AND MX_3

	Radial distribution			Visual method			Final values		
	M–X	X–X	Angle	M–X	X–X	Angle	M–X	X–X	Angle
PF_3	1.47 Å.	2.41 Å.	110°	1.56 Å.	2.37 Å.	99°	1.52 ± 0.04 Å.	2.39 ± 0.03 Å.	104 ± 4°
AsF_3	1.70	...	...	1.73	...	...	1.72 ± .02	... ...	... ..
PCl_3	1.98	3.08	102	2.02	3.09	100	2.00 ± .02	3.09 ± 0.02	101 ± 2
$AsCl_3$	2.13	3.43	107	2.18	3.36	101	2.16 ± .03	3.39 ± .04	103 ± 3
CH_2Cl_2	(1.73)	2.935	...	1.77	2.92	111	1.77 ± .02	2.93 ± .02	112 ± 2
$CHCl_3$	(1.77)	2.931	...	1.78	2.93	111	1.77 ± .02	2.93 ± .02	112 ± 2
Cl_2O	1.65	2.86	120	1.71	2.82	111	1.68 ± .03	2.84 ± .03	115 ± 4
$(CH_3)_2O$	1.38	2.28	111	1.44	2.39	111	1.42 ± .03	2.35 ± .05	111 ± 4
ClO_2	1.53	2.85	137	1.53	...	...	1.53 ± .02	2.85 ± .15	137 ± 15
SO_2	1.43	2.56	127	1.46	...	...	1.45 ± .02	2.56 ± .15	124 ± 15

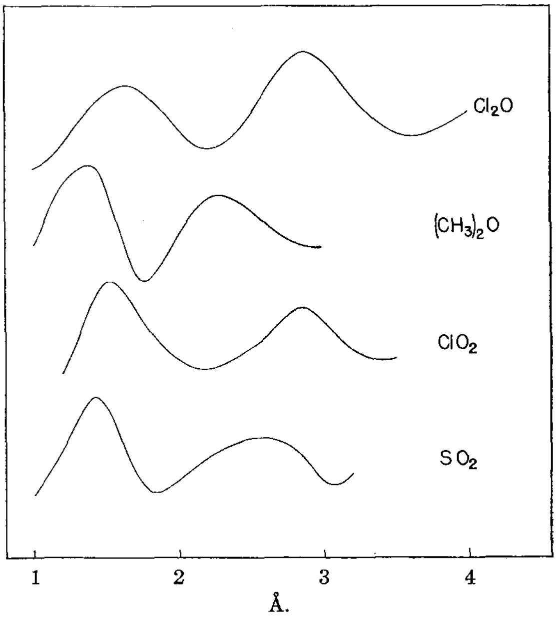


Fig. 8.—Radial distribution curves for chlorine monoxide, dimethyl ether, chlorine dioxide and sulfur dioxide.

The radial distribution method of interpretation is applied to a number of molecules previously investigated, and revised values of interatomic distances and bond angles, obtained by considering the results of this method as well as of the usual visual method, are presented (Tables XI and XII).

It is pointed out that the radial distribution method is particularly satisfying in that it leads directly to the values of the important interatomic distances in the molecule, thus eliminating many possible models and usually limiting the molecule to the structures represented by small ranges of values of the structural parameters.

PASADENA, CALIFORNIA RECEIVED SEPTEMBER 24, 1935

[Reprint from the Journal of the American Chemical Society, 59, 13 (1937).]

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 572]

The Adjacent Charge Rule and the Structure of Methyl Azide, Methyl Nitrate, and Fluorine Nitrate

BY LINUS PAULING AND L. O. BROCKWAY

With the recognition of the fact that in many cases the normal state of a molecule cannot be represented satisfactorily by a single valence-bond structure of the Lewis type but can be approximated by a combination of several such structures (among which it is said to resonate) there arose the problem of determining for each resonating molecule the magnitudes of the contributions of various reasonable structures. Information regarding these magnitudes is being obtained in many ways, such as from the interpretation of experimental values of interatomic distances, force constants, electric dipole moments, etc., and some progress is being made in the formulation of empirical rules expressing this information in a succinct form. Four years ago it was pointed out[1] that the observed moment of inertia of nitrous oxide corresponds to resonance between the structures $:\overset{-}{\ddot{N}}=\overset{+}{N}=\ddot{O}:$ and $:N\equiv\overset{+}{N}-\overset{-}{\underset{\cdot\cdot}{\ddot{O}}}:$, the third reasonable structure, $:\overset{-}{\underset{\cdot\cdot}{\ddot{N}}}-\overset{+}{N}\equiv\overset{+}{O}:$, making no appreciable contribution, whereas the closely similar molecule carbon dioxide resonates among all three analogous structures; and in explanation of this unexpected fact the suggestion was advanced that, in general, structures in which adjacent atoms have electrical charges of the same sign are much less important than other structures, the diminution in importance resulting from the increase in coulomb energy corresponding to the adjacent charges. This *adjacent charge rule* was reported also to apply to the methyl azide molecule.[2] We have now reinvestigated methyl azide by electron diffraction and have similarly studied methyl nitrate and fluorine nitrate. The configurations found for all of these substances are those predicted on the basis of the rule.

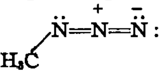
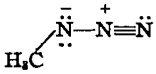
Methyl Azide.—In our earlier investigation of methyl azide[2] it was concluded that the molecules contain a linear azide group with dimensions corresponding to resonance between the structures  and . The photographs used in this work were very light, showing only one measurable apparent maximum and one minimum. With improved technique we have now obtained photographs of methyl azide showing five well-defined apparent maxima, the interpretation of which has led to the verification and refinement of the earlier results. The

TABLE I

METHYL AZIDE

Max.	Min.	I	s, obsd.	s, calcd. for model H-120°	s, calcd. for model I-120°	C-N for model H-120°, Å.	C-N for model I-120°, Å.
1		5	6.17	6.15	6.28	1.465	1.496
2		2	8.32	8.26	8.36	1.460	1.477
	3		10.20	9.70	10.15	1.397	1.461
3		3	11.49	11.49	11.77	1.470	1.507
	4		12.75	12.47	12.70	1.437	1.464
4		1	13.81	13.68	13.66	1.455	1.454
	5		15.54	15.20	15.38	1.438	1.455
5		1	16.77	17.12	17.40	1.500	1.524
					Average C–N =	1.453	1.480
					N–N′ =	1.246	1.229
					N′–N″ =	1.087	1.107

Averaged results:
C–N = 1.47 ± 0.02 Å.
N–N′ = 1.24 ± 0.02 Å.
N′–N″ = 1.10 ± 0.02 Å.

Angle C–N–N = 120 ± 5°

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(1) L. Pauling, *Proc. Nat. Acad. Sci.*, **18**, 498 (1932).

(2) L. O. Brockway and L. Pauling, *ibid.*, **19**, 860 (1933).

sample of methyl azide used was part of that prepared for the first investigation by Dr. G. W. Wheland. The photographs were taken with a film distance of about 10 cm. and electron wave lengths of about 0.06 Å.

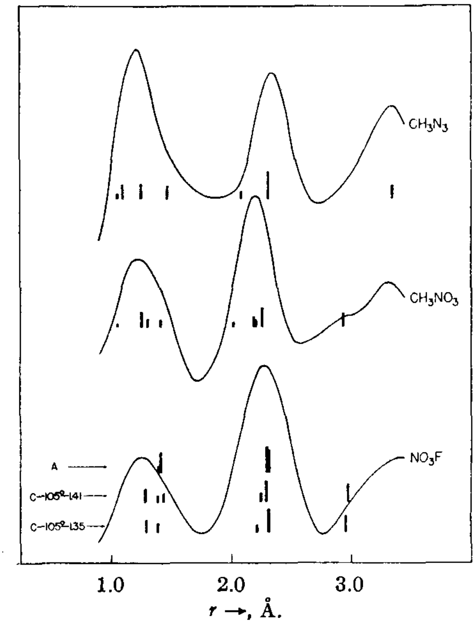
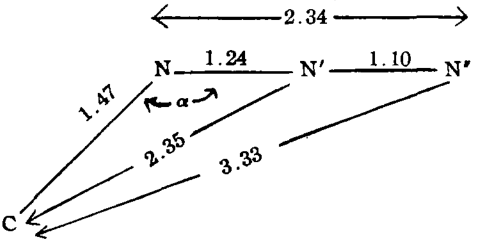


Fig. 1.—Radial distribution curves for methyl azide, methyl nitrate, and fluorine nitrate.

The measured s values and estimated intensities, averaged for sixteen photographs, given in Table I lead to the radial distribution curve shown in Fig. 1, with principal peaks at 1.22, 2.34, and 3.33 Å. These correspond closely with C–N = 1.47 Å. (the sum of the single-bond covalent radii), N–N = 1.24 and 1.10 Å., and the C–N–N angle = 120°, the peak at 1.22 Å. representing the unresolved distances 1.10, 1.24, and 1.47 Å. This correspondence was verified in the usual way by the comparison of the photographs with calculated intensity curves. In Fig. 2 there are shown curves for models containing a linear azide group,[3] defined by the following values of the distances N–N′ and N′–N″, respectively: E, 1.10, 1.10; F, 1.26, 1.26; G, 1.26, 1.16; H, 1.26, 1.10; I, 1.22, 1.10; the angle α having the value 180° for E and 125° for F and G, and the values shown for H and I. The C–N distance was assumed to be 1.47 Å., the C–H distances 1.06 Å., and the carbon angles were assumed to be tetrahedral. All interactions were considered, with one orientation of the methyl group.



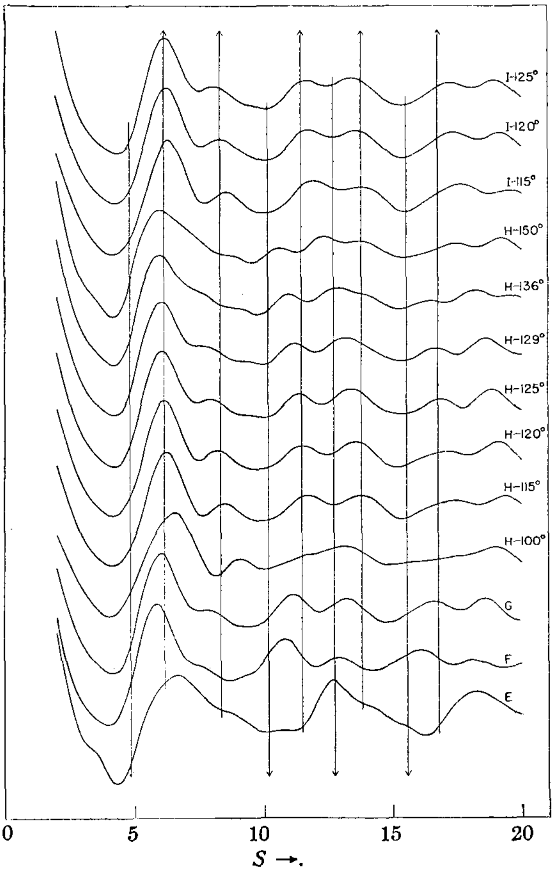


Fig. 2.—Theoretical intensity curves for methyl azide.

It is seen that all of the curves show pronounced disagreement with the photographs except H–120° and I–120° and their immediate neighbors. For these curves the qualitative and quantitative comparisons are satisfactory. The agreement for the second, third, and fourth peaks is somewhat better for the 120° curves than for the 115 or 125° curves, and we accept for the nitrogen bond angle the value 120 ± 5°, which is at the lower edge of the range of values 135 ± 15°

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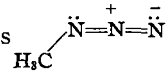
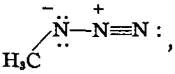
[3] The new photographs, like the old ones, are incompatible with a cyclic configuration.

previously reported. The quantitative comparison (Table I) leads to the interatomic distances C–N = 1.47 ± 0.02 Å., N–N′ = 1.24 ± 0.02 Å., and N′–N″ = 1.10 ± 0.02 Å. This final configuration of the model is identical with that indicated by the radial distribution curve.

These results are in good accord with the assumption that the molecule resonates between the two electronic structures  $H_3C{-}\ddot{N}{=}\overset{+}{N}{=}\overset{-}{\ddot{N}}{:}$ and  $H_3C{-}\overset{-}{\ddot{N}}{-}\overset{+}{N}{\equiv}N{:}$, the N–N′ distance having essentially the double-bond value and the N′–N″ distance the triple-bond value.[4] The value 120° for the nitrogen bond angle, intermediate between those expected for a single and a double bond (125° 16′) and for two single bonds (109° 28′), is also not unreasonable.

Methyl Nitrate.—Methyl nitrate was prepared from methyl alcohol, nitric acid, and urea nitrate by Mr. Willard McRary under the direction of Professor H. J. Lucas. The product was washed repeatedly with water and dried, and then was redistilled three times.

The photographs show six well-defined and nearly uniformly separated rings, with *s* values and estimated intensities as given in Table II.

TABLE II

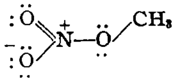
METHYL NITRATE

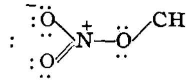
Max.	Min.	I	*s*, obsd.	*s*, calcd. for model II–105°	*s*, calcd. / *s*, obsd.
1		1	3.50	3.23	(0.923)
	2		4.67	4.17	(0.893)
2		5	6.34	6.34	1.000
	3		7.92	7.98	1.008
3		3	9.44	9.40	0.996
	4		10.69	10.50	.982
4		2	11.93	11.60	.973
	5		13.50	13.18	.976
5		1	14.87	15.20	1.022
	6		16.21	16.50	1.018
6		1	17.71	17.68	.998
				Average	0.997

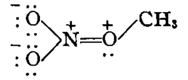
Results (model II–105°): N–O = 1.26, 1.26, 1.36 Å.
O–C = 1.43 Å.
Angle N–O–C = 105 ± 5°

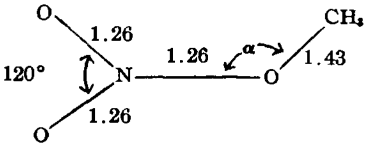
The six-term radial distribution function (Fig. 1) has a broad peak at about 1.24 Å., a sharper peak at 2.21 Å., and another at 3.32 Å. These are compatible with the models discussed below, but provide no basis for choice among them.

The number of parameters determining the structure of the molecule is so great that it was not possible to carry out a thorough investigation involving their independent variation. We have accordingly contented ourselves with the attempt to decide between the two most reasonable structures. The first, representing resonance among the three structures A, B, and C, leads to the predicted dimensions shown below, all three N–O bonds having approximately the double bond distance.


A

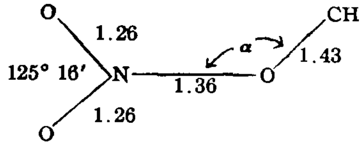

B


C



I

The methyl group is restricted to the plane of the nitrate group by the double-bond character of the N–OCH_3 bond. For α a value of about 120 or 125° would be expected; curves calculated for 120, 125, and 130° are shown in Fig. 3. The second reasonable structure, representing resonance between A and B only, corresponds to essentially the double-bond distance for two of the N–O bonds and the single-bond distance for the third.



II

Steric effects probably tend to keep the methyl group out of the plane of the nitrate group. The curves of Fig. 3 are calculated on this assumption; we have found that they are changed only slightly by the assumption of free rotation of the OCH_3 group about the N–O bond. For α a value close to the tetrahedral value 109° 28′ is expected; curves for α = 100, 105, 110, and 115° are shown.

All of the curves show rough agreement with the photographs; the curves for model I are,

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[4] L. Pauling, L. O. Brockway and J. Y. Beach, THIS JOURNAL, 57, 2705 (1935).

however, all inferior to curve II–105° in regard to the observation of six well-shaped and nearly uniformly spaced rings. Curve II–105° is in nearly complete agreement with the experimental data, the greatest quantitative discrepancy, 3%, being shown by the fourth maximum (see Table II). We accordingly accept model II with α = 105° as supported by the electron diffraction data. The quantitative comparison verifies the interatomic distance values N–O = 1.36 Å. (for the oxygen atom with methyl attached), N–O = 1.26 Å. (for the other oxygen atoms), and O–C = 1.43 Å. to about ± 0.05 Å., the N–O–C bond angle being given the value 105 ± 5°. This configuration is compatible with the radial distribution curve (Fig. 1).

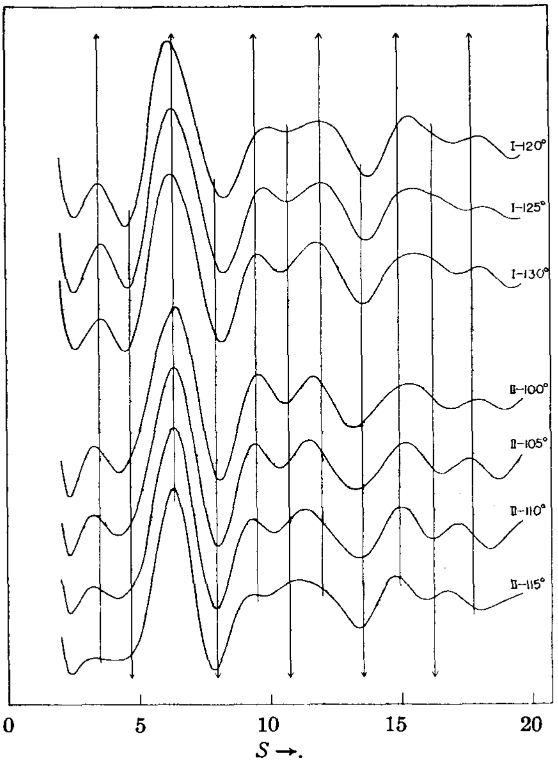

Fig. 3.—Intensity curves for methyl nitrate.

Fluorine Nitrate.—Fluorine nitrate, NO_3F, was first prepared by G. H. Cady[5] in 1934 by bubbling fluorine through dilute nitric acid. At the suggestion of Professor W. A. Noyes, we undertook the electron diffraction investigation of the vapor in order to determine where the fluorine atom is attached and what effect it has on the nature of the bonds in the NO_3 group. Professor D. M. Yost and Mr. A. Beerbower of these Laboratories[6] prepared samples of fluorine nitrate by Cady's method (using the original apparatus of Dr. Cady), and also by another method, consisting in passing fluorine over solid potassium nitrate, and kindly provided us with some of the substance for the electron diffraction work. The vapor of the substance at about 300 mm. pressure was held in a one-liter glass flask connected to the electron diffraction apparatus through an ordinary stopcock. The photographs obtained from the first sample showed four rings. An attempt to prepare heavier photographs from another sample was made unsuccessful by the explosion of the substance at the instant of making the first exposure. It was previously thought that fluorine nitrate gas was stable at room temperature, and the cause of the explosion is still unknown.

The s values and the visually estimated intensities for the four rings observed in the photographs are given in Table IV. The radial distribution function (Fig. 1) shows maxima at 1.27 and 2.29 Å., the second being about twice as large as the first.

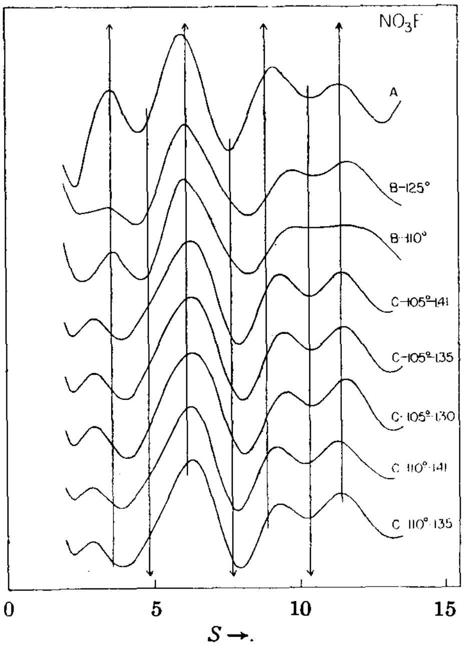

Fig. 4.—Intensity curves for fluorine nitrate.

The molecular models upon which the theoretical intensity curves of Fig. 4 are based have been chosen to distinguish between the three most probable configurations of fluorine nitrate. The

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(5) G. H. Cady, THIS JOURNAL, 56, 2635 (1934).

(6) D. M. Yost and A. Beerbower, *ibid.*, 57, 781 (1935).

first, suggested to us by Professor W. A. Noyes, involves a tetrahedral arrangement of the fluorine and oxygen atoms around the nitrogen atom, in which the bond angles are all 109° 28′ and the ratio of the N–F to the N–O distances is 0.985; the corresponding curve is marked A. The other two models are similar to those considered above for methyl nitrate. In the second (B) the double bond in the NO_3 groups is assumed to resonate equally among the three N–O bonds and the fluorine atom lies in the plane of the other atoms, with the interatomic distances as shown in Table III. In the third (C) the resonance of the double bond does not involve the oxygen atom to which the fluorine is attached (O′) but is restricted to the other two positions; with this structure the molecule is no longer coplanar but instead the NO′F plane is perpendicular to the NO_3 plane.

TABLE III

MODELS FOR NO_3F

Model	NO	NF	NO′	O′F	<ONO	<NO′F
A	1.40	1.38			109° 28′	
B–125°	1.26		1.26	1.34	120°	125°
B–110°	1.26		1.26	1.34	120°	110°
C–105°–1.41	1.26		1.36	1.41	125°	105°
C–105°–1.35	1.26		1.36	1.35	125°	105°
C–105°–1.30	1.26		1.36	1.30	125°	105°
C–110°–1.41	1.26		1.36	1.41	125°	110°
C–110°–1.35	1.26		1.36	1.35	125°	110°

The models for complete resonance, B, are eliminated because in the corresponding curves the third and fourth maxima are not well resolved from each other, as they are in the photographs. The remaining six curves are more satisfactory in this respect, the relative heights of the third and fourth maxima showing better agreement with the photographs for the curves A, C–105°–1.41, and C–105°–1.35 than for the other three.

TABLE IV

FLUORINE NITRATE

Max.	Min.	I	*s*, obsd.	*s*, calcd C–105° –1.41	*s*, calcd C–105° –1.35	*s*, calcd./*s*, obsd. C–105°– 1.41	*s*, calcd./*s*, obsd. C–105°– 1.35
1		2	3.56	2.95	2.97	(0.829)	(0.834)
	2		4.84	3.87	3.97	(0.800)	(0.821)
2		5	6.16	6.29	6.29	1.021	1.021
	3		7.66	7.89	8.04	1.030	1.050
3		2	8.88	9.34	9.46	1.052	1.065
	4		10.36	10.36	10.41	1.000	1.005
4		1	11.45	11.46	11.52	1.001	1.006
					Average	1.021	1.029
					N–O	1.286 Å.	1.296 Å.
					N–O′	1.389	1.400
					O–F	1.440	1.390

Model A cannot be eliminated definitely by the photographs; there are, however, some points which make this model improbable. From the curve for this model the first minimum would be expected to be at least as well pronounced as the second minimum, whereas on the photographs the first minimum is not very well defined. That the qualitative appearance of the photographs supports model C rather than model A is further shown by the fact that the photographs resemble those of methyl nitrate more closely than those of carbon tetrafluoride. Some evidence is also provided by the radial distribution curve (Fig. 1), the first peak being displaced by 0.15 Å. from the position expected for it for model A. For these reasons and the additional reason that it is difficult to correlate the tetrahedral configuration with an electronic structure involving only completed octets, we consider model A not to be satisfactory.[7]

The curves C–105°–1.41 and C–105°–1.35 are in reasonably good qualitative and quantitative agreement with the photographs, the discrepancies shown by the first maximum and second minimum being no larger than usual for inner rings. The quantitative comparison (Table IV) leads to the average interatomic distances N–O = 1.29 Å., N–O′ (with fluorine attached) = 1.39 Å., and O′–F = 1.42 Å., with probable errors of about ± 0.05 Å. The bond angles are O–N–O = 125 ± 5° and N–O′–F = 105 ± 5°. This configuration is compatible with the radial distribution curve (Fig. 1).

The Adjacent Charge Rule.—There are thus now known four substances (nitrous oxide, methyl azide, methyl nitrate, and fluorine nitrate) with configurations supporting the adjacent charge rule. That this rule is reasonable can be seen from the following argument. In general a valence-bond structure involving two charged atoms with opposite signs may correspond to about the same energy value as a structure involving uncharged atoms, the difference between the ionization energy of one atom and the electron affinity of the other being approximately compensated by the coulomb energy of the charges. For example, the coulomb interaction of the charges + *e* and − *e* 2.30 Å. apart stabilizes the structures $\overset{-}{:}\underset{\cdot\cdot}{\ddot{O}}{-}C{\equiv}\overset{+}{O}:$ and $:\overset{+}{O}{\equiv}C{-}\underset{\cdot\cdot}{\ddot{O}}\overset{-}{:}$ for carbon dioxide by 6.3 e. v., which

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[7] Quantitative comparison for this model leads to the interatomic distances N–O = 1.42 Å., N–F = 1.40 Å.

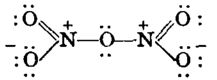
is roughly equal to the estimated energy required to remove an electron from one bound oxygen atom and attach it to another; it is accordingly not unreasonable that these two structures contribute about equally with the structure $:\ddot{O}{=}C{=}\ddot{O}:$ to the normal state of the molecule. For nitrous oxide the two structures ${}^{-}{:}\ddot{N}{=}\overset{+}{N}{=}\ddot{O}:$ and $:N{\equiv}\overset{+}{N}{-}\ddot{O}\overset{-}{:}$ have nearly equal covalent bond energies and coulomb energies and would be expected to make about equal contributions. The structure ${}^{-}{:}\underset{..}{\ddot{N}}{-}\overset{+}{N}{\equiv}\overset{+}{O}:$, however, with adjacent positive charges adding a large positive quantity to the energy of the molecule, corresponds to a higher energy value than the other two structures, and accordingly makes no significant contribution to the normal state of the molecule.

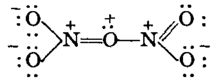
The principal application of the adjacent charge rule is to the compounds of nitrogen. In many compounds a nitrogen atom forms four covalent bonds and has a positive charge; the adjacent charge rule then prevents resonance to structures in which an atom attached to this nitrogen atom also has a positive charge. The covalent azides and nitrates are the principal substances of this type. It is interesting to note that the adjacent charge rule provides an explanation of the large differences in stability shown by covalent and ionic azides and nitrates. Covalent azides and nitrates are restricted by the rule to resonance between two important structures, whereas the ions resonate among three structures. The resonance energy[8] for two structures is about 1 e. v. and for three structures about 2 e. v.; hence ionic azides and nitrates are more stable than the covalent substances by about 25,000 cal. per mole. We accordingly understand why the alkali and alkaline earth azides[9] can be exploded only at high temperatures whereas the heavy metal azides, chlorazide, cyanuric triazide, and other covalent azides are extremely explosive. Similarly the ionic nitrates are relatively stable, whereas the covalent nitrates (methyl nitrate, nitroglycerine, etc.) are exploded easily. It may be pointed out that the covalent nitrates are more closely related to nitro compounds than to the nitrate ion from the resonance point of view, in that in covalent nitrates, as in nitro compounds, the double bond resonates between two oxygen molecules, whereas in the nitrate ion it resonates among three.

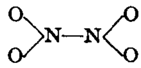
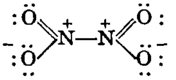
The destabilizing effect of the adjacent charge rule shown in covalent nitrates does not occur in the analogous compounds containing carbon as the central atom, such as carbonates, urea, guanidine, etc., since the quadricovalent carbon atom is neutral.

The question as to whether or not hydrazoic acid and nitric acid are more closely related to the corresponding covalent compounds than to the ions could be answered by determining the configurations of the acids. From general information we would predict that the H–N and H–O bonds are essentially covalent (with perhaps about one-third ionic character) and that the N_3 and NO_3 groups in the acids have the same structures as in methyl azide and nitrates. This prediction is supported by the instability of the acids.

The adjacent charge rule permits resonance of nitrogen pentoxide among the four structures of type A, but excludes the four structures of type B (as well as the structure with two double bonds to the central oxygen atom). We accordingly predict for the molecule a configuration in which the two interatomic distances N–O′ (O′ being the central oxygen atom) have about the single-bond value 1.36 Å. and the four distances N–O have about the double-bond value 1.26 Å., each NO_3 group being coplanar, with the angles ONO equal to about 125° and NO′N to about 110°; the relative orientation of the two NO_3 planes is uncertain, since the single N–O′ bonds permit free rotation.[10]


A


B

The symmetrical configuration  is usually assumed for nitrogen tetroxide.[11] However, the only reasonable electronic structures involving completed octets which can be written for this configuration are the four of the type  which are incompatible with

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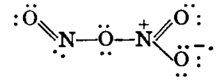
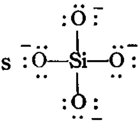
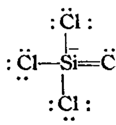
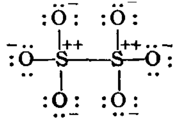
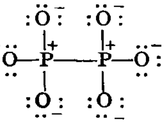
[8] L. Pauling and J. Sherman, *J. Chem. Phys.*, **1**, 606 (1933).

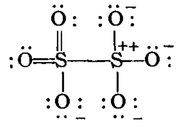
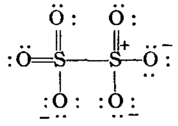
[9] The alkali azides are known to be ionic: S. B. Hendricks and L. Pauling, THIS JOURNAL, **47**, 2904 (1925); L. K. Frevel, *ibid.*, **58**, 779 (1936).

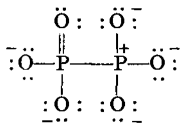
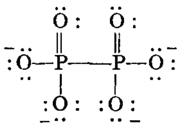
[10] L. R. Maxwell, V. M. Mosley and L. S. Deming, *J. Chem. Phys.*, **2**, 331 (1934), report the values N–O = 1.18 Å. and N–O′ = 1.3–1.4 Å. on the basis of electron diffraction data, in agreement with our structure.

[11] S. B. Hendricks, *Z. Physik*, **70**, 699 (1931); G. B. B. M. Sutherland, *Proc. Roy. Soc.* (London), **A141**, 342, 535 (1933); Maxwell, Mosley and Deming, ref. 10; L. Harris and G. W. King, *J. Chem. Phys.*, **2**, 51 (1934).

the adjacent charge rule. We accordingly believe that nitrogen tetroxide has not this configuration but instead the unsymmetrical configuration corresponding to resonance between the two structures of type .

The adjacent charge rule provides some information regarding the nature of the bonds in the oxygen acids of heavier atoms. It has become customary, following Lewis, to assign to the silicate ion and related groups structures such as , the octet rule being considered to hold for the heavier atoms as well as for the first-row atoms. The discovery of Brockway and Wall[12] that structures such as  are important for silicon tetrachloride and other halides of non-first-row atoms suggests that corresponding structures might be important for the oxygen compounds also. Strong support for this idea is provided by the observed interatomic distances in crystals, as determined by W. L. Bragg, Zachariasen, and others, which are approximately equal to the sums of double-bond radii (Table V), indicating strong resonance to structures involving double bonds.[13] Dithionic acid, $H_2S_2O_6$, and hypophosphoric acid, $H_4P_2O_6$, are stable substances, resisting oxidation even by dichromate.[14] This stability would not be expected for the completed octet structures  and , which run counter to the adjacent charge rule; the rule instead requires us to accept as the important structures for these substances those in which a sulfur atom forms two double bonds and a phosphorus atom one double bond, such as

 ,  etc., and

 ,  etc.

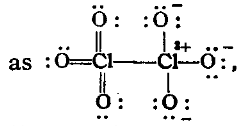
For Cl_2O_6 structures such as , etc., are allowed by the adjacent charge rule. We consider it probable that the dissociation of this substance is due not to its instability (weakness of the Cl–Cl bond) but instead to the unusual stability of the odd molecule ClO_3 through three-electron bond formation, as in the other odd molecules NO_2, NO, ClO_2, etc. It is possible that Cl_2O_6 has an unsymmetrical configuration, O_3Cl–O–ClO_2, analogous to that which we have suggested for N_2O_4; however, chlorine, unlike nitrogen, has more than four orbitals in its outer shell and hence the adjacent charge rule does not eliminate the symmetrical configuration, which we consider to be the more likely one because of analogy with the dithionate and hypophosphate ions.

TABLE V

INTERATOMIC DISTANCES M–O IN IONS MO_4

	SiO_4^{4-}, Å.	PO_4^{3-}, Å.	SO_4^{-} Å.	ClO_4^-, Å.
Observed values	1.60	1.53	1.50	1.48
Sums of single-bond radii	1.83	1.76	1.70	1.65
Sums of double-bond radii	1.65	1.58	1.53	1.48

We wish to thank Dr. G. H. Cady for lending us his apparatus, Professor Don M. Yost and Mr. A. Beerbower for preparing the fluorine nitrate used in this work, Mr. K. S. Palmer for assisting in the preparation of the electron diffraction photographs, and Dr. Sidney Weinbaum and Mrs. M. Lassettre for assisting in their interpretation.

Summary

The investigation of methyl azide, methyl nitrate, and fluorine nitrate by electron diffraction is shown to lead to configurations of the molecules corresponding in each case to resonance between two important valence-bond structures. The unimportance of a third otherwise reasonable structure for these molecules as well as for nitrous oxide is ascribed to instability due to the presence of electric charges of the same sign on adjacent atoms. It is shown that the differ-

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[12] L. O. Brockway and F. T. Wall, THIS JOURNAL, **56**, 2373 (1934).

[13] The observed decrease below the double-bond values may possibly be due to some triple bond formation.

[14] P. Nylén and O. Stelling, *Z. anorg. allgem. Chem.*, **212**, 169 (1933).

ences in chemical properties of covalent and ionic azides and nitrates can be correlated with differences in structure. The use of the adjacent charge rule is illustrated by its application in the discussion of the structures of nitrogen pentoxide, nitrogen tetroxide, and the oxygen acids of heavier atoms.

PASADENA, CALIF. RECEIVED OCTOBER 19, 1936

[Reprint from the Journal of the American Chemical Society, 59, 1223 (1937).]

[Contribution from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, No. 594]

Carbon–Carbon Bond Distances. The Electron Diffraction Investigation of Ethane, Propane, Isobutane, Neopentane, Cyclopropane, Cyclopentane, Cyclohexane, Allene, Ethylene, Isobutene, Tetramethylethylene, Mesitylene, and Hexamethylbenzene. Revised Values of Covalent Radii

By Linus Pauling and L. O. Brockway

In our studies of the dependence of interatomic distances on resonance[1] we have assumed that the carbon–carbon single bond is characterized by the distance 1.54 Å. (as in diamond) and we have attributed shortening of bond distances below 1.54 Å., such as is observed for the central bond in cyanogen,[2] diacetylene,[2] biphenyl,[3] and other conjugated systems, to partial double-bond character resulting from resonance. Some question has been raised as to whether or not this interpretation is justified, on the basis that the single-bond radius for aromatic carbon might be different from that for aliphatic carbon, as is indicated by the X-ray work of Mrs. Lonsdale on hexamethylbenzene.[4] In order to obtain information about this and to investigate also the constancy of carbon–carbon bond distances in non-resonating molecules we have during the past three years determined the configurations of thirteen hydrocarbons by the electron diffraction method; the results of this investigation are reported below.

In the course of the work it was found that the value assumed five years ago for the carbon double-bond covalent radius (obtained by linear interpolation between the single-bond and the triple-bond radius) is 0.02 Å. too large; in consequence of this we have been led to revise the double-bond radii of other atoms also.

Ethane, Propane, Isobutane, and Neopentane.—The samples of ethane, propane, and isobutane used were provided by Dr. B. H. Sage of these Laboratories, and that of neopentane by Dean F. C. Whitmore, from a preparation made by Mr. G. H. Fleming at Pennsylvania State College. Electron diffraction photographs, showing six to eight rings, were prepared by the usual method,[5] the distance from the gas nozzle to film being about 10 cm. and the electron wave length about 0.06 Å. Values of $s_0 = (4\pi \sin \theta/2)/\lambda$ for the apparent maxima and minima, obtained by averaging the measurements on about ten films for each substance, are given in Tables I to IV, together with visually estimated values of the intensities of the rings for use in application of the radial distribution method.[6]

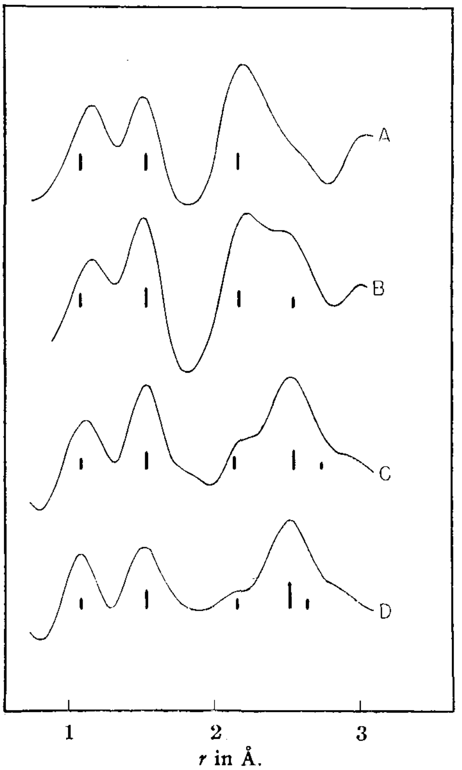

Fig. 1.—Radial distribution curves for (A) ethane, (B) propane, (C) isobutane and (D) neopentane. The positions of the heavy arrows indicate the interatomic distances determined by the comparison of the photographs with theoretical intensity curves; their heights show the relative scattering power associated with each distance.

The six-term radial distribution function for ethane (Fig. 1, curve A) shows maxima at 1.16,

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(1) (a) L. Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932); (b) L. Pauling, L. O. Brockway, and J. Y. Beach, This Journal, **57**, 2705 (1935).

(2) L. O. Brockway, *Proc. Nat. Acad. Sci.*, **19**, 868 (1933).

(3) J. Dhar, *Indian J. Phys.*, **7**, 43 (1932).

(4) K. Lonsdale, *Proc. Roy. Soc.* (London), **A123**, 494 (1929).

(5) L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

(6) L. Pauling and L. O. Brockway, This Journal, **57**, 2684 (1935).

1.52, and 2.21 Å. With consideration of the incomplete resolution of the first two maxima, this indicates that the C–C bond distance is somewhat greater than 1.52 Å. and the C–H bond distance somewhat less than 1.16 Å. Intensity curves calculated for (A) C–H = 1.06 Å., C–C = 1.54 Å., (B) C–H = 1.09 Å., C–C = 1.54 Å., and (C) C–H = 1.12 Å., C–C = 1.54 Å., with all angles given the tetrahedral value 109°28′, are represented in Fig. 2, the *trans* configuration of methyl groups indicated by recent thermochemical studies[7] being assumed in evaluating the H–H separations, which make only a small contribution. The curves do not differ greatly in qualitative aspect; the intensities of the three strong rings on the photographs, however, indicate that model B is somewhat better than either of the others. The quantitative comparison for this model, given in Table I, leads to the final values C–C = 1.55 ± 0.03 Å. and C–H = 1.09 ± 0.03 Å., in approximate agreement with the value C–C = 1.52 ± 0.10 Å. (with C–H = 1.10 Å. assumed) obtained by Wierl[8] by measurement of the three strong rings appearing on his photographs.

In ethane it was possible to consider the C–H distance as a parameter and to evaluate it as 1.09 ± 0.03 Å. In the case of the other hydrocarbons studied in this investigation (aside from ethylene) there are so many structural parameters that the experimental evaluation of the C–H distance cannot be carried out conveniently. We have accordingly assumed values for this distance in these substances, namely, C–H = 1.09 Å. for a carbon atom which forms four single bonds to other atoms (as in a methyl group) and C–H = 1.06 Å. for a carbon atom which forms a double bond. There is very little doubt that these values are correct to within about 0.03 Å., and in no case would a change of 0.03 Å. in the assumed C–H values change the values given in our investigation for the other interatomic distances by as much as 0.01 Å. The reasons for our choice of C–H values are the following. The table of covalent radii gives the value C–H = 1.06 Å., with use of the hydrogen radius provided by the hydrogen halides. This value is found experimentally to be valid for a carbon atom which forms a triple bond, 1.057 Å. being reported for both acetylene and hydrogen cyanide.[9] The value 1.06 ± 0.03 Å. for carbon forming a double bond is given by our study of ethylene, described later in this paper. On the other hand, the somewhat larger value 1.09 Å. which we have reported for ethane is supported by the spectroscopic values 1.08 and 1.093 Å. for methane.[10]

TABLE I

ETHANE

Max.	Min.	I	s_0	s^a	C–C, Å.
1		1	3.50		
2		6	6.15	6.40	(1.60)[b]
	3		7.51	7.81	(1.60)
3		5	9.07	9.00	1.528
	4		10.80	10.83	1.545
4		4	12.59	12.76	1.561
5		3	17.60	18.07	1.581
6		2	21.52	21.27	1.522
				Average	1.547 Å.

[a] Calculated for the model with C–H = 1.09 Å., C–C = 1.54 Å. and the angle H–C–H = 109°28′.

[b] In this table and the following ones the less reliable values, not included in taking the average, are shown in parentheses.

The principal peak on the radial distribution curve of propane (Fig. 1, curve B), at 1.53 Å., represents the C–C bond distance. The small and accordingly unreliable peak representing the C–H distance has its maximum at 1.17 Å. The rest of the curve is compatible with a model with C–H $\cong$ 1.09 Å., C–C = 1.54 Å., and all angles close to the tetrahedral value 109°28′; the principal distances for this model, 10 C–H at 2.17 Å. and C–C at 2.51 Å., are represented by a peak at 2.23 Å. and an unresolved hump at about 2.5 Å.

Intensity curves calculated for the ratio C–H/C–C = 1.09/1.54 and for the values 109°28′, 111°30′, and 113°30′ for the C–C–C bond angle, the H–C–C angles being taken as 109°28′, are shown in Fig. 2. These curves all reproduce satisfactorily the appearance of the photographs;[11] the quantitative agreement with the 111°30′ curve is somewhat better than that for either of the others, however, permitting us to assign to the C–C–C angle the value 111°30′ ± 3°. The quantitative comparison[12] is shown in Table II; it leads to the value C–C = 1.54 ± 0.02 Å., with C–H = 1.09 Å. Wierl[8] reported C–C = 1.52 ±

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(7) J. D. Kemp and K. S. Pitzer, *J. Chem. Phys.*, **4**, 749 (1936); THIS JOURNAL, **59**, 276 (1937); J. B. Howard, *Phys. Rev.*, **51**, 53 (1937).

(8) R. Wierl, *Ann. Physik*, **13**, 453 (1932).

(9) G. Herzberg, F. Patat and H. Verleger, *Z. Physik*, **102**, 1 (1936); P. F. Bartunek and E. F. Barker, *Phys. Rev.*, **48**, 516 (1935).

(10) R. G. Dickinson, R. T. Dillon and F. Rasetti, *Phys. Rev.*, **34**, 582 (1929); N. Ginsburg and E. F. Barker, *J. Chem. Phys.*, **3**, 668 (1935).

(11) The apparent faint first ring on the photographs is not represented by a very well-defined peak on the curves.

(12) The values given by the first and fifth maxima have been omitted in taking the average. The reason for the poor agreement shown by the fifth maximum is not known to us.

0.05 Å., assuming C–H = 1.10 Å. and all angles tetrahedral, from the measurement of photographs showing four rings. Bauer,[13] using his analytic method of interpretation, reported C–C = 1.50 Å., C–H = 1.08 Å., and the angle C–C–C = 114°; we believe that these values are somewhat less reliable than those found in the present investigation, partly because our new photographs are better than those used by Bauer.

The radial distribution function for isobutane (Fig. 1, curve C) shows well-defined peaks at 1.13, 1.54, and 2.53 Å., and indications of a distance 2.2 Å. also. The peak at 1.54 Å. represents the C–C bond distance, and that at 2.53 Å. the larger C–C distance, the ratio of these corresponding to the value 110°30′ for the C–C–C bond angle.

Intensity curves calculated for C–H = 1.09 Å., C–C = 1.54 Å., angles H–C–C = 109°28′, and angles C–C–C = 109°28′, 111°30′, and 113°30′, shown in Fig. 2, agree well in general with the appearance of the photographs, as indicated by the data in Table III; there can also be seen on the photographs a faint ring (too faint to be measured) between the fourth and fifth maxima of the table, corresponding to the small peak on the curves. The C–C–C bond angle can be evaluated with use of the third ring and its shelf, for which we estimate the intensity ratio 3/2, which corresponds to the 111°30′ curve. The quantitative comparison with this curve leads to the average value C–C = 1.54 ± 0.02 Å., with the angle C–C–C equal to 111°30′ ± 2°.

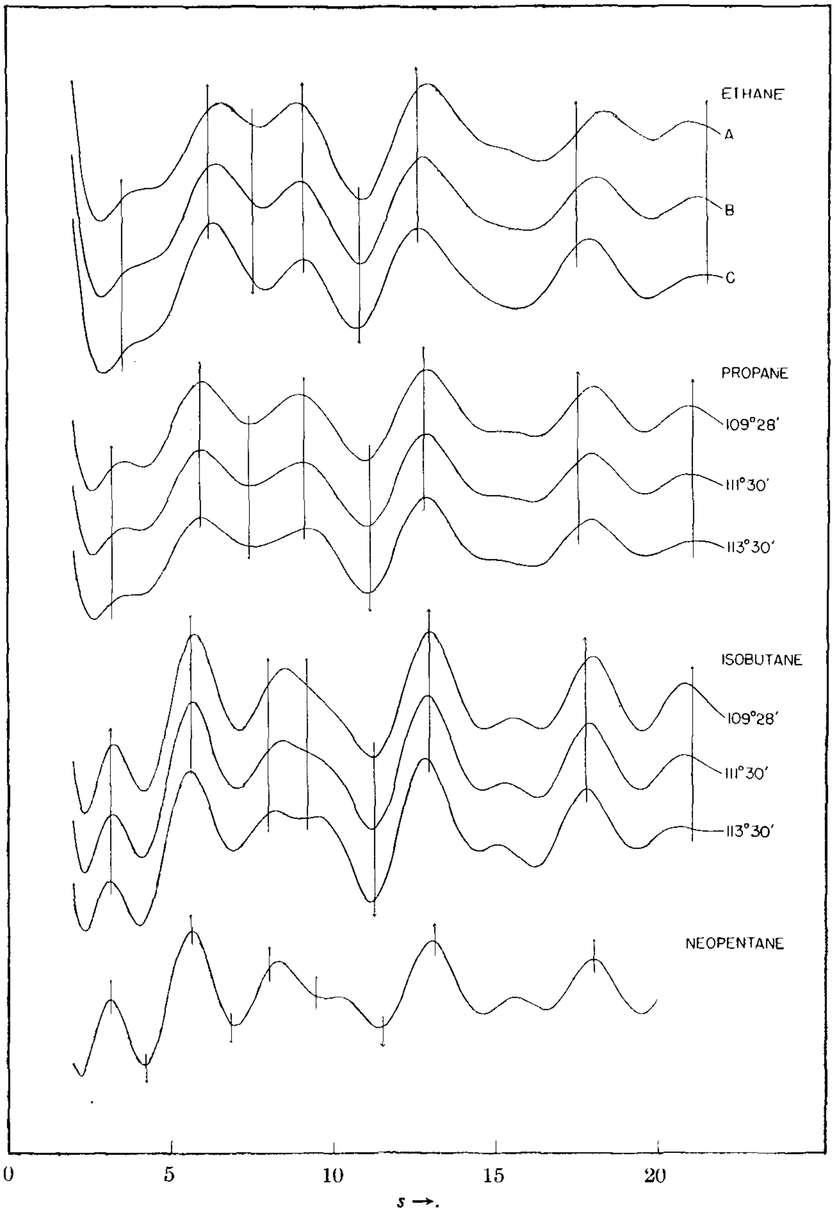

Fig. 2.—Theoretical intensity curves for ethane, propane, isobutane and neopentane. The arrows show the positions of the maxima and minima measured on the photographs.

The photographs of neopentane show five rings, the third of which has an outer shelf; the general appearance of the photographs is closely indicated by the calculated intensity curve shown in Fig. 2. (A faint ring, not included in the table, can be seen at about s = 15.5.) The radial distribution curve corresponding to the measured s_0

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(13) S. H. Bauer, *J. Chem. Phys.*, **4**, 407 (1936).

TABLE II

PROPANE

Max.	Min.	I	s_0	s^a	C–C, Å.
1		1	3.18	3.63	(1.76)
2		4	5.87	5.93	1.556
	3		7.40	7.40	1.540
3		3	9.11	9.09	1.537
	4		11.13	11.03	1.526
4		3	12.78	12.85	1.548
5		2	17.51	17.94	(1.577)
6		1	21.09	21.04	1.536
				Average	1.541 Å.

[a] Calculated for the model with C–H = 1.09 Å., C–C = 1.54 Å., and the angle C–C–C = 111°30′.

TABLE III

ISOBUTANE

Max.	Min.	I	s_0	s^a	C–C, Å.
1		1	3.13	3.22	(1.58)
2		5	5.60	5.66	1.557
3		3	7.97	8.43	(1.63)
Shelf		2	9.17		
	4		11.25	11.19	1.532
4		4	12.94	12.89	1.534
5		3	17.77	17.87	1.549
6		2	21.12	20.83	1.519
				Average	1.538 Å.

[a] Calculated for the model with C–H = 1.09 Å., C–C = 1.54 Å., angles H–C–C = 109°28′, and angles C–C–C = 111°30′.

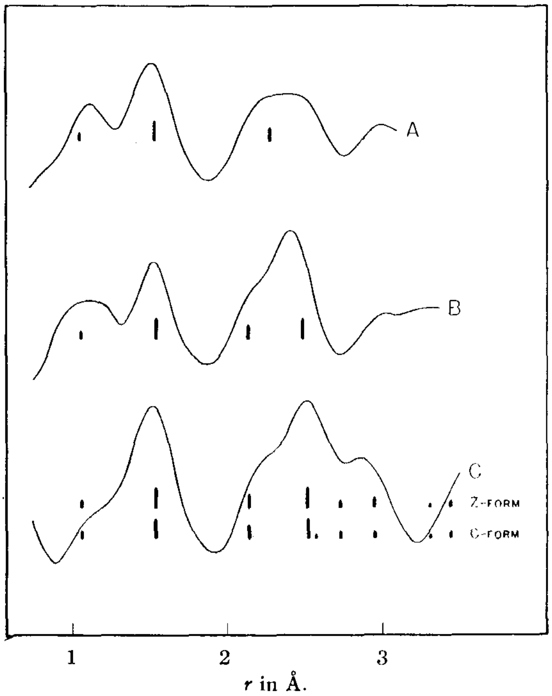


Fig. 3.—Radial distribution curves for (A) cyclopropane, (B) cyclopentane and (C) cyclohexane.

and I values given in Table IV (Fig. 1, curve D) shows peaks at 1.09, 1.53, and 2.52 Å., and humps indicating distances about 2.15 and 2.95 Å. The C–C bond distance is given directly by the 1.53 Å. peak as 1.53 Å., and by the 2.52 Å. peak as 1.54 Å.

TABLE IV

NEOPENTANE

Max.	Min.	I	s^0	s	C–C, Å.
1		1	3.12	3.17	(1.565)
	2		4.22	4.20	1.533
2		4	5.60	5.62	1.545
	3		6.84	6.97	1.559
3		3	8.00	8.32	(1.60)
Shelf		1	9.44	10.08	(1.64)
	4		11.50	11.42	1.533
4		4	13.10	13.00	1.532
5		2	18.02	18.00	1.539
				Average	1.540 Å.

The quantitative comparison of s_0 values and s values calculated for the tetrahedral model with C–H = 1.09 Å. and C–C = 1.54 Å. leads to C–C = 1.54 ± 0.02 Å., the inner ring being ignored as usual and the third ring with its shelf omitted from consideration because of its unsymmetrical shape.

The photographs of neopentane provide some information regarding the orientation of methyl groups in this molecule. There are two configurations with non-rotating methyl groups which preserve holohedral tetrahedral symmetry for the molecule; in these the methyl groups are oriented with their C–H bonds in the planes determined by the central carbon atom and two other carbon atoms, with the hydrogen atoms of each methyl group either *cis* or *trans* to the other methyl groups. Intensity curves calculated for both of these configurations are unsatisfactory, in that they show a pronounced maximum between the third and fourth rings on the photographs, where only a shelf is observed. It is possible that the configuration obtained by rotating each methyl group through 30° from either of the two orientations described above, which causes the hydrogen atoms of different methyl groups to fit together like cogs, would be considered satisfactory; its curve shows a shelf on the third ring and is otherwise like the photographs except that the peak at about s = 15.5 is too large. The average curve calculated for 30° intervals in azimuthal angle for each methyl group, simulating free rotation, is, on the other hand, completely satisfactory (Fig. 2).

It was noticed that the longer C–H distances are of little importance in the curve for the free-rotation model; the curve calculated by ignoring all C–H terms except those for the bond distance and the next larger distance (which is unchanged by rotation) is qualitatively indistinguishable from the free-rotation curve, and the s values for the peaks of the two curves differ on the average by only 0.02. In our treatment of propane and isobutane we have made use of this simplification.

Cyclopropane, Cyclopentane, and Cyclohexane.—The sample of cyclopropane used was provided by Professor G. S. Parks of Stanford University. Of the two samples of cyclopentane photographed, one was prepared for us by Dr. G. W. Wheland by the catalytic hydrogenation of cyclopentadiene and the other was provided by Mr. T. A. Boyd of the General Motors Research Laboratory. Kahlbaum cyclohexane was used with no further purification.

Cyclopropane gave photographs showing four rings, with qualitative appearance corresponding closely to the calculated curve of Fig. 4. The s_0 and I values given in Table V lead to the radial distribution curve shown in Fig. 3 (curve A), with peaks at 1.12 Å. (C–H bond distance), 1.52 Å. (C–C bond distance) and 2.2–2.5 Å. (larger C–H distance). The intensity curve of Fig. 4 is calculated for a model with the three carbon atoms at the corners of a regular triangle and the hydrogen atoms at tetrahedron corners out of the plane of the carbon ring, the H–C–H angle being taken as 109°28′ and the C–C and C–H distances in the ratio 1.54/1.09. With omission of the inaccurate readings for the first maximum, second minimum and the broad third maximum, the carbon–carbon distance is found to have the value 1.53 ± 0.03 Å.[14]

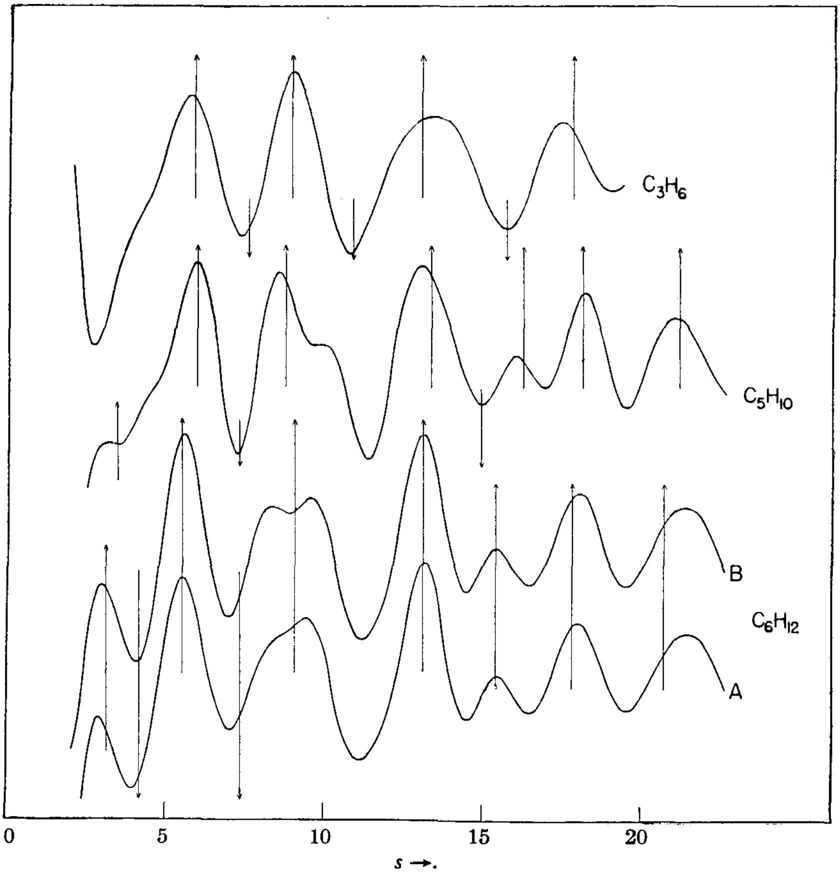


Fig. 4.—Theoretical intensity curves for cyclopropane, cyclopentane and cyclohexane.

TABLE V

CYCLOPROPANE

Max.	Min.	I	s_0	s	C–C, Å.
1		4	5.83	5.72	(1.51)
	2		7.55	7.30	(1.48)
2		4	8.90	8.92	1.543
	3		10.84	10.70	1.519
3		3	13.00	13.46	(1.59)
	4		15.69	15.62	1.532
4		2	17.77	17.42	1.509
				Average	1.526 Å.

The photographs of cyclopentane have the general appearance indicated by the calculated curve of Fig. 4. The shelf on the third ring, which can barely be seen on the photographs, seems to be displaced outward, however, the fourth minimum appearing flat rather than sharp; neither of the two corresponding s_0 values could be measured reproducibly. The estimated relative intensities

[14] In a note added at the end of his last paper[8] Wierl stated that he had found for the carbon–carbon distance in cyclopropane the value 1.6 ± 0.1 Å.

of the last three rings do not correspond well with those shown by the curve.

The radial distribution curve (Fig. 3, curve B) corresponding to the s_0 and I values of Table VI has peaks at 1.1, 1.53, and 2.42 Å., the first two representing the C–H and C–C bond distances. The comparison of s_0 and s values for a model based on a regular plane pentagon of carbon atoms, with C–C = 1.54 Å. and C–H = 1.09 Å., leads to the averaged result C–C = 1.52 ± 0.03 Å., in good agreement with Wierl's value[8] 1.51 ± 0.08 Å.

TABLE VI

CYCLOPENTANE

Max.	Min.	I	s_0	s	C–C, Å.
1		1	3.44	3.11	(1.40)
2		5	5.98	5.94	1.528
	3		7.28	7.20	1.523
3		5	8.72	8.50	1.500
Shelf		1	11.12		
4		4	13.30	12.91	1.500
	5		14.86	14.84	1.539
5		2	16.20	15.95	1.516
6		2	18.10	18.07	1.546
7		2	21.40	20.94	1.507
				Average	1.520 Å.

The s_0 and I values for the photographs of cyclohexane (Table VII), showing seven rings, lead to the radial distribution curve represented in Fig. 3 (curve C). The two principal peaks are at 1.52 and 2.51 Å., corresponding closely to the values 1.54 and 2.51 Å. expected for single-bonded carbon atoms at tetrahedral angles. Intensity curves calculated for C–C = 1.54 Å., C–H = 1.09 Å., and all bond angles 109°28′ are given in Fig. 4, A representing the Z form (staggered ring) and B the C form. These reproduce reasonably well the appearance of the photographs except in the neighborhood of the third ring, which is observed as a rather broad ring with a faint outer shelf. Except for the presence of the shelf, the appearance of the third ring is about as expected for model A, whereas for model B a resolved double peak would be seen; otherwise the two curves are equally suitable. The quantitative comparison for model A is shown in Table VII. The average of the more reliable values for the carbon–carbon bond distance is 1.540 Å.; considering also the radial distribution result, we write for cyclohexane C–C = 1.53 ± 0.03 Å., in approximate agreement with the value 1.51 ± 0.03 Å. reported by Wierl[15] from the measurement of photographs showing four rings.

TABLE VII

CYCLOHEXANE

Max.	Min.	I	s_0	s^a	C–C, Å.
1		3	3.08	2.85	(1.43)
	2		4.13	3.89	(1.45)
2		10	5.48	5.47	1.538
3		3	9.03	9.37	(1.59)
Shelf		0.5	11.14		
4		4	13.07	13.08	1.540
5		1	15.38	15.34	1.536
6		2	17.78	17.86	1.547
7		1	20.69	21.35	(1.589)
				Average	1.540 Å.

[a] Calculated for the model consisting of a staggered ring in the Z-configuration with C–C = 1.54 Å., C–H = 1.09 Å. and all bond angles 109°28′.

Allene.—A sample of allene was kindly given us by Dr. W. E. Vaughan of Harvard University. Electron diffraction photographs of this substance were found to show four well-defined rings, the first having a noticeable outer shelf, the second a pronounced outer shelf or subsidiary ring, and the third a faint outer shelf (not measured).

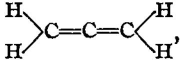
The measured ring diameters and estimated intensity values given in Table VIII (averages for eleven photographs) lead to the radial distribution curve shown in Fig. 5 (curve A). The structure of allene,  $H_2C{=}C{=}CH_2$, is determined by three significant parameters, the C=C bond distance, the C–H bond distance, and the H–C–H bond angle. Of the five interatomic distances (other than H–H) in the molecule, the C=C bond distance contributes twice as much to the diffraction pattern as any other; its value is given by the principal peak, at 1.34 Å., in the radial distribution curve. Without doubt the C–H bond distance is close to 1.06 Å. and the H–C–H bond angle to 109°28′; the interatomic distances corresponding to these values and to C=C = 1.34 Å. agree well with the radial distrib-

TABLE VIII

ALLENE

Max.	Min.	I	s_0	s^a	C–C, Å.
1		10	5.92	5.93	1.342
1a		2	7.26		
	2		8.77	8.57	(1.309)
2		5	9.93	9.95	1.343
2a		2	12.00	11.65	(1.301)
3		4	15.04	15.05	1.341
4		2	19.50	19.36	1.331
				Average	1.339 Å.

[a] Calculated for the model with C=C = 1.34 Å., C–H = 1.06 Å. and the angle H–C–H = 109°28′.

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(15) R. Wierl, *Ann. Physik*, **8**, 521 (1931).

ution curve, the C–H bond distance (1.06 Å.) appearing as a hump on the first peak, the C–H and C–C distances 2.11 and 2.68 Å. appearing only partially resolved at 2.25 and 2.60 Å., and the longest C–H distance 3.40 Å. appearing as a separate peak at 3.40 Å.

Verification of this structure is provided by the comparison with calculated intensity curves. In Fig. 6 curve A represents the model described above and curve B a similar model with the C=C bond distance equal to 1.38 Å., as given by the original table of covalent radii. Each of these curves reproduces closely the qualitative aspect of the photographs; curve A also shows quantitative agreement, whereas curve B shows a systematic difference of about 3%. The quantitative comparison of measured ring diameters and s values for the maxima and minima of curve A is shown in Table VIII. The mean of the values given for the C=C distance by the four principal maxima is 1.339 Å. A similar comparison for the four principal maxima with curve B gives 1.346 Å. Considering also the radial distribution value 1.34 Å., we accept for the C=C double-bond distance in allene the value 1.34 ± 0.02 Å.; the C–H distance was assumed to be within 0.04 Å. of 1.06 Å. and the H–C–H bond angle close to 109°28′, their independent evaluation being impossible because of the small contribution of the C–H terms to the diffraction pattern.

Our result agrees approximately with that of Wierl,[8] who found the value C=C = 1.31 ± 0.05 Å. from measurement of two rings.

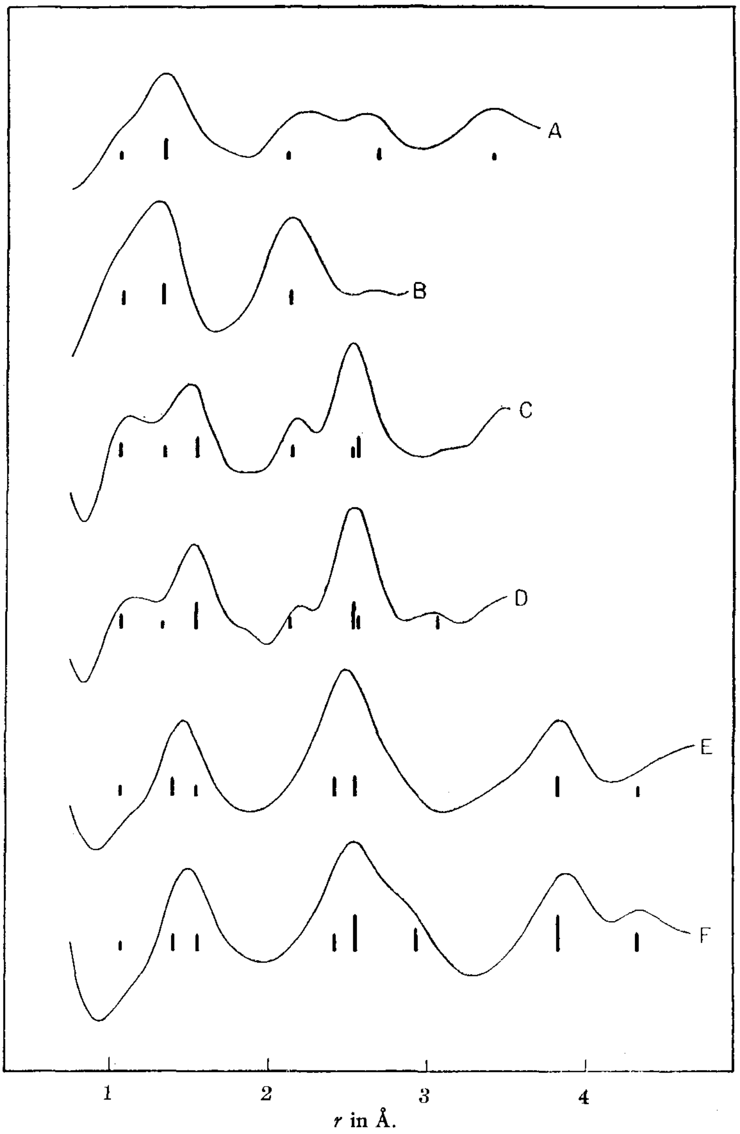

Fig. 5.—Radial distribution curves for (A) allene, (B) ethylene, (C) isobutane, (D) tetramethylethylene, (E) mesitylene and (F) hexamethylbenzene.

Ethylene.—Photographs of ethylene were found to show five rings, of uniformly decreasing intensity except for the third, which is weak and appears as an outer shelf on the second. The radial distribution curve calculated with the s_0 and I values in Table IX (Fig. 5, curve B) shows only two peaks, the first, at 1.32 Å., representing the C=C bond distance with the C–H bond appearing as a hump, and the second, at 2.14 Å., the longer C–H distance.

The calculated intensity curves A, B, and C in Fig. 6 are for coplanar models with the ratios 1.06/1.38, 1.09/1.38, and 1.12/1.38, respectively, for C–H/C=C, the H–C–H bond angle being given the reasonable value 109°28′. Curve B reproduces the appearance of the photographs closely; it shows a small defect in that the third ring is about equidistant from the second and fourth, rather than closer to the second as observed. Curve A is unsatisfactory because of the further shift of the third ring toward the fourth, and curve C because it gives the third ring too great intensity. The effect of increase in H–C–H bond angle is to shift the third ring toward the fourth, as is seen from curve D, which is similar to B except for increase in the angle to 115°; this curve and similar curves for 120 and 125° are all unsatisfactory for this reason.

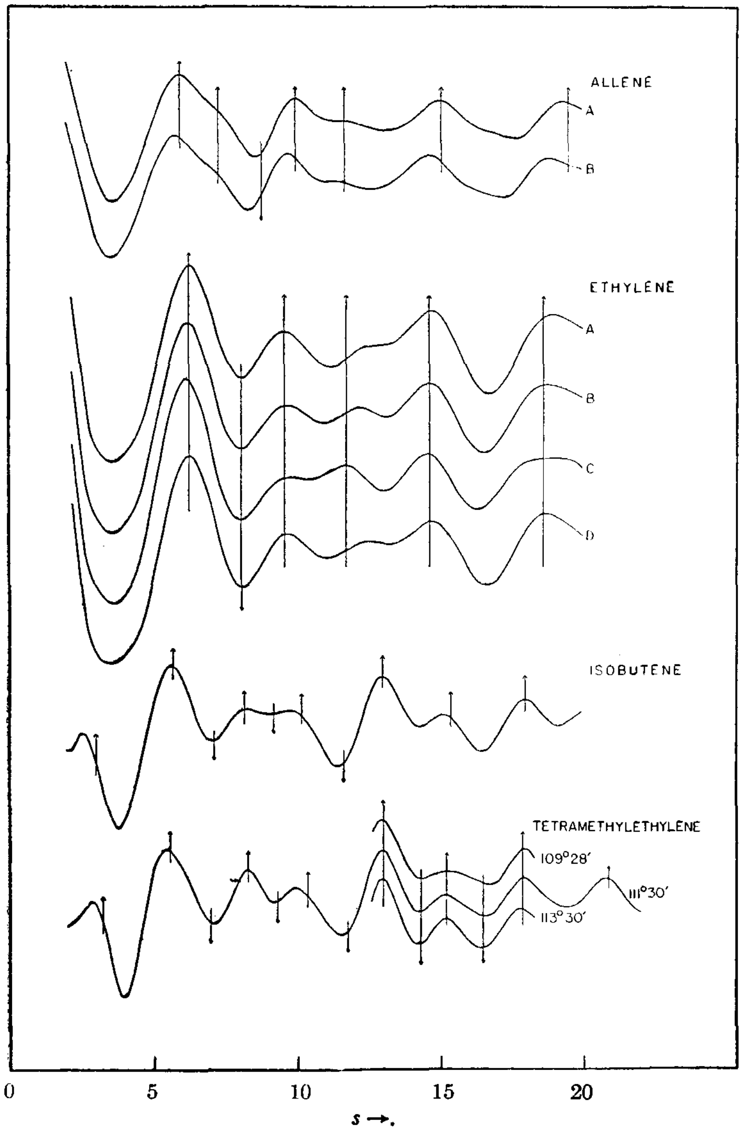

Fig. 6.—Theoretical intensity curves for allene, ethylene, isobutene and tetramethylethylene. The s-scale for ethylene has been decreased by 3%, to show the quantitative agreement between the measured s values and the curve with C=C = 1.34 Å.

Quantitative comparison of s_0 and s values for model B (Table IX) leads to C=C = 1.34 ± 0.02 Å. and C–H = 1.06 ± 0.03 Å., the H–C–H bond angle having the value 110 ± 5°. This model agrees well with the radial distribution curve; the peak at 1.32 Å. represents the distances 1.06 and 1.34 Å. only partially resolved, and the peak at 2.14 Å. occurs at exactly the place required by the 110° model. Wierl[8] reported C=C = 1.30 ± 0.10 Å. from measurement of two rings on his photographs.

The structure which we assign to ethylene corresponds to the values 33.7, 28.7, and 5.0 × 10^{-40} for the three principal moments of inertia of the molecule. These are in reasonably good agreement with the values 33.2, 27.5, and 5.7 × 10^{-40} found spectroscopically by Badger,[16] and the single value 28.85 × 10^{-40} reported by Scheib and Lueg.[17] Penney[18] has recently interpreted Badger's values as corresponding to the distances C–H = 1.08 Å. and C=C = 1.33 Å. and the angle H–C–H = 118°. Our photographs are compatible with these distances but suggest a smaller value for the angle.

Isobutene and Tetramethylethylene.—Using a sample of isobutene provided by Professor H. J. Lucas of these Laboratories and a sample of tetramethylethylene provided by Professor G. B. Kistiakowsky and Dr. W. E. Vaughan of Harvard University, we obtained photographs showing seven or eight rings, with the average s_0 values and estimated intensities given in Tables X and XI. The radial distribution curves (Fig. 5, curves C and D) for the two substances are compatible with the double-bond and single-bond distances C=C = 1.34 Å. and C–C = 1.54 Å., but because of lack of resolution of the peaks the values are not verified individually.

(16) R. M. Badger, *Phys. Rev.*, **45**, 648 (1934).

(17) W. Scheib and P. Lueg, *Z. Physik*, **81**, 764 (1933).

(18) W. G. Penney, *Proc. Roy. Soc.* (London), **A158**, 306 (1937).

TABLE IX

ETHYLENE

Max.	Min.	I	s_0	s^a	C–C, Å.
1		6	6.46	6.22	1.329
	2		8.30	8.10	1.346
2		3	9.90	9.68	1.349
3		1	12.07	12.17	(1.391)
4		2	15.07	14.62	1.339
5		1	19.08	18.76	1.356
				Average	1.344 Å.

[a] Calculated for the model with C=C = 1.38 Å., C–H = 1.09 Å. and the angle H–C–H = 109°28′.

TABLE X

ISOBUTENE

Max.	Min.	I	s_0	s^a	s/s_0
1		1	2.99	2.66	(0.89)
2		10	5.69	5.68	0.998
	3		7.10	7.02	.989
3		2	8.15	8.29	1.017
	4		9.20	9.20	1.000
4		2	10.14	9.90	0.976
	5		11.66	11.65	.999
5		3	13.00	13.05	1.004
6		1	15.39	15.40	1.001
7		2	18.03	18.04	1.001
				Average	0.998

C–C = 1.537 Å.
C=C = 1.337 Å.

[a] Calculated for the model with C–H = 1.09 Å., C–C = 1.54 Å., C=C = 1.34 Å., angle C–C–C = 111°30′, and angles H–C–C = 109°28′.

TABLE XI

TETRAMETHYLETHYLENE

Max.	Min.	I	s_0	s^a	s/s_0
1		1	3.22	2.87	(0.88)
2		6	5.52	5.43	0.984
	3		6.95	7.06	1.016
3		3	8.24	8.31	1.009
	4		9.27	9.20	0.992
4		2	10.31	9.92	(.962)
	5		11.71	11.51	.983
5		4	12.95	12.92	.998
	6		14.27	14.23	.997
6		1	15.19	15.15	.997
	7		16.43	16.48	1.003
7		2	17.85	17.85	1.000
8		$^1/_2$	20.86	20.76	0.995
				Average	0.998

C–C = 1.537 Å.
C=C = 1.337 Å.

[a] Calculated for the model with C–H = 1.09 Å., C–C = 1.54 Å., C=C = 1.34 Å., angles C–C–C = 111°30′, and angles H–C–C = 109°28′.

Calculated intensity curves are shown in Fig. 6. For each substance there is shown a complete curve calculated for the distances C–H = 1.09 Å., C–C = 1.54 Å. and C=C = 1.34 Å. and the angles H–C–C = 109°28′ and C–C–C = 111°30′; in addition there are shown for tetramethylethylene segments of curves for models similar to this except for the value of the angle C–C–C, which is changed to 109°28′ and to 113°30′, the curves being appreciably different from the 111°30′ curve only in the region covered by these segments. The estimated intensities of the three rings in this region are 4, 1, and 2; it is seen that these correspond more closely to the 111°30′ curve than to either of the other two, so that we obtain for the C–C–C bond angle the value 111° 30′ ± 2°. This evaluation of the bond angle is not invalidated by a change of as much as 0.04 Å. in the assumed C=C distance.

A similar determination of the bond angle for isobutene cannot be carried out, the curves being practically unchanged by a change of 2° in the angle. It is of course probable that the angle has the same value in this substance as in tetramethylethylene.

The calculated intensity curves are changed in shape only very slightly by changing C=C from 1.34 to 1.38 Å., so that the carbon–carbon double-bond distance in these substances cannot be evaluated independently. We think that the value is within 0.02 of 1.34 Å.; if we were to assume 1.38 Å., the values quoted below for the carbon–carbon single-bond distance would be decreased to 1.52 Å. for isobutene and 1.53 Å. for tetramethylethylene.

The quantitative comparison of s_0 and s shown in Tables X and XI leads to 1.54 ± 0.02 Å. for the C–C distance in each of the two substances, the value 1.34 Å. for C=C being assumed. No other investigation of interatomic distances in these hydrocarbons has been reported.

Mesitylene and Hexamethylbenzene.—Photographs showing eight or nine rings were prepared of mesitylene, provided by Dr. W. E. Vaughan, and of hexamethylbenzene (Eastman Kodak Co.), with s_0 and I values given in Tables XII and XIII.

There is little doubt that the C–C distance in the benzene ring retains in its methyl derivatives the value 1.39 Å. found for benzene itself.[19] The main question regarding these substances is whether the distance from methyl carbon to ring carbon is determined by the usual single-bond radius, having thus the value 1.54 Å., or whether

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(19) R. Wierl, ref. 15; Pauling and Brockway, *J. Chem. Phys.*, **2**, 867 (1936). V. Schomaker, working in these Laboratories, has recently obtained benzene photographs with rings extending to $s = 20$ which leads to C–C = 1.39 Å. This value has also been substantiated to within 0.03 Å. by the interesting investigation of the phthalocyanines by J. M. Robertson, *J. Chem. Soc.*, 1195 (1936).

TABLE XII

MESITYLENE

Max	Min.	I	s_0	s^a	s/s_0
1		4	3.32	3.12	(0.94)
	2		4.34	4.23	(.975)
2		10	5.54	5.48	.989
	3		7.39	7.18	(.972)
3		3	8.60	8.79	1.022
	4		9.43	9.39	0.996
4		4	10.33	10.22	.989
5		$^1/_2$	11.59	11.88	(1.025)
6		4	13.49	13.58	1.007
7		1	15.30	15.06	0.984
8		2	18.31	18.60	1.016
				Average	1.000

C_{ar}–C_{al} = 1.540 Å.

C_{ar}–C_{ar} = 1.390 Å.

[a] Calculated for the model with C_{ar}–C_{ar} = 1.39 Å., C_{ar}–C_{al} = 1.54 Å. and C–H = 1.09 Å.

TABLE XIII

HEXAMETHYLBENZENE

Max.	Min.	I	s_0	s^a	s/s_0
1		4	3.27	3.15	(0.964)
	2		4.21	4.13	(.981)
2		10	5.30	5.34	1.008
Shelf		1	6.24		
	3		7.04	7.16	(1.017)
Shelf		1	7.61		
3		4	8.76	8.86	1.011
	4		9.51	9.52	1.001
4		4	10.29	10.22	0.993
5		$^1/_2$	11.80	12.08	(1.023)
6		4	13.31	13.42	1.008
7		1	15.16	15.20	1.003
8		2	18.25	18.22	0.998
9		$^1/_2$	20.35	20.20	.993
				Average	1.002

C_{ar}–C_{al} = 1.543 Å.

C_{ar}–C_{ar} = 1.393 Å.

[a] Calculated for the model with C_{ar}–C_{ar} = 1.39 Å., C_{ar}–C_{al} = 1.54 Å. and C–H = 1.09 Å.

it is the sum of the radius 0.77 Å. for an aliphatic carbon atom and the radius 0.70 or 0.71 Å. for an aromatic carbon atom, giving the value $C_{ar}-C_{al}$ = 1.47 or 1.48 Å., as suggested originally by Mrs. Lonsdale.[4] Accepting a value close to 1.09 Å. for C–H, we thus have two principal models to be tested, one (model A) with $C_{ar}-C_{al}$ = 1.54 Å. and the other (model B) with $C_{ar}-C_{al}$ = 1.48 Å., both having $C_{ar}-C_{ar}$ = 1.39 Å.

The radial distribution curves, shown in Fig. 5 (curves E and F), support model A rather than B. For example, the first peak for hexamethylbenzene, at 1.49 Å., lies closer to the value given by A, 1.47 Å. (the mean of 1.39 Å. and 1.54 Å. contributing equally), than to that given by B, 1.43 Å.; and the second peak, at 2.53 Å., also lies closer to the value given by A for the principal interatomic distance in this region, 2.54 Å., than to that given by B, 2.48 Å. For mesitylene these peaks are observed at 1.46 and 2.49 Å., the expected values for A being 1.44 and 2.48 Å. and for B 1.42 and 2.45 Å. These four peaks thus have values greater than expected by an average amount of only 0.01 Å. for model A, and of 0.05 Å. for model B.

The qualitative aspect of the photographs also supports model A. On the photographs of hexamethylbenzene there is observed between the fourth and sixth rings a very weak fifth ring, with apparent intensity estimated to be about one-eighth as great as for its neighbors. A corresponding small peak appears on the intensity curve calculated for model A (Fig. 7), but not on that for model B. The appearance of the photographs is in general well reproduced by curve A; in particular, mention may be made of the shelves adjacent to the third minimum.

The quantitative comparison of measured s_0 values and s values calculated for models A for mesitylene and hexamethylbenzene is given in Tables XII and XIII. With omission of the innermost maximum and minimum, the unreliable third minimum, and the very weak fifth maximum for each substance, the average values s_A/s_0 = 1.000 and 1.002, respectively, are found. These correspond to the interatomic distances $C_{ar}-C_{al}$ = 1.54 ± 0.01 Å. and $C_{ar}-C_{ar}$ = 1.39 Å. in both substances, the $C_{ar}-C_{al}$ distance being equal to the single-bond distance in aliphatic compounds and the $C_{ar}-C_{ar}$ distance to that in benzene to within the probable error of the determination.

In her X-ray study of crystals of hexamethylbenzene[4] Mrs. Lonsdale found the value $C_{ar}-C_{al}$ = 1.48 Å. to be in better agreement with the observed intensities than the value 1.42 Å.; her work provides no evidence against the value 1.54 Å., however, which she did not test.

An electron-diffraction study of benzene, *p*-xylene, mesitylene, and hexamethylbenzene has been made recently by Jones,[20] who, on the basis of measurements extending to s_0 = 14, reported the values $C_{ar}-C_{al}$ = 1.50 ± 0.01 Å. and $C_{ar}-C_{ar}$ = 1.40 ± 0.01 Å. Jones' s_0 values are about 1.3% greater than ours, and comparison of them with our calculated values of s_A leads to

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(20) P. L. F. Jones, *Trans. Faraday Soc.*, **31**, 1036 (1935).

$C_{ar}-C_{al}$ = 1.52 Å. and $C_{ar}-C_{ar}$ = 1.37 Å., these distances being 0.02 Å. smaller than those given by our photographs. The rings given by mesitylene and hexamethylbenzene are unusually sharp and well defined, and we estimate, by comparison with other substances for which the electron-diffraction method has been tested,[21] that the error in our values of s_0 is not greater than about 0.5%.

Summary of Results

Values of interatomic distances and bond angles found in this investigation are collected in Table XIV. It should be mentioned that Wierl's early electron-diffraction work seems to be more reliable than he considered it to be; the mean difference of his C-C values and ours for the six hydrocarbons common to the two investigations is 0.03 Å., much less than the mean of the errors assigned by him, 0.07 Å.

The results shown in the table provide further evidence of the extraordinary extent to which the tetrahedral carbon atom of van't Hoff and Le Bel determines the structure of organic molecules. The values found for the angle between two single carbon–carbon bonds are in all cases (except cyclopropane) within 2° of the theoretical value 109°28′.

Table XIV

Interatomic Distances and Bond Angles in Hydrocarbons

	C–H, Å.	C–C, Å.	C=C, Å.	Angle C–C–C
Ethane	1.09 ± 0.03	1.55 ± 0.03		
Propane	(1.09)[a]	1.54 ± .02		111°30′ ± 3°
Isobutane	(1.09)	1.54 ± .02		111°30′ ± 2°
Neopentane	(1.09)	1.54 ± .02		
Cyclopropane	(1.09)	1.53 ± .03		(60°)
Cyclopentane	(1.09)	1.52 ± .03		(108°)
Cyclohexane	(1.09)	1.53 ± .03		(110°)
Allene	(1.06)		1.34 ± 0.02	
Ethylene	1.06 ± 0.03		1.34 ± .02	
Isobutene	(1.09)	1.54 ± .02	(1.34)	(111°30′)
Tetramethylethylene	(1.09)	1.54 ± .02	(1.34)	111°30′ ± 2°
Mesitylene	(1.09)	1.54 ± .01		
Hexamethylbenzene	(1.09)	1.54 ± .01		

[a] Values enclosed in parentheses were assumed.

The Constancy of the Carbon–Carbon Single-Bond Distance.—For the eleven hydrocarbons containing carbon–carbon single bonds studied in this investigation the values found for the corresponding interatomic distance lie between the limits 1.52 and 1.55 Å., all being equal to the diamond value 1.54 Å. to within their estimated probable errors. The results found for isobutene, tetramethylethylene, mesitylene, and hexamethylbenzene show definitely that the carbon–carbon single-bond distance is not affected by adjacent carbon–carbon double bonds[22] or aromatic nuclei, provided that the conditions for resonance across the single bond are not satisfied.

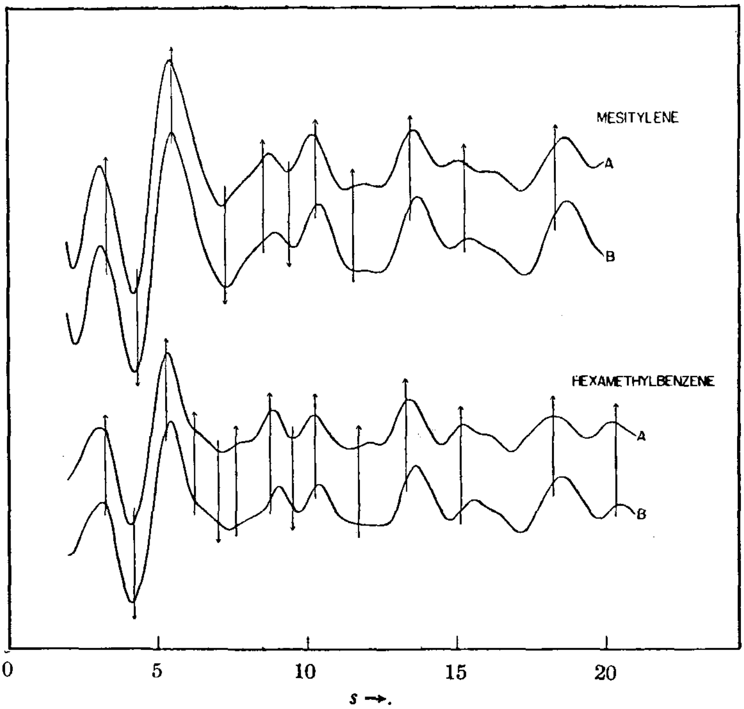

Fig. 7.—Theoretical intensity curves for mesitylene and hexamethylbenzene.

It has been reported recently[23] that the spectroscopic study of methylacetylene leads to the value 1.462 ± 0.005 Å. for the carbon–carbon single-bond distance in this substance. This is 0.08 Å. less than the value 1.54 Å. which we expect on the basis of the argument that constancy of the single-bond distance should be retained in the presence of an adjacent triple as well as of an adjacent double bond or aromatic nucleus. An electron-diffraction investigation of this substance is under way in these Laboratories.

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[21] Pauling and Brockway, *J. Chem. Phys.*, **2**, 867 (1936).

[22] It has been found that a carbon–oxygen double bond decreases the single-bond radius of the carbon atom involved: Pauling and Brockway, paper to be submitted to This Journal.

[23] G. Herzberg, F. Patat and H. Verleger, *J. Phys. Chem.*, **41**, 123 (1937).

It might be expected that the strain in cyclopropane, in which the C–C–C bond angles are distorted from 109°28′ to 60°, would weaken the bonds and thus lead to an increase in the bond distance. This effect is not observed, however, the carbon–carbon distance in cyclopropane being the same as in the other hydrocarbons to within the accuracy of the investigation. There is even some small indication that the C–C distance in cyclic aliphatic hydrocarbons is slightly smaller (by about 0.01 Å.) than the normal distance, the three values reported being 1.53, 1.52, and 1.53 Å.

It may be pointed out that the carbon–hydrogen bond seems not to show the constancy of interatomic distance found for the carbon–carbon single bond. The spectroscopic value for methane, 1.09 Å., and the value found in ethane, 1.09 Å., are definitely larger than the accurately known spectroscopic value 1.06 Å. for acetylene and cyanogen. In the CH molecule the observed distance is 1.12 Å.; it is possible that here the bonding orbital of carbon is different (with more 2p character) from that for quadrivalent carbon. The radius of the hydrogen atom is apparently more variable than those of other atoms, perhaps because the spatial extent of the valence orbital is much smaller than for other atoms. In the hydrogen molecule the covalent radius of hydrogen is 0.37 Å. and in the hydrogen halides 0.27 to 0.29 Å. Other stable hydrogen compounds show values within these limits: 0.29 to 0.32 Å. in hydrocarbons, 0.31 in ammonia, 0.30 in water, and 0.31 in hydrogen sulfide; in spectroscopic hydrides such as CH interatomic distances are usually about 0.03 Å. larger than in stable molecules.

Revised Values of Double-Bond Covalent Radii.—This investigation has led to the value 1.34 Å. for the carbon–carbon double-bond distance, 0.04 Å. less than the value provided by the table of covalent radii.[1a,24] Five years ago, when this table was extended to multiple bonds, there were few reliable experimental data on which the selected values for double-bond and triple-bond radii could be based. The single-bond radii were obtained from the study of a large number of interatomic distances found experimentally by crystal-structure and spectroscopic methods. The spectroscopic value of the triple-bond radius of nitrogen (in N_2) was found to bear the ratio 0.79 to the single-bond radius, and this ratio was assumed to hold for other atoms also. For the double-bond radii no similarly reliable experimental value was at hand. Wierl had reported 1.30 ± 0.10 Å. for the carbon–carbon double-bond distance in ethylene and 1.31 ± 0.05 Å. for that in allene; these correspond to 0.85 for the ratio of double-bond distance to single-bond distance, whereas the much larger ratio 0.92 is given by the oxygen–oxygen distance 1.20 Å. observed for the normal $^3\Sigma$ state of the oxygen molecule, which might be expected to approximate closely to the double-bonded state. Under these circumstances it seemed sensible to interpolate between the triple-bond factor 0.79 and unity, and the value 0.90 for the double-bond factor was chosen.[25]

The new carbon–carbon double-bond distance corresponds to the value 0.87 for the double-bond factor. Moreover, there are now available three accurately known triple-bond distances; 1.204 for C≡C in acetylene, 1.154 Å. for C≡N in hydrogen cyanide, and 1.094 for N≡N in the nitrogen molecule, whereas five years ago only the last was known. The ratios of these distances to the corresponding sums of single-bond radii are 0.782, 0.785, and 0.781, respectively. We accordingly now select 0.78 as the value of the triple-bond factor. Revised covalent radii[26] for first-row atoms are given in Table XV.

TABLE XV

COVALENT RADII

	C	N	O	F
Single bond	0.77	0.70	0.66	0.64
Double bond	.67	.61	.57	.55
Triple bond	.60	.55	.51	
	Si	P	S	Cl
Single bond	1.17	1.10	1.04	0.99
Double bond	1.06	1.00	0.95	.90
Triple bond	0.99	0.93	.88	

It is probable that the factors for atoms other than first-row atoms have values somewhat different from 0.87 and 0.78. Because of the small tendency of these atoms to form multiple bonds,

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[24] M. L. Huggins, *Phys. Rev.*, **28**, 1086 (1926); L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

[25] Sidgwick in 1933 ("The Covalent Link in Chemistry," Cornell University Press, 1933, p. 82), accepting 1.32 Å. for the carbon–carbon double-bond distance as indicated by Wierl's work, adopted 0.86 for the double-bond factor and 0.77 for the triple-bond factor.

[26] The revision leads to a difference of 0.06 Å. between the interatomic distance in the normal oxygen molecule and the sum of the double-bond radii. This may be attributed to the presence of an unusual structure, consisting of a single bond plus two three-electron bonds. We assign this structure both to the normal $^3\Sigma$ state, with r_0 = 1.204 Å., and to the excited $^1\Sigma$ state, with r_0 = 1.223 Å., the two differing in the relative spin orientations of the odd electrons in the two three-electron bonds. We expect for the double-bonded $^1\Delta$ state the separation r_0 = 1.14 Å.

few pertinent interatomic-distance data are available. The observed distances[27] 1.86 Å. in P_2 and 1.49 Å. in PN correspond to 0.93 Å. for the triple-bond radius of phosphorus, indicating the value 0.85 for the triple-bond factor for the second row. We further suggest 0.91 for the second-row double-bond factor, from comparison with the first-row factors. Second-row radii calculated in this way are also included in Table XV.

Interatomic Distances and Resonance.—Two years ago[1b] we constructed an empirical curve showing the dependence of the carbon–carbon distance on bond type for single bond–double bond resonance, using data for diamond (1.54 Å., single bond), graphite (1.42 Å., one-third double bond), and benzene (1.39 Å., one-half double bond), and accepting 1.38 Å. for the pure double-bond distance. With the aid of this curve a number of conclusions were drawn regarding bond type in resonating molecules.

The decrease of 0.04 Å. in the double bond distance requires that the resonance curve be revised. It is fortunate that this revision invalidates none of the earlier conclusions, for the reason that only the part of the curve from 0 to 50% double-bond character was made use of, and the new curve does not differ appreciably from the old one in this region.

The new curve representing the dependence of carbon–carbon interatomic distance on double-bond character is shown in Fig. 8. As mentioned above, this curve does not differ appreciably from the old one up to 50% double-bond character, and in this region it may be used as before to determine bond type from measured interatomic distances. The change in the curve between 50 and 100% double-bond character enhances its value; the new curve can be used to determine bond type in this region also, where the old one was useless because of its small slope.

The most extensive application which was made of the resonance curve was to the carbon–chlorine bond in phosgene and the chloroethylenes. In the electron-diffraction study of these substances[28] the carbon–carbon and carbon–oxygen double-bond values 1.38 and 1.28 Å. were assumed; the question accordingly arises as to what effect the new double bond values would have on the carbon–chlorine distances. The new double-bond distances are smaller than the old by 0.04 Å. It is probable, however, that in the chlorine-substituted ethylenes the carbon–carbon distance is about 1.36 Å. and in phosgene the carbon–oxygen distance is about 1.26 Å., for the following reason. Conjugation of the unshared pair of a chlorine atom with the double bond gives the carbon–chlorine bond some double-bond character and at the same time gives the double bond some single-bond character, amounting to 20 or 30%. Reference to Fig. 8 shows that this corresponds to a distance about 0.02 Å. larger than the double-bond distance, and thus about 0.02 Å. smaller than the old double-bond distance. To make this decrease of 0.02 Å. in the models each atom would be moved in 0.01 Å. toward the midpoint of the two. This change would have only an inappreciable effect on the calculated intensity curves, so that the models accepted in the original investigation would still be acceptable after revision in this way. Considering the angles involved, we see that the revision leads to carbon–chlorine distances which differ from the original ones by less than 0.005 Å., a negligible amount; the conclusions reached regarding double-bond character of the carbon–chlorine bonds are accordingly still valid.

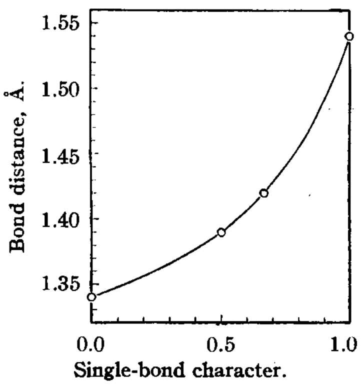

Fig. 8.—Curve showing the dependence of carbon–carbon bond distance on the relative degree of single-bond–double-bond character.

It is interesting that the resonance curve of Figure 8 can be represented by the equation

$$d = 1.54 - 0.20 \frac{3x}{(2x + 1)} \qquad (1)$$

in which x represents the double-bond character. This equation can be derived in the following simple way, based on Morse's interpretation of the

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[27] G. Herzberg, *Ann. Physik*, **15**, 677 (1932); J. Curry, L. Herzberg and G. Herzberg, *J. Chem. Phys.*, **1**, 749 (1933); *Z. Physik*, **86**, 348 (1933).

[28] L. O. Brockway, J. Y. Beach, and L. Pauling THIS JOURNAL, **57**, 2693 (1935).

curve.[29] Let the potential function for a resonating bond be given as the sum of two parabolas, representing single-bond and double-bond potential functions, with coefficients 1 − x and x

$$V(r) = (1 - x)C_1 (r - r_1)^2 + xC_2(r - r_2)^2 \qquad (2)$$

By equating to zero the differential of this with respect to r, we find the equilibrium distance as a function of x and the ratio of force constants C_2/C_1. For $C_2/C_1 = 3$, $r_2 = 1.34$, and $r_1 = 1.54$, this function is that given by Equation 1. The value 3 for the ratio of force constants is somewhat larger than that indicated by Badger's rule, which is about 2.3; it is probable that this increase is needed to compensate for the neglect of resonance energy in the assumed potential function.

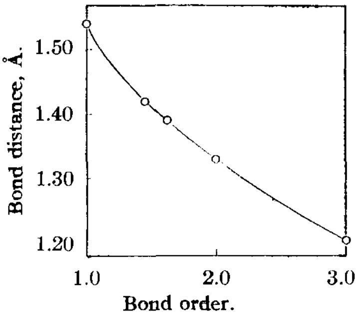

Fig. 9.—Curve showing the dependence of carbon–carbon bond distance on the order of bond (Penney).

In drawing the original resonance curve we pointed out that the assignment of 33.3% double-bond character to graphite and 50% to benzene is somewhat arbitrary; we selected the treatment leading to these numbers (division of valences of carbon among the available bonds) rather than a treatment based on a more complete quantum-mechanical discussion for the sake of simplicity, feeling that the discussion of resonance of molecules should be kept as close as possible to the accepted ideas and methods of chemistry. The arbitrariness of our procedure has again been pointed out by Penney,[18] who has introduced a new concept, that of the "order" of a bond. The order of a bond in a resonating molecule can be calculated by a quantum-mechanical method which is an extension of the valence-bond treatment applied in the calculation of resonance energies.[30] In benzene the bonds are of order 1.623, somewhat closer to double bonds (of order 2) than to single bonds (of order 1); this corresponds essentially to considering the resonance energy to increase the strength of the bonds. In graphite the bonds are found by a long calculation to be of order 1.45. Penney's curve relating interatomic distance to order of bond is shown in Fig. 9. It is very interesting that a simple curve passes through not only the four points represented in Fig. 8 but also the point 1.20 Å. at order 3 representing a triple bond; this becomes understandable when it is recognized that in a molecule containing equivalent bonds the order of the bonds is a measure of the total bond energy of the molecule, including resonance energy, since we might well expect a simple relation to hold between interatomic distance and bond energy for closely similar bonds.

Acknowledgments.—We are indebted to Dr. B. H. Sage, Professor F. C. Whitmore, Professor G. S. Parks, Dr. G. W. Wheland, Mr. T. A. Boyd, Professor G. B. Kistiakowsky, Dr. W. E. Vaughan, and Professor H. J. Lucas for samples of substances used in this work, to Mr. K. S. Palmer for assistance in preparing some of the photographs, and especially to Dr. S. Weinbaum and Mrs. M. R. Lassettre for carrying out many laborious calculations.

Summary

Values found for interatomic distances and bond angles in the thirteen hydrocarbons studied are given in Table XIV. The carbon–carbon single-bond distance is found to have the constant value 1.54 ± 0.02 Å., being unaffected by the presence of an adjacent double bond or benzene nucleus (provided that it does not form part of a conjugated system). The carbon–carbon double-bond distance in allene and acetylene has the value 1.34 Å. This is 0.04 Å. less than that formerly given by the table of covalent radii, which has accordingly been revised. The effect of the revision on the bond distance-resonance curve is discussed.

PASADENA, CALIF. RECEIVED APRIL 26, 1937

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(29) See footnote 3 of reference 1b.

(30) L. Pauling and G. W. Wheland, *J. Chem. Phys.*, **1**, 362 (1933).

[Reprinted from the Journal of the American Chemical Society, **61**, 1769 (1939).]

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 686]

The Electron Diffraction Investigation of the Structure of Benzene, Pyridine, Pyrazine, Butadiene-1,3, Cyclopentadiene, Furan, Pyrrole, and Thiophene

BY V. SCHOMAKER AND L. PAULING

The determination of values of interatomic distances in molecules has been found to provide much information regarding electronic structure, especially in the case of substances which resonate among two or more valence–bond structures. The interpretation of interatomic distances in terms of the types of bonds involved is made with use of an empirical function formulated originally for single bond–double bond resonance of the carbon–carbon bond.[1] There are given in this paper the results of the determination of the configurations of two molecules involving Kekulé resonance, pyridine and pyrazine, of two molecules with conjugated double bonds, butadiene and cyclopentadiene, and of three five-membered heterocyclic molecules, furan, pyrrole, and thiophene, together with the conclusions regarding their electronic structures reached by application of the bond type–interatomic distance function. In addition, because of the improvement in electron diffraction technique since the study of benzene in these Laboratories four years

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[1] L. Pauling, L. O. Brockway and J. Y. Beach, THIS JOURNAL, **57**, 2705 (1935); L. Pauling and L. O. Brockway, *ibid.*, **59**, 1223 (1937).

ago[2] and because of its similarity to pyridine and pyrazine, this substance was re-investigated.

Experimental Method.—The diffraction photographs were prepared with the apparatus and technique described by Brockway.[3] Ten or more photographs were made for each substance, the electron wave length used being about 0.0613 Å. and the camera distance 10.83 cm. The values of $s_0 = 4\pi(\sin \theta/2)/\lambda$ given in the tables are averages of the values found by visual measurement of ring diameters for ten or more films.

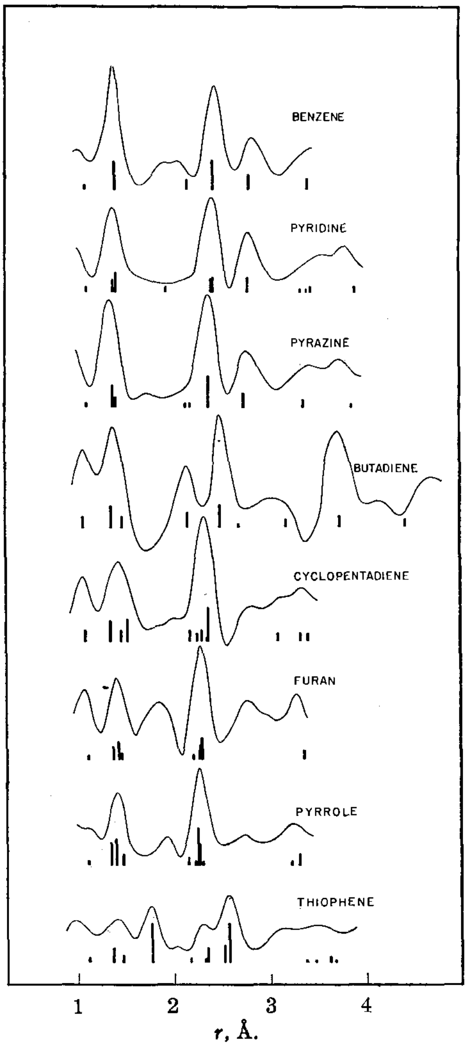

Fig. 1.—Radial distribution curves.

The radial distribution treatment,[4] with refinements soon to be described in This Journal, was applied as the first step in the interpretation of the data for each substance. Further selection from among the small range of molecular models compatible with the radial distribution curve for each substance was then made by the usual visual method, involving comparison with simplified theoretical intensity curves for the models under discussion.

The sample of benzene used was prepared by redistilling thiophene-free benzene and rejecting the first and last portions. A similar treatment was given to pyridine (Kahlbaum), pyrrole (Eastman), and thiophene (Eastman). Butadiene was prepared by treating tetrabromobutane in ethyl alcohol solution with granulated zinc and redistilling the product several times. Cyclopentadiene was prepared by distilling dicyclopentadiene; in order that appreciable repolymerization should not take place in the sample the diffraction photographs were made immediately after the distillation (within one hour). Furan was prepared by the decarboxylation of furoic acid and purified by fractional distillation. A sample of pyrazine kindly given us by Professor F. W. Bergstrom was used without further purification.

Benzene, Pyridine, and Pyrazine.—New photographs of benzene were obtained showing four more measurable rings than those used in the

Table I

Benzene

Max.	Min.	I	C_k[a]	s_0	s[b]	s/s_0
1		4	2	3.20	2.89	(0.904)[c]
	2	−10	− 7	4.30	4.19	(0.974)
2		10	14	5.71	5.75	1.006*
	3	− 1	− 2	7.60	7.57	0.996
3		4	11	9.48	9.89	(1.043)
	4	− 1	− 3	10.26	10.92	(1.063)
4		3	11	11.20	11.15	(0.991)
	5	− 7	−27	12.46	12.50	1.003*
5		4	19	13.63	13.89	1.020
	6	− 2	− 9	14.85	...[d]	...
6		2	10	15.98	15.80	0.989
	7	− 5	−23	17.42	17.40	0.999*
7		3	15	18.61	18.84	1.012*
	8	− 1/2	− 2	20.18	20.29	1.005
8		1 1/2	7	21.30	21.17	0.994
	9	− 2	− 8	22.70	22.20	0.979
9		2	8	23.80	24.00	1.008
10		1	3	(27.0)	...[d]	...

Average 1.002
Average deviation 0.008
(C–C = 1.39 × 1.002 = 1.393 Å.)
(C–H = 1.075 × 1.002 = 1.077 Å.)
C–C = 1.39 ± 0.02 Å
C–H = 1.08 ± 0.04 Å.

[a] The coefficients of the terms $(\sin l s_k/l s_k)$ of the radial distribution function. [b] Calculated for coplanar hexagonal model with C–H = 1.075 Å. and C–C = 1.39 Å. [c] Less reliable values, not included in taking the average, are shown in parentheses. [d] The theoretical curve does not indicate a precisely measurable feature at this point. * In finding the average value of s/s_0, the starred values are given double weight, for we believe them to be more reliable than the others. Doubly weighted values of s/s_0 are similarly indicated in the following tables.

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(2) L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

(3) L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

(4) L. Pauling and L. O. Brockway, This Journal, **57**, 2684 (1935).

earlier investigation in these Laboratories. The radial distribution curve calculated with the C and s values of Table I (Fig. 1) shows three principal peaks, at 1.37 Å., 2.43 Å. (= $\sqrt{3} \times$ 1.40 Å.), and 2.83 Å. (= $2 \times$ 1.415 Å.), representing the C–C separations for a regular hexagon with edge about 1.39 Å. The small peaks do not provide reliable information about the C–H bond distance. In order to make an approximate evaluation of this distance, intensity curves were calculated for plane hexagonal models with C–C = 1.39 Å. and C–H varying between 1.00 and 1.18 Å. at intervals of 0.03 Å. These curves (Fig. 2) differ significantly only in the region from the third to the sixth ring. (Note that in the tables a feature of the photographs is for convenience designated by "max." or "min." even though it appears to be a shelf or the inner edge of a shelf, respectively, and that in the text the numbers assigned to the rings correspond to those for maxima in the tables.) The visual intensity estimates for the third and fourth rings have the ratio $^4/_3$; this is not in accordance with the curves with C–H = 1.12 Å. or more, which make the fourth ring as strong as the third. Moreover, the 1.03 curve (as well as the 1.00 curve) shows only a very poorly defined shelf in place of the fourth ring. The 1.06 and 1.09 curves satisfactorily reproduce all of the features observed on the photographs, including the fifth and sixth rings. The quantitative comparison of observed s values with those calculated for C–C′ = 1.39 Å. and C–H = 1.075 Å. (the mean for the 1.06 and 1.09 curves), given in Table I, leads to C–C = 1.393 ± 0.02 Å. and C–H = 1.08 ± 0.04 Å. This value for the C–H distance agrees well with the value C–H = 1.090 ± 0.005 Å. which may be inferred from the C–H stretching frequencies and our knowledge of the relation of these frequencies to C–H bond distances.[5]

Wierl[6] and Pauling and Brockway[2] have previously reported C–C = 1.39 Å. in benzene. Jones[7] has reported the values C–C = 1.40 ± 0.01 Å. and C–H = 1.14 ± 0.01 Å. It seems probable that the latter value is in error.

An intensity curve was calculated also for a plane trigonal model, with C–H = 1.09 Å., C–C = 1.36 and 1.42 Å. alternately around the ring, the angles C–C–C = 120°, and the angles H–C–C = 123 and 117°, corresponding to quite incomplete resonance between the Kekulé structures. This curve is practically indistinguishable from that for the corresponding plane hexagonal model with C–H = 1.09 Å. and C–C = 1.39 Å. The electron diffraction method is accordingly unable to add to the existing theoretical and experimental evidence[8] for complete resonance in the benzene molecule.

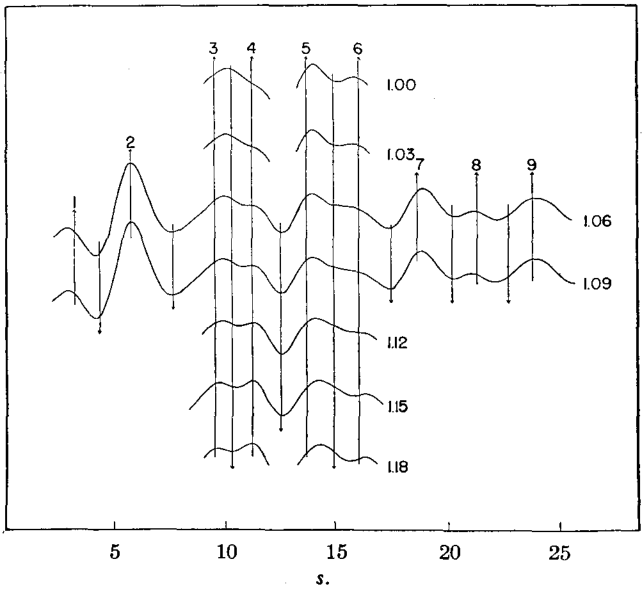

Fig. 2.—Calculated intensity curves for benzene.

The photographs obtained for pyridine and pyrazine are so closely similar to those of benzene as to leave no doubt that the three molecules have nearly identical structures. The radial distribution curve for pyridine (Fig. 1) calculated from the data given in Table II has well-defined peaks at 1.38, 2.39 (= $\sqrt{3} \times$ 1.38), and 2.76 (= $2 \times$ 1.38) Å. The sharpness of the 2.39 peak indicates that the six meta distances in the ring are nearly equal. The calculated intensity curve for the model with C–C = 1.39 Å., C–N = 1.33 Å., C–H = 1.08 Å., the angle C–N–C = 119° and the angles C–C–C = 121°, and having nearly equal "meta" and "para" distances, is shown in Fig. 3. The comparison of s_0 and s values for this model (Table II) leads to the values C–H =

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[5] E. Eyster, *J. Chem. Phys.*, **6**, 580 (1938).

[6] R. Wierl, *Ann. Physik*, **8**, 521 (1931).

[7] P. L. F. Jones, *Trans. Faraday Soc.*, **31**, 1036 (1935).

[8] C. K. Ingold, *Proc. Roy. Soc.* (London), **A169**, 149 (1938).

TABLE II

PYRIDINE

Max.	Min.	I	C	s_0	Model I[a] s	Model I[a] s/s_0	Benzene "1.09," "1.39" s	Benzene "1.09," "1.39" s/s_0
1		4	2	3.19	2.99	(0.947)	2.89	(0.906)
	2	−10	−7	4.37	4.16	(0.952)	4.19	(0.959)
2		10	14	5.69	5.83	1.025*	5.75	1.011*
	3	−1	−2	7.58	7.68	1.027	7.57	0.999
3		4	11	9.14	9.94	(1.087)	9.89	(1.082)
	4	−1	−3	10.21	10.74	(1.053)	10.92	(1.070)
4		3	11	11.24	11.30	(1.004)	11.15	(0.992)
	5	−7	−27	12.73	12.75	1.002*	12.50	0.982*
5		4	19	13.88	14.23	1.025	13.89	1.001
	6	−2	−9	15.12	15.85	(1.048)	...	...
6		2	10	16.20	16.31	1.007	15.80	0.975
	7	−5	−23	17.60	17.66	1.003*	17.40	.988*
7		3	15	18.86	19.10	1.013*	18.84	.999*
	8	−$^1/_2$	−2	20.33	20.60	1.013	20.29	.997
8		$1^1/_2$	7	21.44	21.40	0.997	21.17	.987
	9	−2	−8	22.65	22.47	0.992	22.20	.980
9		2	8	23.82	24.27	1.018	24.00	1.007
10		1	3	28.0	28.18	1.007	...	...
					Average	1.011		0.994
					Average deviation	0.009		0.010

[a] Models described in text.

1.09, C–C = 1.405, and C–N = 1.344 Å., with average ring bond distance 1.385 ± 0.01 Å. The comparison with the s values for a regular hexagonal model leads to the same value 1.385 Å. for the average ring bond distance. It seems unlikely that the C–C distance differs from 1.39 Å., and the results accordingly suggest that the C–N distance is about 1.37 ± 0.03 Å.

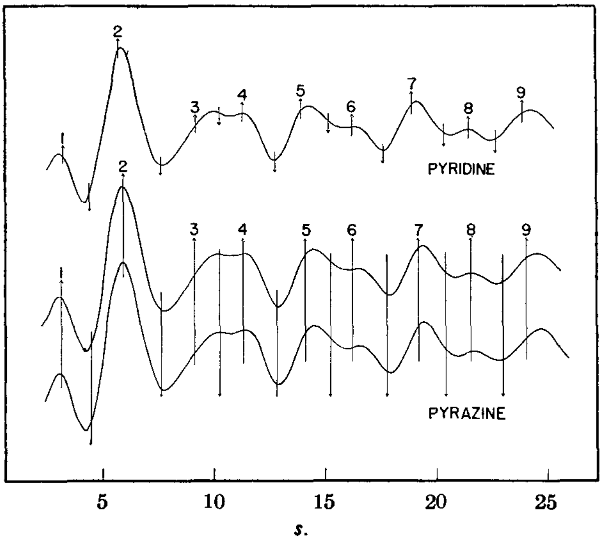


Fig. 3.—Calculated intensity curves for pyridine and pyrazine.

The principal peaks on the radial distribution curve for pyrazine (Fig. 1) lie at 1.36, 2.37 (= $\sqrt{3} \times 1.37$), and 2.76 (= 2 × 1.38 Å.). Intensity curves for model I, with C–C = 1.39 Å., C–N = 1.33 Å., C–H = 1.09 Å., and all ring angles 120°, and for model III, with the same bond distances but with the ring angles at nitrogen 123° and at carbon 118°30′, making the meta distances equal, are shown in Fig. 3. These curves, as well as the benzene curve (representing a regular hexagonal model), agree qualitatively with the photographs. The quantitative comparison for all three leads to the value 1.366 ± 0.01 Å. for the average ring bond distance. With C–C = 1.39 Å., this corresponds to C–N = 1.35 ± 0.02 Å.

Butadiene-1,3 and Cyclopentadiene.—The photographs of butadiene which were obtained are diffuse and were measured only with difficulty, so that the determination of the configuration of the molecule is less precise than usual. Thirteen rings could be seen, with the s_0 and I values given in Table IV. These correspond to the radial distribution curve shown in Fig. 1, with peaks at 1.07, 1.38, 2.12, 2.48, (3.0), 3.71, (4.13), and (4.65) Å., the values in parentheses being unreliable. The carbon–carbon peak at 1.38 Å. represents the mean of the values for the two double bonds and the intervening single bond, which has some double bond character. If the double bonds have about the normal distance 1.34 Å. found in ethylene and allene,[1b,5] the value 1.46 Å. is indicated for the conjugated single bond. The peak

TABLE III

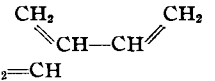
PYRAZINE

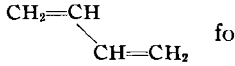
	Max.	Min.	I	C_k	s_0	Model 1[a] s	Model 1[a] s/s_0	Model 111 s	Model 111 s/s_0	Benzene "1.09," "1.39"	
	1		4	2	3.09	3.02	(0.977)	3.06	(0.990)	2.90	(0.938)
		2	−10	−10	4.41	4.23	(.959)	4.20	(0.952)	4.19	(.950)
	2		10	16	5.89	5.87	.996*	5.89	1.000*	5.75	.976*
		3	− 2	− 5	7.59	7.77	1.023	7.71	1.016	7.60	1.002
	3		4	12	9.08	10.23	(1.127)	10.24	(1.128)	9.87	(1.087)
		4	− 1/2	− 2	10.20	10.70	(1.049)	10.62	(1.042)	10.90	(1.068)
	4		4	16	11.27	11.37	(1.008)	11.35	(1.007)	11.20	(0.994)
		5	− 7	−31	12.76	12.90	1.012*	12.89	1.011*	12.50	.980*
	5		4	19	14.07	14.43	1.026	14.45	1.027	13.93	.991
		6	− 1	− 4	15.21	16.02	(1.053)	15.92	(1.047)	...[b]	...
Shelf	6		2	10	16.20	16.50	1.018	16.55	1.022	15.80	.975
		7	− 5	−25	17.73	17.90	1.010*	17.95	1.007*	17.40	.982*
	7		3	14	19.16	19.40	1.013*	19.41	1.013*	18.85	.984*
		8	− 1	− 4	20.37	20.85	1.024	20.90	1.026	20.30	.997
	8		1	4	21.51	21.60	1.004	21.70	1.008	21.13	.983
		9	− 2	− 7	22.97	22.70	0.988	22.78	0.992	22.20	.967
	9		2	6	24.04	24.55	1.021	24.65	1.025	24.00	.988
					Average		1.012		1.012		0.984
					Average deviation		0.008		0.008		0.007

[a] Models described in text. [b] The theoretical curve does not show a measured feature at this point.

at 2.48 Å. corresponds to the 1,3 and 2,4 carbon–carbon distances; this value leads to about 125° for the C=C—C bond angle.

Of the two probable configurations *cis*



and *trans*  for the molecule, the latter is suggested by the presence of a large radial distribution peak at 3.71 Å., which is just the value calculated for the *trans* model. The small radial distribution peak at 3.0 Å. is probably without significance.

The intensity curves I, II, III, and IV of Fig. 4 are calculated for coplanar *trans* models with C–H = 1.06 Å., the angle H—C=C = 115°, and the angle H—C—H = 109.5°. Although these hydrogen parameters are so chosen as to agree as well as possible with minor peaks of the radial distribution function, no great reliance can be placed on them, and indeed it is likely that for this molecule the C–H bond distance is 1.09 Å. The models have the following additional parameters

Model	C=C	C—C	Angle C=C—C
I	1.38 Å.	1.38	126°10′
II	1.36	1.44	124°40′
III	1.34	1.48	123°5′
IV	1.32	1.54	120°10′

The average of the carbon–carbon bond distances has for each model approximately the radial distribution value 1.38 Å. and the angle C=C—C is such as to give the radial distribution value 2.48 Å. for the 1,3- and 2,4-distances. The agreement with the photographs is reasonably satisfactory for curves II and III, but not for I and IV. For example, the relative intensities of rings 9 and 10 are not well reproduced by curve IV, and those of rings 11 and 12 are not given satisfactorily by either curve I or curve IV. The appearance on the photographs of a doublet (rings 6 and 7) rather than a single ring may be due to an inflection in curves II and III in this region; otherwise the agreement is excellent. Curves were also calculated for about ten models differing slightly from these, with no improvement.

It is concluded that the butadiene molecule has the configuration described by the following parameter values: C–H = 1.06 Å. (assumed), C=C = 1.35 ± 0.02 Å., C–C = 1.46 ± 0.03 Å., angle C=C—C = 124 ± 2°. The configuration is probably essentially coplanar and *trans;* the evidence for this view provided by the radial distribution function is not conclusive inasmuch as it is not supported by a strong dependence of the theoretical intensity curves on the relative rotation of the vinyl groups of the butadiene model. The electron diffraction data are not incompatible with a mixture of *cis* and (predominantly) *trans* molecules. However, other experimental evidence (reviewed by Mulliken[9]) together with theoretical

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(9) R. S. Mulliken, *J. Chem. Phys.*, **7**, 121 (1939). See, however, **7**, 373 (1939).

considerations[10] indicates that butadiene molecules must be essentially coplanar and *trans*.

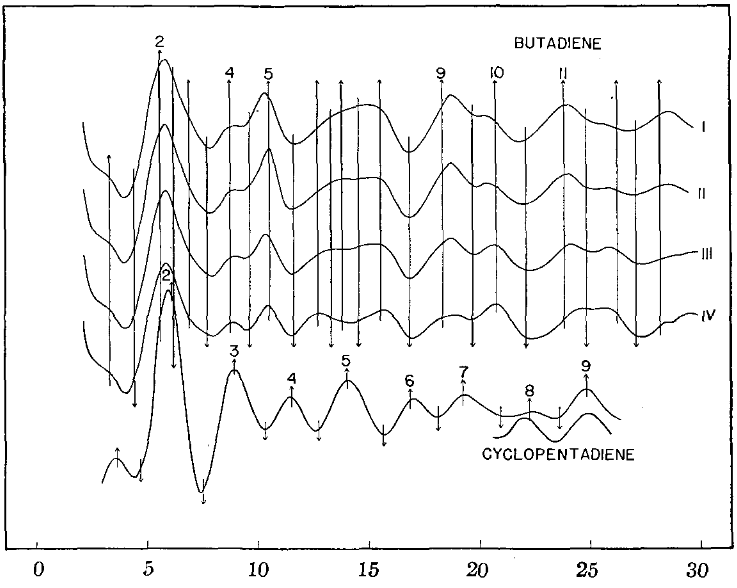
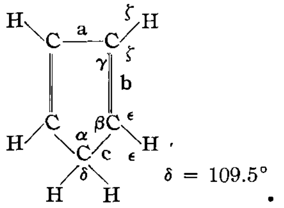


Fig. 4.—Calculated intensity curves for butadiene and cyclopentadiene.

The spectroscopic conclusion of Bartholomé and Karweil[11] that in butadiene there is essentially free rotation about the C–C bond with a barrier not greater than 200 cal./mole is almost certainly incorrect.

Data for the excellent photographs of cyclopentadiene, showing nine rings, are given in Table V. The corresponding radial distribution curve (Fig. 1) has peaks at 1.06, 1.42, and 2.33 Å. The number of parameters determining the structure of this molecule is so great as to prevent their independent evaluation. The molecule



without doubt has the single bond distance *c* equal to about 1.53 Å., as in the cycloparaffins, and the double bond distance *b* equal to about 1.35 Å., as in butadiene. The conjugated single bond *a* is probably about 1.46 Å. Many models with approximately these values for the carbon–carbon distances, with various ring angles, and with C–H = 1.09 Å. were found to give calculated curves showing by their qualitative appearance that $\alpha = 101 \pm \sim 3°$ and leading on quantitative comparison to the value 1.445 ± 0.01 Å. for the average ring bond distance. This is exactly the average of the values suggested above. Assuming the average of the values of *b* and *c* to be reliable, we write C–C = 1.46 ± 0.04 Å. as the value determined for the conjugated double bond. The curve shown in Fig. 4, with *s* values given in Table V, is that for the model with the values $a = 1.44$, $b = 1.34$, and $c = 1.54$ Å., and the angles $\alpha = 101°$, $\beta = 109°$, $\gamma = 110°$. While this curve is slightly better than any of the others we have calculated, it is not possible to base a satisfactory determination of the relative values of the bond distances on the qualitative appearance of the diffraction pattern. The curve gives an excellent representation of the appearance of the photographs except that the fourth minimum of the curve is much too deep relative to the fifth minimum, and the eighth maximum is much too weak. On the films the eighth ring appears to be as strong as the ninth. These discrepancies arise from ignoring the temperature effect,[12] that is, the effect on the diffraction pattern of the variation of the interatomic distances resulting from molecular vibrations. We have found that when probable variations of the various interatomic distances are considered, the slight trouble of the fourth and fifth minima is resolved, as is the greater difficulty of the eighth maximum. This is illustrated for the region of the eighth maximum by the last curve of Fig. 4, which has been plotted for the best cyclopentadiene model (C–C = 1.53, 1.46; C=C = 1.35; $\alpha = 101°$), with the carbon–hydrogen interactions omitted as an approximation to the effect at large diffraction angles of the temperature factor corresponding to the large amplitudes of vibration of the hydrogen atoms.

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(10) L. Pauling and J. Sherman, *J. Chem. Phys.*, **1**, 679 (1933); W. G. Penney, *Proc. Roy. Soc.* (London), **A158**, 306 (1937).

(11) E. Bartholomé and J. Karweil, *Z. physik. Chem.*, **B35**, 442 (1937).

(12) L. O. Brockway, *Rev. Modern Phys.*, **8**, 238 (1936). The temperature effect may be somewhat significant also for the other molecules discussed in the paper. Its dominating importance for cyclopentadiene is perhaps coincidental. We expect to investigate this question further.

TABLE IV

BUTADIENE

					Model II		Model III	
Max.	Min.	I	C_k	s_0	s	s/s_0	s	s/s_0
	1	− 3	0	2.37	...	(.....)	...	(.....)[a]
1		5	2	3.35	...	(.....)	...	(.....)
	2	−10	− 7	4.47	4.01	(0.897)	4.10	(0.918)
2		15	14	5.62	5.92	(1.053)	5.94	(1.057)
	3	− 1	− 1	6.24	...	(.....)	...	(.....)
3		7	11	6.98	...	(.....)	...	(.....)
	4	− 2	− 4	7.74	7.90	1.020	7.95	1.026
4		4	8	8.79	9.00	1.023	9.05	1.029
	5	− 1	− 2	9.68	9.30	0.961	9.40	0.971
5		6	16	10.56	10.62	1.006*	10.40	.985*
	6	− 4	−11	11.67	11.55	0.990*	11.60	.994*
6		3	10	12.74	...	(.....)	...	(.....)
	7	− 1	− 3	13.33	...	(.....)	...	(.....)
7		3	9	13.82	...	(.....)	...	(.....)
	8	− 2	− 6	14.60	...	(.....)	...	(.....)
8		3	10	15.58	...	(.....)	...	(.....)
	9	− 4	−13	16.90	16.92	1.001*	16.93	1.002*
9		3	10	18.37	18.78	1.022*	18.79	1.022*
	10	− 1	− 3	19.72	19.94	1.011*	19.80	1.004*
10		1	3	20.79	20.40	0.981*	20.72	0.997*
	11	− 2	− 5	22.13	22.00	0.994*	22.35	1.010*
11		2	4	23.88	23.97	1.004*	24.12	1.010*
	12	− 1	− 2	24.87	...	(.....)	...	(.....)
12		1	2	26.26	...	(.....)	...	(.....)
	13	− 1	− 1	27.10	...	(.....)	...	(.....)
13		1	1	28.20	...	(.....)	...	(.....)
					Average	1.001		1.003
					Average deviation	0.012		0.001

[a] The theoretical curve does not have a well-defined maximum or minimum corresponding to the measured ring.

TABLE V

CYCLOPENTADIENE

					Model I[a]	
Max.	Min.	I	C_k	s_0	s	s/s_0
1		28	1	3.66	...	...
	2			4.71	4.45	(0.946)
2		70	14	6.13	6.00	(.979)
	3			7.54	7.46	.990
3		28	15	8.98	9.01	1.003
	4			10.37	10.41	1.004
4		12	11	11.54	11.53	0.999
	5			12.78	12.68	0.992
5		18	24	14.09	14.14	1.003
	6			15.68	15.80	1,007
6		7	12	16.90	17.07	1.009
	7			18.16	18.15	0.999
7		7	13	19.29	19.40	1.006
	8			20.99	21.40	1.019
8		3	5	22.28	22.45	1.007
	9			23.62	23.43	0.992
9		3	5	24.87	24.86	0.999
			Average			1.002
			Average deviation			0.005
			Average ring bond distance			1.443 Å.

[a] Model for which a = 1.44 Å., b = 1.34 Å., c = 1.54 Å., α = 101°.

TABLE VI

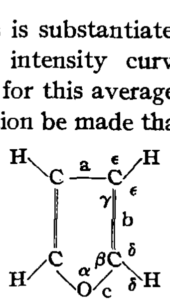
FURAN

Max.	Min.	I	C_k	s_0	s[a]	s/s_0
	1			2.42	2.52	(0.961)
1		11	0	3.61	3.82	(1.057)
	2			4.78	4.50	(0.941)
2		20	4	6.15	6.07	.987
	3			7.76	7.70	.991
3		12	7	9.13	9.43	(1.032)
	4			10.60	10.75	(1.013)
4		6	15	11.73	11.60	(0.989)
	5			13.16	12.90	(0.980)
5		10	28	14.44	14.56	1.008
	6			16.23	16.30	1.004
6		3	13	17.65	17.73	1.004
	7			18.89	18.55	(0.982)
7		3	15	19.88	19.77	0.994
	8			21.55	21.63	1.003
8		$1^1/_2$	11	23.26	23.20	0.997
	9			24.26	24.57	1.012
9		$1^1/_2$	5	25.46	25.55	1.003
			Average			1.000
			Average deviation			0.0065
			Average ring bond distance			1.395 Å.

[a] Model XIX: C–O = 1.41, C=C = 1.35, C—C = 1.46, α = 105°, β = 110.8°, γ = 106.7°.

Furan, Pyrrole, and Thiophene.—The data for furan (Table VI) lead to a radial distribution curve (Fig. 1) with principal peaks at 1.39 and 2.26 Å., indicating an average ring bond distance of 1.39 Å. This is substantiated by comparison with calculated intensity curves, which gives 1.395 ± 0.01 Å. for this average.

If the assumption be made that in the molecule



the values of a and b are 1.46 and 1.35 Å., respectively, as in butadiene and cyclopentadiene, it is found that there is excellent qualitative and quantitative agreement between the photographs and models with C–H = 1.09 Å., c = 1.41 ± 0.02 Å., α = 107 ± 4°, β = 109 ± 3°, and γ = 107 ± 2°, as is illustrated for model XIX by Fig. 5 and Table VI. The quantitative agreement is impaired by change in c, and the qualitative agreement by change in α (with corresponding changes in β and γ). It is interesting to note that the value of c is only slightly less than the single bond C–O value, 1.43 Å.

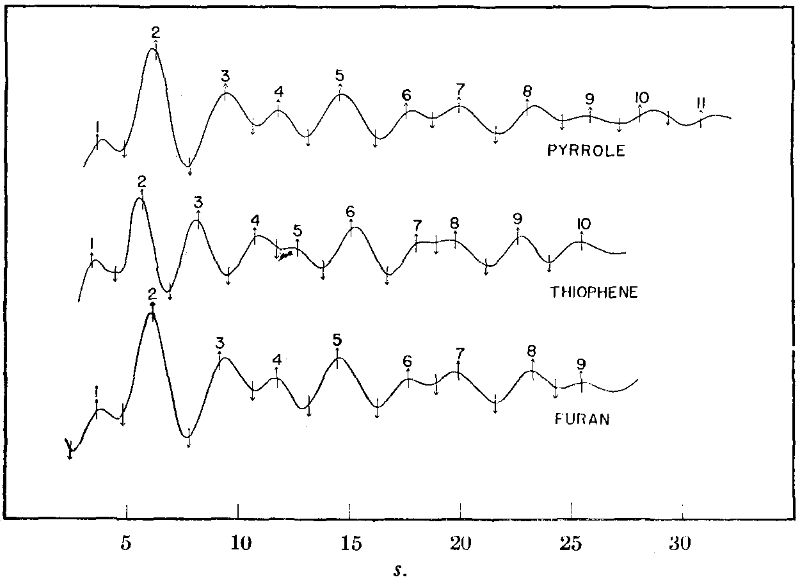


Fig. 5.—Calculated intensity curves for furan, pyrrole, and thiophene.

The curve for model XIX represents the appearance of the photographs very well, except that the sixth and seventh maxima actually appear to be equally strong. Several of the twenty theoretical curves calculated for furan are nearly as satisfactory, and one, for the model with C—O = 1.42, C=C = 1.34, C—C = 1.44, and α = 104°, is somewhat better, the sixth and seventh maxima on it being equally high. This improvement is probably not significant, especially since the temperature effect may here play a role as with cyclopentadiene. We find that it is not possible to determine the relative values of the bond distances in the heterocyclic molecules containing only light atoms within reasonable limits by the qualitative comparison, and we have accordingly assumed appropriate values for C=C and C—C. For any reasonable given set of ring bond distances qualitative agreement is obtained only when the bond angles are so chosen as to make the cross-ring distances equal to within a few hundredths of an ångström unit.

The photographs for pyrrole are very closely similar to those for furan, and lead to the same value, 1.395 ± 0.01 Å., for the average ring bond distance. The radial distribution function shown in Fig. 1 has important sharp peaks at 1.40 and 2.25 Å. With a = 1.46 and b = 1.35 Å., the average ring bond distance leads to c = 1.41 Å., which is 0.06 Å. less than the C–N single bond value. In accordance with the discussion given below, it seems probable that this decrease, indicating double bond character, is accompanied by further decrease in a, and that the values in the molecule are C—H = 1.09 Å. (assumed), a = 1.44 Å. (assumed), b = 1.35 Å. (assumed), and c = 1.42 ± 0.02 Å. The angles have the values α = 105 ± 4°, β = 110 ± 3°, and γ = 108 ± 2°. The agreement of the photographs with a model falling within this range is shown in Fig. 5 and Table VIII. Other models give the same average ring bond distance.

The data from the photographs of thiophene, showing ten rings (Table VIII), lead to the radial distribution curve of Fig. 1, with peaks at 1.40 Å. (C–C), 1.74 Å. (S–C), 2.29 Å. (C–C, meta), and 2.55 Å. (S—C). If the values C—C = 1.44 and C=C = 1.35 Å. be assumed in this molecule, as in pyrrole, the radial distribution curve leads to the configuration with S—C = 1.74 ± 0.03 Å., angle C—S—C = 91 ± 4°, angle S—C=C = 112 ± 3°, and angle C=C—C = 113 ± 3°. The curve calculated for this model (with C—H = 1.09 Å.) agrees very well with the photographs, as shown in Fig. 5 and Table VIII.

Discussion

Pyridine and Pyrazine.—The values found

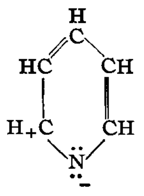
TABLE VII

PYRROLE

Max.	Min.	I	C_k	s_0	Model I^a s	Model I^a s/s_0
1		10	0	3.61	...	(...)
	2			4.85	...	(...)
2		30	8	6.26	6.09	0.972
	3			7.79	7.71	0.989
3		12	7	9.36	9.49	1.014
	4			10.62	10.83	1.019
4		5	7	11.79	11.81	1.001
	5			13.12	13.04	0.994
5		10	22	14.53	14.67	1.009
	6			16.18	16.47	1.018
6		4	13	17.54	17.85	1.017
	7			18.72	18.77	1.003
7		4	15	19.93	19.95	1.001
	8			21.60	21.79	1.009
8		4	17	22.98	23.38	1.017
	9			24.57	24.65	1.003
9		1	4	25.82	25.70	0.995
	10			27.14	27.15	1.000
10		2	7	28.07	28.80	(...)
	11			29.34	30.19	(...)
11		1	3	30.81	31.55	(...)
		Average				1.004
		Average deviation				0.010
		Average ring bond distance				1.395 Å.

[a] Model: $a = 1.47$ Å., $b = 1.34$ Å., $c = 1.40$ Å., $\alpha = 105°$, $\beta = 110°$, $\gamma = 106°$.

for the C–N Kekulé-type bond distance in pyridine and pyrazine, 1.37 ± 0.03 Å. and 1.35 ± 0.02 Å., respectively, are somewhat larger than the expected value 1.33 Å. for 50% double bond character. It is possible that this is the result of the large electronegativity of the nitrogen atom, leading to significant additional resonance with ionic structures such as



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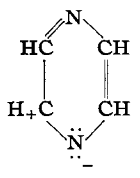

Probably the effect on the C–N distance is greater for pyridine than for pyrazine because in pyridine there are three structures giving the nitrogen atom a negative formal charge and only single bonds, while in pyrazine there are four such structures of which only two affect a given one of the nitrogen atoms. Investigations of the C–N distances in related compounds such as pyridazine, pyrimidine, and cyanuric and cyameluric[13] derivatives would be of interest in this connection.

TABLE VIII

THIOPHENE

Max.	Min.	I	C_k	s_0	Model I^a s	Model I^a s/s_0
1		2	0	3.37	3.53	(1.047)[b]
	2			4.42	4.50	(1.019)
2		10	5	5.64	5.52	(0.978)
	3			6.90	6.80	.986
3		8	9	8.17	8.05	.985
	4			9.53	9.50	.997
4		3	5	10.71	10.92	(1.019)
	5			11.70	12.08	(1.032)
5		1	3	12.63	12.42	(0.983)
	6			13.80	13.78	0.999
6		3	11	15.05	15.30	1.016
	7			16.68	16.82	1.008
7		1	5	17.98	18.30	(1.017)
	8			18.88	18.85	(0.998)
8		1	6	19.71	19.60	(0.994)
	9			21.10	21.30	1.009
9		1	9	22.53	22.79	1.010
	10			23.97	24.04	1.003
10		½	5	25.41	25.33	0.997
				Average		1.001
				Average deviation		0.008

[a] Model described in text. [b] Many of the features of the thiophene photographs are of types known to be difficult to measure. Here the inner rings and the components of the two doublets have been thrown out of the average, since measurements of both types of features are known to be unreliable. The effect of the choice of rings to be thrown out is here somewhat greater than usual and may amount to ±0.005 in s/s_0.

It may be mentioned that this interpretation is in agreement with the deactivating and β directing influence of nitrogen in pyridine and its analogs[14] with respect to substitution reactions.

Butadiene-1,3 and Cyclopentadiene.—The value 1.46 Å. for the single bond between conjugated double bonds in butadiene-1,3 and cyclopentadiene has been discussed already in connection with the values found in other hydrocarbons containing conjugated systems.[15] Penney's[10] predicted value for the conjugated bond in butadiene, 1.43 Å., appears to be a little too low.

Furan, Pyrrole, and Thiophene.—The carbon–heteroatom distances found in furan, pyrrole, and thiophene correspond to 5 ± 5%, 12 ± 6%, and 17 ± 10% double-bond character, respectively. Resonance of the normal structure I with structures of the types II and III (X = O, NH, S) is assumed to be responsible for this double-bond character, while excited structures characteristic

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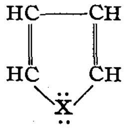
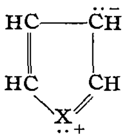
[13] L. Pauling and J. H. Sturdivant, *Proc. Natl. Acad. Sci.*, **23**, 615 (1937), have discussed the cyanuric and cyameluric derivatives.

[14] G. W. Wheland and L. Pauling, THIS JOURNAL, **57**, 2086 (1935).

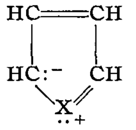
[15] L. Pauling, H. D. Springall, and K. J. Palmer, *ibid.*, **61**, 927 (1939).



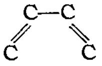
I

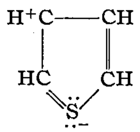


II

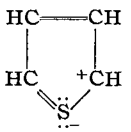


III

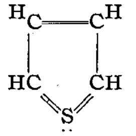
of the conjugated system  together with structures of the type III lead to the shortening of the C—C bond and the lengthening of the C=C bond. The C–C distance is assumed to be 1.46 Å. for furan and 1.44 Å. for pyrrole and thiophene, corresponding approximately to the expected contributions of various structures in these molecules. Besides those already mentioned, we may write for thiophene further reasonably stable structures, of types IV, V, and VI, involving the violation of the octet rule by sulfur, and contributing to the shortening of the C–S and C–C bonds. The



IV



V



VI

extent of their contribution is discussed below.

It is of interest to compare our results regarding furan, pyrrole, and thiophene with other information about these molecules. First of all, it is understandable that the very electronegative oxygen atom should not like to assume the positive charge of the excited structures written for furan, and that in consequence resonance with these structures should be less important than in pyrrole and thiophene, where the less electronegative atoms nitrogen and sulfur are involved. The values of the stabilizing resonance energy 21, 23, and 31 kcal./mole, respectively, for furan, pyrrole, and thiophene reported by Pauling and Sherman[16] are not in agreement with the great difference of degree of resonance in furan and pyrrole indicated by the electron diffraction investigation. We have recalculated values of the resonance energy from combustion data[17] for several furan and pyrrole derivatives; these values are listed in Table IX, together with our estimates of that part of the resonance energy which is to be attributed to the heterocyclic nuclei, obtained by subtracting the following corrections: 39 kcal./mole for benzene resonance, 6 kcal./mole for conjugation with phenyl, vinyl, or aldehyde group, 1.5 kcal./mole for conjugation with methyl or ethyl group, and 3 kcal./mole for conjugation with a hydroxyl group. These values[18] indicate that the resonance energy of the pyrrole nucleus is actually greater than that of the furan nucleus by about 8 kcal./mole, the probable values being approximately 23 and 31 kcal./mole, respectively. It accordingly seems likely that the value given in the literature for the heat of combustion of pyrrole is about 8 kcal./mole high.

TABLE IX

VALUES OF RESONANCE ENERGY OF DERIVATIVES OF FURAN AND PYRROLE

Substance	Resonance energy, kcal./mole	Resonance energy of nucleus, kcal./mole
Furan	23	23
Furfural	29.5	23.5
Furylethylene	28	22
Furfuryl alcohol	32	29
Pyrrole	23	23
Pyrrole aldehyde	40	34
N-Phenylpyrrole	76	31
2,4,5-Trimethyl-3-ethylpyrrole	33.5	27.5
2,4-Dimethyl-3-ethylpyrrole aldehyde	42.4	32

The new value for the resonance energy of pyrrole is just equal to that for thiophene. Unfortunately we have been unable to find combustion data for derivatives of thiophene to use in verifying the thiophene value. The interatomic distance data indicate greater resonance for thiophene than for pyrrole, which presumably would be accompanied by greater resonance energy; it is possible, however, that the magnitude of the resonance integrals for a molecule involving a heavier atom (sulfur) is less than for molecules containing only light atoms, and that the resonance energies of thiophene and pyrrole cannot be directly compared to obtain the relative amounts of resonance in the two molecules.

The electric dipole moments in units 1 × 10^{-18} e. s. u. of these molecules and their derivatives by hydrogenation measured[19] in benzene solution are the following: furan, 0.670; 2,5-dihydrofuran, 1.53; tetrahydrofuran, 1.68; pyrrole, 1.80; pyrroline, 1.42; pyrrolidine, 1.57; thiophene, 0.54; and tetrahydrothiophene, 1.87. We now give a very rough interpretation of these quantities based on the bond moments given

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[16] L. Pauling and J. Sherman, *J. Chem. Phys.*, **1**, 606 (1933).

[17] M. S. Kharasch, *Bur. Standards J. Research*, **2**, 359 (1929); Landolt–Börnstein, "Tabellen."

[18] Our recalculation for furan itself led to a small change from the value given by Pauling and Sherman.

[19] H. de Vries Robles, *Rec. trav. chim.*, **58**, 111 (1939); appendix to Symposium, *Trans. Faraday Soc.*, **30**, 904 (1934).

TABLE X

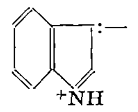
SUMMARY OF DISTANCES AND ANGLES

	C-H, Å.	C-C, Å.	C-X	C=C	Angle CXC	Angle XC=C	Angle C=C—C
Benzene	1.08±0.04	1.39±0.02	......	......	...	...	...
Pyridine	1.09	1.39	1.37±0.03	......	Angles ~ 120°, "meta"		
Pyrazine	1.09	1.39	1.35± .02	......	distances approximately equal		
Butadiene[a]	1.06	1.46± .03	......	1.35±0.02	...	...	124±2°
Cyclopentadiene	1.09	1.46± .04	1.53	1.35	101±4°	109±3°	110±2°
Furan	1.09	1.46	1.41± .02	1.35	107±4°	109±3°	107±2°
Pyrrole	1.09	1.44	1.42± .02	1.35	105±4°	110±3°	108±2°
Thiophene	1.09	1.44	1.74± .03	1.35	91±4°	112±3°	113±3°

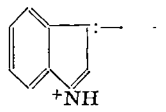
[a] Probably coplanar *trans* configuration.

by Smyth[20] and on the usual approximate treatment[21] of the effect on electric dipole moment of resonance with polar structures. A simple calculation suggests that the difference 0.15 *D* in moment between the dihydro and tetrahydro derivatives of furan and pyrrole may be accounted for as the result of change in the direction and number of C–H bonds having moments of about 0.4 *D*. The differences of moments of tetrahydrofuran and furan, and tetrahydrothiophene and thiophene, which are 1.01 and 1.33 *D*, respectively, consist of contributions of 0.05 to 0.10 *D* due to the change of C–H moments, combined with resonance moments, in the same direction, of about 0.95 and 1.25 *D*, respectively, the effects of changing the angles in the ring being neglected. The interpretation of the moments of the pyrroles is complicated by uncertainty regarding the orientation of the N–H bond in these molecules. It seems to be impossible to make a reliable estimate of the resonance moment for pyrrole; various methods of making the calculation give values lying between 1.0 and 2.5 *D*, with 1.5 *D* the most probable value. These resonance moments, 0.95 *D* for furan, 1.5 *D* for pyrrole, and 1.25 *D* for thiophene, correspond to approximately the following total contribution of structures of Types II and III (assumed to be equally important): furan 15%, pyrrole 23%, and thiophene 16%, while the assumed C–X distances correspond to total contributions by excited structures of 10, 24, and 34%, respectively. The agreement of the estimates made in the two ways is reasonably good for furan and pyrrole. The low value found for thiophene by the dipole moment calculation indicates that structures of types IV, V, and VI are of considerable significance; the consideration of the data suggests about 10% contribution by these structures, involving more than eight electrons in the outer shell of the sulfur atom, and 20% by the structures of types II and III.

Finally, it may be said that the general chemical behavior of furan, pyrrole, and thiophene indicates this order of increasing stability and aromatic character, in agreement with this discussion. An interesting example which seems to support this conclusion is the reaction[22] with maleic anhydride of furan to give (by the Diels-Alder reaction) a product which does not contain the furan nucleus, and that of pyrrole[23] to give in part by a simple condensation a compound in which the pyrrole nucleus is retained. The α directing influence on substitution reactions of the hetero atoms in furan, pyrrole, and thiophene indicates that excited structures of type III predominate over those of type II, as would be expected from their smaller charge separation. It is interesting to note that β-substitution occurs in indole; this is the result of the fact that of the ionic excited structures, two



and



place a negative charge on the β-carbon atom, whereas only one such structure occurs for each of the other carbon atoms. This striking difference between pyrrole and indole thus has a simple explanation in terms of resonance.

We wish to thank Professor F. W. Bergstrom for the sample of pyrazine, Dr. W. E. Vaughan for that of tetrabromobutane, Dr. K. J. Palmer for his help with experimental work, Dr. Sidney Weinbaum for assistance in the preparation of the figures, and Dr. E. R. Buchman for discussion of the chemical properties of the substances. We are especially indebted to Professor L. O.

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[20] C. P. Smyth, THIS JOURNAL, **60**, 183 (1938).

[21] See L. E. Sutton, *Trans. Faraday Soc.*, **30**, 789 (1934).

[22] O. Diels and K. Alder, *Ber.*, **62**, 554 (1929).

[23] O. Diels and K. Alder, *Ann.*, **486**, 211 (1931).

Brockway for checking our measurements of the photographs, for general assistance, and for many helpful discussions.

Summary

The results of the electron diffraction investigation reported in this paper are collected in Table X. The re-investigation of benzene confirms the value 1.39 Å. for the C–C distance and provides a rough experimental value for the C–H distance. In pyridine and pyrazine the C–N distance is greater than expected for Kekulé resonance; the effect is attributed to extra resonance with ionic structures. The electron diffraction results, electric dipole moment data, resonance energies, chemical information, and simple theoretical considerations indicate, almost uniformly, the order furan < pyrrole < thiophene for the degree of resonance stabilization of these molecules. The contributions of excited structures, other than those characteristic of the conjugated double bonds, are about 10, 24, and 34%, respectively. Part of the resonance of thiophene is with structures with ten electrons in the valence shell of the sulfur atom.

PASADENA, CALIFORNIA RECEIVED APRIL 17, 1939

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[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 1027]

An Instrument for Determining the Partial Pressure of Oxygen in a Gas[1]

BY LINUS PAULING, REUBEN E. WOOD, AND J. H. STURDIVANT

On October 3, 1940, at a meeting in Washington called by Division B of the National Defense Research Committee, mention was made of the need for an instrument which could measure and indicate the partial pressure of oxygen in a gas. During the next few days we devised and constructed a simple and effective instrument for this purpose. This instrument measures the volume magnetic susceptibility of the gas; its use as an oxygen meter is based on the fact that the magnetic susceptibility of molecular oxygen is very much greater than that of any other common gas. The volume magnetic susceptibility of oxygen at 20° and one atmosphere pressure (standard conditions) is $+142 \times 10^{-9}$ c. g. s. m. u.; all other common gases are diamagnetic, with susceptibilities very much smaller in magnitude: nitrogen -0.40×10^{-9}; hydrogen -0.165×10^{-9}; carbon dioxide -0.83×10^{-9}; helium -0.078×10^{-9}; etc. The magnetic susceptibility of a mixture of common gases is hence de-

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(1) This work was done in whole under the Contracts Nos. NDCrc-38, NDCrc-200, OEMsr-326, and OEMsr-584 between the California Institute of Technology and the Office of Scientific Research and Development, which assumes no responsibility for the accuracy of the statements contained herein. A brief description of this instrument has been published in *Science*, **103**, **2672** (1946).

pendent mainly on the partial pressure of oxygen in the gas; a change of a few hundred millimeters of mercury in the partial pressure of the diamagnetic gases would affect the magnetic susceptibility only as much as a change of one millimeter of mercury in the partial pressure of oxygen.[2]

The forces due to the action of achievable magnetic fields on a gas, even such a strongly magnetic gas as oxygen, are very small, and their measurement is not easy. The instrument as originally proposed was to embody the following features. A strong inhomogeneous magnetic field would be created between suitably shaped pole pieces of a permanent magnet, made from a highly retentive alloy such as Alnico. Suspended in this field on a taut silica fiber would be a glass test body and attached mirror so arranged that the test body and mirror could rotate through regions of varying magnetic field strength by twisting and untwisting the fiber. The magnetic force acting on a small test body in an inhomogeneous magnetic field is proportional to the product of the field strength, the gradient of the field strength, and the difference in volume magnetic susceptibility of the test body and the gas surrounding it. The equilibrium orientation of the test body, as determined by the magnetic force and the torsional force of the fiber, would accordingly be dependent on and would provide a measure of the magnetic susceptibility of the gas. The orientation could be indicated by a light beam reflected from the mirror onto a scale; the scale could be calibrated to read directly the partial pressure of oxygen in the gas.

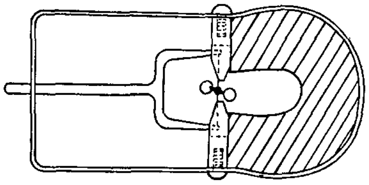

Fig. 1.—The first experimental magnetic oxygen meter.

This design was closely followed in the experimental model and in the later instruments. The experimental model (October, 1940) had as test body a dumbbell of two thin-walled glass spheres 4 mm. in diameter sealed to a glass rod 6 mm. long. A silica fiber $8\ \mu$ in diameter was stretched between the prongs of a silica fork,[3] and the glass dumbbell was cemented with shellac to the middle of the fiber, perpendicular to it. A plane glass mirror 2 mm. square was also cemented near the middle of the fiber. The suspension was balanced approximately by use of shellac, and was coated with aluminum by evaporation.

A four-ounce Alnico permanent magnet was mounted in a brass yoke. Two wedge-shaped pole pieces of soft iron, each with a slot sawed part way through it, were also attached, and the dumbbell assembly was inserted with the ends of the silica fiber in the slots and the spheres of the dumbbell between the pole pieces, one sphere being a little in front and the other a little behind the plane of the pole pieces, as shown in Figure 1.

This instrument was laid in a vacuum desiccator with the fiber vertical. A flashlight bulb was set up outside the desiccator, and the position of the spot of light reflected by the meter mirror was observed on a piece of tissue paper pasted to the desiccator wall. The experimental results given in Table I were obtained.

Table I

Results Obtained with the First Experimental Magnetic Oxygen Meter

Gas in desiccator	Angular displacement of light beam (radians)
Air, 1 atm.	(0)
Air, 0.02 atm.	+0.18
Nitrogen, 1 atm.	+0.18
Oxygen, 1 atm.	−0.52
Oxygen, 0.20 atm.	0.00

The readings are seen to be determined by the partial pressure of oxygen in the gas.

Some changes in design have been incorporated in later models of the instrument. The improved dumbbell assembly is shown in Fig. 2. The dumbbell consists of two thin-walled glass spheres, matched for volume (diameter about 3 mm.) and weight, fused to the ends of a glass rod about 4 mm. long. This rod is bent at its midpoint through a small angle, in order that the silica fiber to which it is cemented by silver chlo-

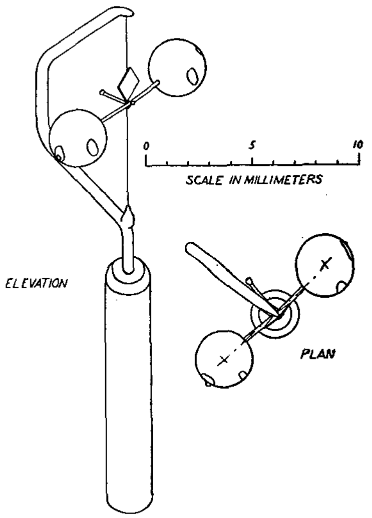

Fig. 2.—The assembly of dumbbell, mirror, and balancing rod mounted on a taut silica fiber.

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[2] The gases nitric oxide, nitrogen dioxide, and chlorine dioxide, each of which consists of molecules containing an odd number of electrons, are strongly paramagnetic, and hence their presence in appreciable amounts in a gas would interfere with the use of the magnetic instrument as an oxygen meter. Each of these gases has about one-half the volume magnetic susceptibility of oxygen.

[3] We are grateful to Professor H. Victor Neher of the Norman Bridge Laboratory of Physics for advice and instruction in silica-fiber technique.

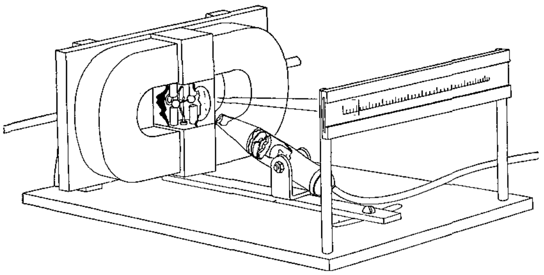

Fig. 3.—Diagram of instrument, showing dumbbell assembly mounted between pole pieces of two small permanent magnets, source of light, and scale.

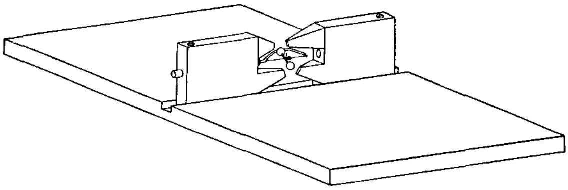

Fig. 4.—Dumbbell assembly and pole pieces (of different design), with magnets removed from back plate.

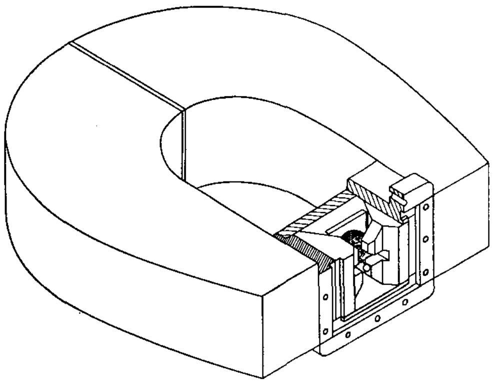

Fig. 5.—Large magnet with test chamber enclosing pole pieces and dumbbell assembly; windowed cover and gasket have been removed from test chamber.

ride may pass through the center of volume of the dumbbell. Another small glass rod, used in balancing the assembly, is fused to the dumbbell during its construction, and the small mirror is cemented to the dumbbell. The moving part of the instrument (dumbbell and mirror) now weighs about 3 mg. The Y-shaped fork has been replaced by a silica yoke such that the cylindrical brass sleeve into which its end is cemented is coaxial with the fiber. The dumbbell is balanced roughly by attaching minute droplets of a low-melting lead borate glass and then precisely by evaporating silver halides onto it from an electrically heated wire.

The permanent magnets are now made of Alnico V, which has a higher retentivity than Alnico II, which was first used. It has been customary to use a pair of magnets weighing five ounces each, arranged as shown in Fig. 3. Pole pieces of various designs have been found to be satisfactory; examples are illustrated in Figs. 3, 4, and 5. A sensitive instrument containing a single large magnet, weighing about six pounds, has also been designed and built (Fig. 5).

Three methods of taking care of effects of change of temperature have been used. The simplest method is to calibrate the instrument at various temperatures and to provide correction tables or graphs. Another method is to adjust the temperature coefficient of the magnetic susceptibility of the dumbbell suitably (its paramagnetic component at mid-point of temperature range numerically twice the diamagnetic component) and to cause the magnetic field strength to vary with temperature in such a way (direct proportionality to absolute temperature) as to compensate the other effects of temperature on the reading of the instrument; this compensation can be effected by placing across the permanent magnet a shunt made from an iron-nickel alloy with a very high negative temperature coefficient of magnetic permeability. The third method is to provide a heater and thermostatic regulator

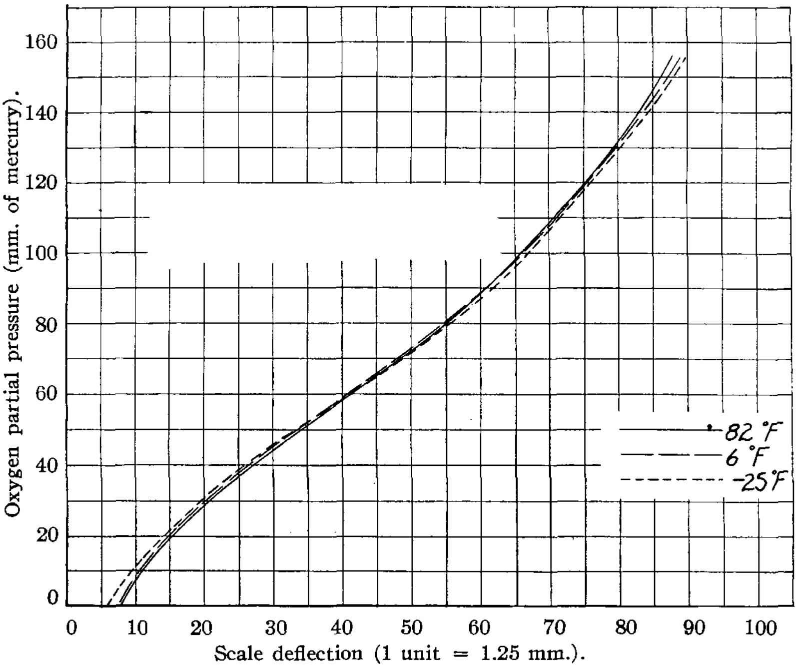

Fig. 6.—Calibration curves for a meter at three temperatures.

for the meter, and thus to maintain it and the sample of gas at the calibration temperature.

The gas to be tested may be drawn or forced at the rate of a few cubic centimeters per minute through the test chamber, which in present models has a volume of about 4 ml., or it may be introduced after evacuating the test chamber. The instrument indicates correctly the magnetic susceptibility of the gas in the test chamber within a few seconds; the main delay in reading the instrument is caused by the time required to introduce the gas.

Meters have been constructed to cover various ranges of partial pressure of oxygen, including 0 to 20 mm. of mercury, 0 to 80, 0 to 160, 110 to 190, and 0 to 800. Dr. A. O. Beckman has also devised a meter which can be switched from one partial-pressure region to another.

Calibration curves for a typical "Model P" meter at three different temperatures are shown in Figure 6. This meter has been compensated for temperature changes in the manner described above. The accuracy of a meter is usually about 1% of the range covered.

The instrument may also be used for determining the magnetic susceptibility of paramagnetic and diamagnetic gases or for any analysis dependent on magnetic susceptibility, such as the determination of nitric oxide or nitrogen dioxide in a gas not containing oxygen.

Several dozen meters were constructed at the California Institute of Technology before the summer of 1942. Dr. Arnold O. Beckman, 11 West State Street, Pasadena 2, California, who then took over the production of the meter, has manufactured several hundred. Descriptions of the various models will be published elsewhere. Some recording models of the instrument are available.

We are glad to acknowledge the assistance of David P. Shoemaker, James B. Edson, Harold Herd, Dr. Herbert Sargent, Dr. Charles D. Wagner, and Beckie Bradford in the development of this instrument at the California Institute of Technology.

Summary

A simple instrument for determining the partial pressure of oxygen in a gas is described. This instrument, the use of which as an oxygen meter depends on the fact that the magnetic susceptibility of oxygen is very much greater than that of other common gases, consists of a small glass dumbbell with attached mirror suspended on a stretched fused-silica fiber in an inhomogeneous magnetic field produced by a small permanent magnet. In the simpler models of the instrument the partial pressure of oxygen is indicated on a scale by a beam of light reflected from the mirror.

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Chapter 8

MOLECULAR PROPERTIES ANALYZED BY QUANTUM MECHANICS

Contents

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Vol. 12, No. 1. January, 1926.

THE QUANTUM THEORY OF THE DIELECTRIC CONSTANT OF HYDROGEN CHLORIDE AND SIMILAR GASES

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Communicated December 14, 1925

Under the influence of an electric field a gas whose molecules have a permanent electric moment and in addition can have a further moment induced in them by deformation becomes polarized in the direction of the field, the amount of polarization per unit volume being[1]

$$P = \frac{3}{4\pi}\frac{\epsilon - 1}{\epsilon + 2} F = N\mu\, \overline{\overline{\cos\theta}} + N\alpha F. \qquad (1)$$

Here ϵ is the dielectric constant of the gas, F the strength of the applied field, N the number of molecules in unit volumes, μ the permanent electric moment of a molecule, and α the coefficient of induced polarization of a molecule; $\overline{\overline{\cos\theta}}$ is the average value of $\overline{\cos\theta}$ for all molecules in the gas, and $\overline{\cos\theta}$ is the time-average of $\cos\theta$ for one molecule in a given state of motion, θ being the angle between the dipole axis and the lines of force of the applied field.

On the basis of the classical theory it was shown by Debye[2] that $\overline{\overline{\cos\theta}}$ is given by the Langevin function

$$\overline{\overline{\cos\theta}} = \coth\frac{\mu F}{kT} - \frac{kT}{\mu F}. \qquad (2)$$

This reduces, for values of μF small in comparison with kT, to

$$\overline{\overline{\cos\theta}} = {}^1/_3\,\frac{\mu F}{kT}. \qquad (3)$$

This result must now, however, be replaced by one based upon the quantum theory. In this case a generally applicable expression cannot be obtained, and it is necessary to consider particular molecular models. W. Pauli, Jr.[3] has treated the diatomic dipole, which is of interest to us, and his treatment forms the basis of this discussion.

The Hamiltonian function for this dynamical problem, using polar coördinates with the polar axis in the direction of the lines of force, is

$$H = \frac{1}{2I}\left(p_\theta^2 + \frac{p_\varphi^2}{\sin^2\theta}\right) - \mu F\cos\theta. \qquad (4)$$

In this expression p_θ and p_φ are the momenta corresponding to the coördinates θ and φ, and I is the moment of inertia of the rotator about an axis through its center of mass and normal to the line joining the atomic nuclei. Applying the Wilson-Sommerfeld quantum conditions we write

$$\left.\begin{aligned} \oint p_\theta\, d\theta + \oint p_\varphi\, d\varphi &= mh, \\ \oint p_\varphi\, d\varphi = 2\pi\, p_\varphi &= nh. \end{aligned}\right\}. \tag{5}$$

The time-average value of cos θ for a given rotator characterized by the quantum numbers m and n is found to be, in case μF is small in comparison with the energy-constant W,

$$\overline{\cos\theta} = \frac{4\pi^2 \mu F I}{m^2 h^2}\left(\frac{3}{2}\frac{n^2}{m^2} - {}^1/_2\right). \tag{6}$$

Pauli assigned to m the values 1, 2, 3, ... ∞, and to n the values ± 1, ± 2, ± 3, ... $\pm m$. We shall give m the values $^1/_2$, $^3/_2$, $^5/_2$, ... ∞, and n the value $\pm{}^1/_2$, $\pm{}^3/_2$, $\pm{}^5/_2$, ... $\pm m$; for these half-quantum numbers for m are indicated by the infra-red oscillation-rotation absorption spectrum[4] of hydrogen chloride and definitely required by the recently observed[5] pure rotation absorption spectrum, and it can be shown that similar values for n are reasonable. Assigning equal *a priori* probabilities to all of the possible quantum states characterized by half-integral values of m and n we have for the probability of a given state

$$w\,(m, n) = \frac{e^{-\frac{W}{kT}}}{\sum\limits_{m={}^1/_2}^{\infty}\ \sum\limits_{n=\pm{}^1/_2}^{\pm m} e^{-\frac{W}{kT}}}. \tag{7}$$

Introducing the variable $\sigma = \frac{\Theta}{T} = \frac{h^2}{8\pi^2 IkT}$ we obtain the following expression for $\overline{\overline{\cos\theta}}$:

$$\overline{\overline{\cos\theta}} = \frac{\mu F}{kT}\,\frac{1}{2\sigma}\,\frac{\sum\limits_{m={}^1/_2}^{\infty}\ \sum\limits_{n=\pm{}^1/_2}^{\pm m} \frac{1}{m^2}\left(\frac{3}{2}\frac{n^2}{m^2} - {}^1/_2\right) e^{-\sigma m^2}}{\sum\limits_{m={}^1/_2}^{\infty}\ \sum\limits_{n=\pm{}^1/_2}^{\pm m} e^{-\sigma m^2}}. \tag{8}$$

Pauli, who obtained a similar expression with whole quantum numbers, evaluated the sums by assuming σ to be very small. This is not justifiable, however, in cases of practical interest, for which σ has values near 0.05, for it then leads to results in error by 30% or more. Replacing m by $r - {}^1/_2$ and n by $s - {}^1/_2$ and summing for s one obtains

$$\overline{\overline{\cos\theta}} = \frac{\mu F}{kT}\, C, \tag{9}$$

where

$$C = \frac{1}{4\sigma}\,\frac{\sum\limits_{r=1}^{\infty}\frac{r}{(r-1/2)^3}\,e^{-\sigma(r-1/2)^2}}{\sum\limits_{r=1}^{\infty} r\,e^{-\sigma(r-1/2)^2}}. \tag{10}$$

C has been evaluated for a range of values of σ by direct substitution. The values obtained are given in table 1.

TABLE 1

σ	C	σ	C
0.20	2.848	0.04	3.690
0.10	3.264	0.03	3.796
0.07	3.445	0.02	3.929
0.05	3.599	0	4.570

In order to apply the results of the theory in the interpretation of the experimental measurements on hydrogen chloride, made by Zahn,[6] it is necessary to know Θ for this substance. Czerny[5] gives for $\frac{hc}{8\pi^2 I}$ the value 10.397, which leads to a value of 14.9° for Θ. It is found that Zahn's experimental results conform reasonably well with the theoretical curve corresponding to a value of 0.3316×10^{-18} c.g.s.u. for μ and 0.00077 for $4\pi N_0\alpha$, with N_0 the number of molecules per cc. at standard conditions. These values differ considerably from those obtained from the same data with the classical theory, 1.034×10^{-18} and 0.00104.

The experimental points, which surprisingly enough lie very close to a curve of the type required by the classical theory, show deviations as large as 2% from the best quantum theory curve. Nevertheless it is not easy to reject the straight-forward and well-grounded quantum theory calculations given in this paper; possibly the discrepancies can be attributed to errors in the experimental measurements. Further measurements testing this point are needed.

The quantum theory value for $4\pi N_0\alpha$ is confirmed by independent evidence; for it conforms with Maxwell's relation $4\pi N_0\alpha = n_0^2 - 1$, in which n_0 is the index of refraction of the gas at standard conditions for light of frequency far from any frequency characteristic of the molecule. It is known that n as determined with light of ordinary wave-length is larger than n_0; hence the observed value 0.000888 for $n^2 - 1$ for hydrogen chloride with the sodium D-lines cannot be reconciled with the classical value 0.00104 for $4\pi N_0\alpha$, but supports the quantum theory value 0.00077.

Similar calculations for hydrogen bromide lead to the values 0.252×10^{-18} for μ and 0.00102 for $4\pi N_0\alpha$. The data for hydrogen iodide are inaccurate because of dissociation, and cannot be used.

The electric moment found for hydrogen chloride is equal to that of a dipole composed of a proton and an electron 0.0694 Å apart; for hydrogen bromide the equivalent distance is 0.0528 Å.

A more extensive account of these calculations will be presented to the *Physical Review* for publication.

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* National Research Fellow in Chemistry.

[1] See, for example, Debye in Marx "Handbuch der Radiologie," Leipzig Akademische Verlagsgesellschaft, **1925,** V. 6, p. 619.

[2] P. Debye, *Physik. Zeit.*, **13,** 97 (1912).

[3] W. Pauli, Jr., *Z. Physik*, **6,** 319 (1921).

[4] Colby, *Astrophys. J.*, **58,** 303 (1923).

[5] Czerny, *Z. Physik*, **34,** 227 (1925).

[6] Zahn, *Physic. Rev.*, **24,** 400 (1924).

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The Theoretical Prediction of the Physical Properties of Many-Electron Atoms and Ions. Mole Refraction, Diamagnetic Susceptibility, and Extension in Space*

By LINUS PAULING, Fellow of the John Simon Guggenheim Memorial Foundation.

(Communicated by A. Sommerfeld, For.Mem.R.S.—Received January 1, 1927.)

I.—*Introduction.*

It is customary to express the empirical data concerning term values in the X-ray region by introducing an effective nuclear charge $Z_{\mathrm{eff.}}e$ in the place of the true nuclear charge Ze in an equation theoretically applicable only to a hydrogen-like atom. Often a screening constant S is used, defined by the equation

$$Z_{\mathrm{eff.}} = Z - S;$$

and this screening constant is qualitatively explained as due to the action of electrons which are nearer the nucleus than the electron under consideration, and which in effect partially neutralise the nuclear field. Thus the relativistic or magnetic doublet separation may be represented by the equation

$$\Delta\nu = \frac{R\alpha^2}{n^3k(k-1)}(Z-s_0)^4 + \ldots.$$

This equation, including succeeding terms, was obtained originally by Sommerfeld from relativistic considerations with the old quantum theory; the first term, except for the screening constant s_0, has now been derived by Heisenberg and Jordan[†] with the use of the quantum mechanics and the idea of the spinning electron. The value of the screening constant is known for a number of doublets, and it is found empirically not to vary with Z.

It has been found possible to evaluate s_0 theoretically by means of the following treatment: (1) Each electron shell within the atom is idealised as a uniform surface charge of electricity of amount $-z_ie$ on a sphere whose radius is equal to the average value of the electron-nucleus distance of the electrons in the shell. (2) The motion of the electron under consideration is then determined by the use of the old quantum theory, the azimuthal quantum number being chosen so as to produce the closest approximation to the quantum

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[*] The phrase "mole refraction" will be used in this paper in place of "coefficient of refraction" or "molal coefficient of refraction," in conformity with the use of the German word Molrefraktion.

[†] 'Z. f. Physik,' vol. 37, p. 263 (1926).

mechanics. (3) Since s_0 does not depend on Z, it is evaluated for large values of Z, by expanding in powers of z_i/Z and neglecting powers higher than the first, and then comparing the expansion with that of the expression containing $Z - s_0$ in powers of s_0/Z. The values of s_0 obtained in this way* are in satisfactory agreement with the empirical ones, the agreement being excellent in the case of orbits of large excentricity, for which the idealisation of the electron shells would be expected to introduce only a small error.

The important problem of the theoretical evaluation of the properties of many-electron atoms and ions has so far received little attention, compared with that devoted to spectral term values. The wave mechanics of Schrödinger provides an atomic model which suggests that the method of treatment given s_0 can be used in deriving theoretical values of screening constants to be used in the equations representing the mole refraction or polarisability, diamagnetic susceptibility, extension in space, and other properties of atoms and monatomic ions. This procedure is followed in this paper, the assumption being made that the nuclear charge is large in comparison with the charge of an electron shell. This requirement is not well fulfilled by actual atoms and ions. However, from a comparison with the accurately known experimental values of the mole refraction of the rare gases and of some ions in aqueous solution it is found that the calculated values of the mole refraction screening constant are not greatly in error. The indicated corrections are made; so that, with the aid of this one empirical change, theoretical values are obtained for the mole refraction and the diamagnetic susceptibility of a large number of atoms and ions. A third screening constant is also evaluated, which permits the calculation of the electron distribution in atoms and ions and the estimation of interatomic distances. In this connection it is shown that the investigation of the diffraction of X-rays by crystals provides a method for the direct experimental verification of the form of Schrödinger's eigenfunctions.

II.—*The Wave Mechanics of the Hydrogen Atom and the Idealisation of an Electron Shell.*

In the wave mechanics of Schrödinger† a conservative Newtonian dynamical system is represented by a wave function or amplitude function ψ, obtained from the partial differential equation

$$\text{div. grad. } \psi + \frac{8\pi^2}{h^2}(\mathrm{W} - \mathrm{V}(q_\kappa))\,\psi = 0,$$

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* Pauling, 'Z. f. Physik,' vol. 40, p. 344 (1926).

† Schrödinger, 'Ann. d. Physik,' vol. 79, p. 361 (1926); vol. 79, p. 489; vol. 80, p. 437; vol. 81, p. 109; cited hereafter as I, II, III, IV.

with the conditions that ψ be everywhere continuous, single-valued, and bounded. W and $V(q_\kappa)$ are the energy constant and the potential energy; and the indicated operations are with respect to co-ordinates whose line element is given by

$$ds^2 = 2T(q_\kappa, \dot{q}_\kappa)\, dt^2,$$

in which T is the kinetic energy expressed as a function of the velocities. Only certain functions (called eigenfunctions) satisfy these requirements in any given case; correspondingly there are certain characteristic values of the energy constant W. For the hydrogen-like atom with fixed nucleus the potential energy is $-e^2Z/r$; on writing for the eigenfunctions

$$\Psi_{nlm} = X_{nl}(r)\, Y_{lm}(\vartheta)\, Z_m(\phi), \tag{1}$$

the wave equation can be resolved into three total differential equations, with the solutions*

$$\left.\begin{aligned} X_{nl}(r) &= \left\{\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}\right\}^{\frac{1}{2}} e^{-\xi/2}\xi^l L_{n+l}^{(2l+1)}(\xi) \\ &\qquad \text{with } \xi = \frac{2Z}{a_0 \, . \, n} . r \\ Y_{lm}(\vartheta) &= \left\{(l+\tfrac{1}{2})\frac{(l-m)!}{(l+m)!}\right\}^{\frac{1}{2}} P_l^m(\cos\vartheta) \\ Z_m(\phi) &= \frac{1}{\sqrt{2\pi}} e^{im\phi} \end{aligned}\right\}. \tag{2}$$

$L_{n+l}^{(2l+1)}(\xi)$ represents the $(2l+1)$th derivative of the $(n+l)$th Laguerre polynomial; and $P_l^m(\cos\vartheta)$ is Ferrer's associated Legendre function of the first kind, of degree l and order m. $Y_{lm}\, Z_m$ thus constitutes a surface harmonic. The Ψ's are in this form orthogonal and normalised with respect to unity, so that they fulfil the conditions

$$\int \Psi_{nlm} \Psi_{n'l'm'}\, dV = \begin{cases} 1 \text{ for } n = n', l = l', m = m' \\ 0 \text{ otherwise.} \end{cases}$$

The parameter n can assume the values 1, 2, 3, ..., and is to be identified with the principal quantum number characterising the energy of the atom; l can assume the values $0, 1, 2, \ldots n-1$, and is to be identified with $k-1$, k being the azimuthal quantum number of the old quantum theory; while m, the magnetic quantum number, can assume the values $0, \pm 1, \pm 2, \ldots \pm l$.

Schrödinger (IV) has interpreted $\Psi\overline{\Psi}$ ($\overline{\Psi}$ being the conjugate complex of Ψ) as giving the weight or probability to be assigned to the corresponding micro-

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* See Schrödinger I; Waller, 'Z. f. Physik,' vol. 38, p. 635 (1926).

scopic state of the system; in the hydrogen-like atom $\Psi\overline{\Psi}$ would then give the *electron density* as a function of r, ϑ, and ϕ, the electron being considered as distributed through space in accordance with this expression (following Schrödinger), or as achieving this distribution through a time average of its instantaneous positions. Unsöld* has shown that this conception provides a simple explanation of Schrödinger's perturbation theory, to the effect that it gives the interaction of the perturbing field and this distribution of electricity. Thus it can easily be shown that the first-order Stark effect energy given by the wave mechanics (Schrödinger, III) is just the field energy of the electric dipole corresponding to such an electron density (the wave equation being separated in parabolic co-ordinates in this case). Accepting these views, the fractional number of electrons in a spherical shell of unit thickness at the distance r from the nucleus is

$$\mathrm{D} = 4\pi r^2\,\Psi\overline{\Psi} = r^2\,\mathrm{X}^2_{nl}(r). \qquad (3)$$

An atom in the S state, with $l = m = 0$, has $\mathrm{Y}_{00}{}^2(\vartheta)\,\mathrm{Z}_0{}^2(\phi) = 1/4\pi$, so that Ψ_{n00} is spherically symmetrical. Unsöld has further shown that the sum of the quantities $\Psi\overline{\Psi}$ for the electrons of a completed sub-group (n and l constant, $m = -l, -l+1, \dots 0, \dots +l$) is not dependent on ϑ and ϕ. Accordingly the electron distribution in an atom in the S state or containing only completed sub-groups† is spherically symmetrical, and a function of r alone.

The dependence on r of several eigenfunctions is shown by the following equations, and by fig. 1, in which $-\mathrm{X}_{nl}(r)\,.\,\mathrm{Z}^{-3/2}\,.\,10^{-12}$ is plotted as a function of ξ.

$$\mathrm{X}_{10}(r) = -2\left(\frac{\mathrm{Z}}{a_0}\right)^{3/2}.\,e^{-\xi/2},$$

$$\mathrm{X}_{20}(r) = \frac{2}{2^{5/2}}\left(\frac{\mathrm{Z}}{a_0}\right)^{3/2}.\,e^{-\xi/2}(\xi-2),$$

$$\mathrm{X}_{30}(r) = -\frac{2}{3^{5/2}\,2\,!}\left(\frac{\mathrm{Z}}{a_0}\right)^{3/2}.\,e^{-\xi/2}(\xi^2-6\,\xi+6),$$

$$\mathrm{X}_{40}(r) = \frac{2}{4^{5/2}\,3\,!}\left(\frac{\mathrm{Z}}{a_0}\right)^{3/2}.\,e^{-\xi/2}(\xi^3-12\,\xi^2+36\,\xi-24),$$

$$\mathrm{X}_{50}(r) = -\frac{2}{5^{5/2}\,4\,!}\left(\frac{\mathrm{Z}}{a_0}\right)^{3/2}.\,e^{-\xi/2}(\xi^4-20\,\xi^3+120\,\xi^2-240\,\xi+120),$$

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* 'Dissertation,' Munich, 1927.

† The sub-groups for which this theorem is derived are not the Stoner sub-groups. However, it is highly probable that the inclusion of the spinning electron in the theory will lead to the result that the theorem is actually true for the Stoner sub-groups.

$$X_{21}(r) = -\frac{2}{2^2\sqrt{3\,!}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\xi/2}\,.\,\xi,$$

$$X_{31}(r) = \frac{2}{3^2\sqrt{4\,!}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\xi/2}\,.\,\xi(\xi-4),$$

$$X_{41}(r) = -\frac{2}{4^2\sqrt{5\,!\,.\,2\,!}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\xi/2}\,.\,\xi(\xi^2-10\,\xi+20),$$

$$X_{51}(r) = \frac{2}{5^2\sqrt{6\,!\,.\,3\,!}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\xi/2}\,.\,\xi(\xi^3-18\,\xi^2+90\,\xi-120).$$

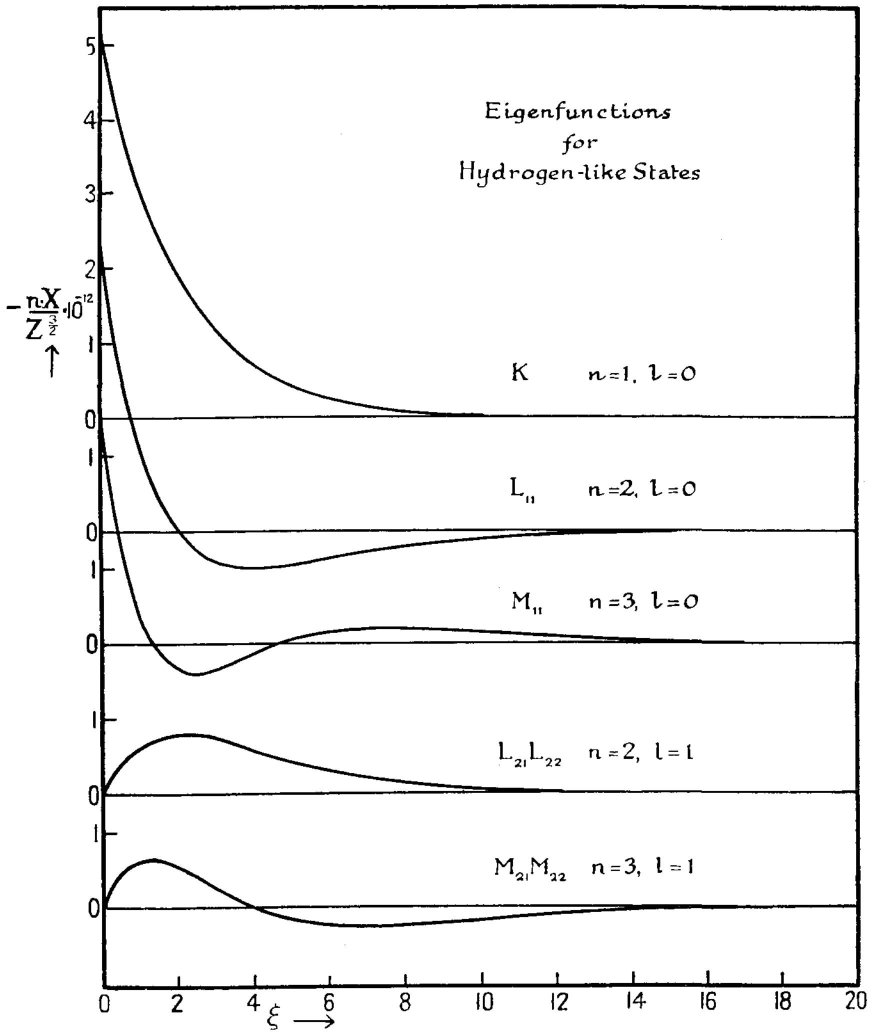

FIG. 1.—Eigenfunctions for hydrogen-like states; as ordinates are shown values of $-nX_{nl}(\xi)\,.\,Z^{-3/2}\,.\,10^{-12}$ with values of ξ as abscissæ.

It will be observed that the function differs appreciably from zero only within a radius of the order of magnitude of the major axis of the corresponding ellipses of the old quantum theory; namely, $r = 2a_0n^2/Z$, or $\xi = 4n$, as was remarked by Schrödinger (I). In fig. 2 are given values of D as a function of

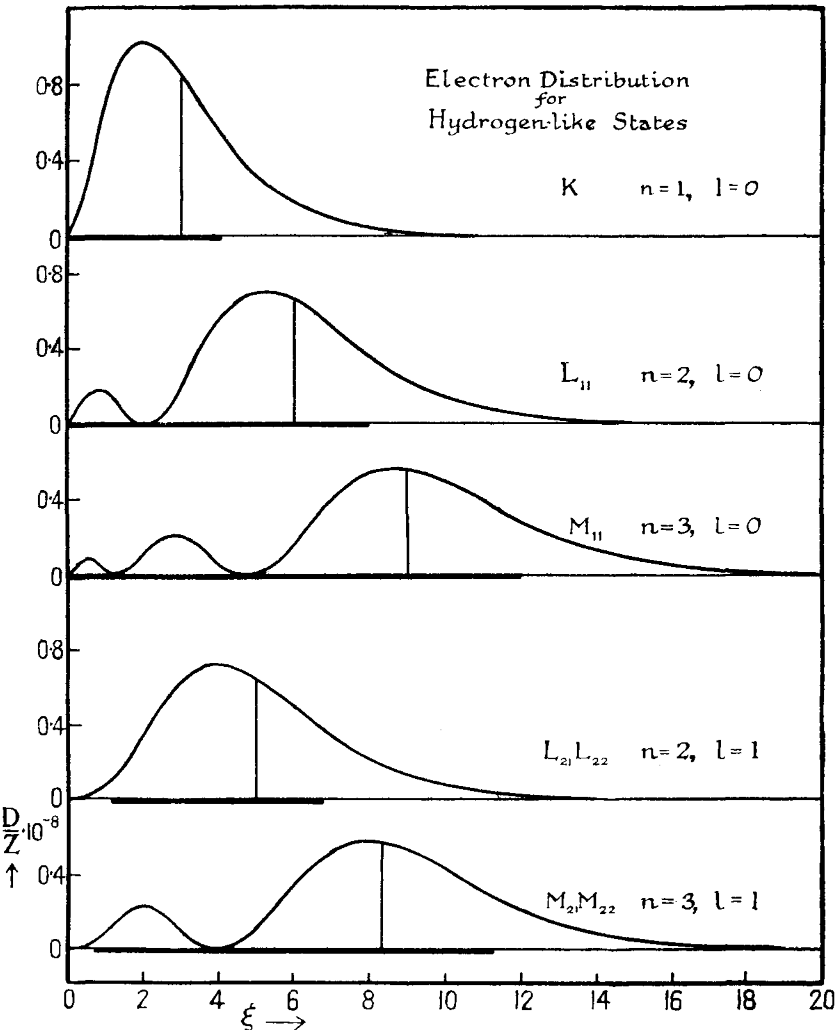

FIG. 2.—Electron distribution for hydrogen-like states; the ordinates are values of $D \,.\, Z^{-1} \,.\, 10^{-8}$, in which $D = 4\pi r^2\rho$, with ρ the electron density. The vertical lines correspond to $\bar{r}$, the average value of r.

ξ, showing the distribution of the electron with respect to r. The limits indicated on the ξ-axis correspond to the electron-nucleus distances at aphelion and perihelion given by the old quantum theory with k^2 placed equal to $l\,(l+1)$.

The idealisation of an electron shell as a uniform distribution of electricity on the surface of a sphere was innovated by Schrödinger,* who calculated the term-values of penetrating orbits by this method, with the old quantum theory. It was pointed out by Heisenberg† and Unsöld‡ that the same idealisation is permitted by the wave mechanics, the potential of the $e\Psi\overline{\Psi}$ distribution of electricity approximating $-e^2/r$ for large values of r, and being equal to $-e^2Z/a_0n^2$ for $r=0$. The spherical symmetry shown by Unsöld to hold for completed sub-groups is, of course, retained in this idealisation. As the best value for the radius ρ_0 of the equivalent shell we shall choose the average value of r,

$$\bar{r} = \int r\Psi\overline{\Psi}\,dV.$$

The method of evaluating this integral has been given by Waller,§ whose equations lead to the result

$$\bar{r} = \frac{a_0n^2}{Z}\left[1+\tfrac{1}{2}\left\{1-\frac{l\,(l+1)}{n^2}\right\}\right]. \tag{4}$$

(The old quantum theory expression for the time average of r contained k^2 in place of $l\,(l+1)$.)

Following Heisenberg and Unsöld, let us consider the potential for the state $n=1$. It is, at the radius R,

$$\begin{aligned}\Phi_{10} &= -e\left\{\int_0^R \frac{1}{R}\cdot X_{10}^2\,(r)\,r^2\,dr + \int_R^\infty \frac{1}{r}\,X_{10}^2\,(r)\,r^2\,dr\right\}\\ &= -e\left\{\frac{1}{R} - e^{-(2Z/a_0)R}\left(\frac{Z}{a_0}+\frac{1}{R}\right)\right\}.\end{aligned}$$

The potential of the electron distributed over the surface of a sphere of radius ρ_0 is

$$\begin{aligned}\Phi &= -\frac{e}{R} \quad \text{for} \quad R > \rho_0\\ &= -\frac{e}{\rho_0} \quad \text{for} \quad R < \rho_0.\end{aligned}$$

Φ will provide the most satisfactory approximation to Φ_{10} when the difference $\Phi - \Phi_{10}$, properly weighted and integrated throughout space, is zero.

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* 'Z. f. Physik,' vol. 4, p. 347 (1921).

† 'Z. f. Physik,' vol. 39, p. 499 (1926).

‡ Dissertation,' Munich, 1927.

§ Waller, 'Z. f. Physik,' vol. 38, p. 635 (1926).

Reference to fig. 2 shows that for small values of r, for which Φ and Φ_{10} differ appreciably, the dependence of D on r is roughly linear for all states, which we may consider to represent other electrons which interact with the electron in the state $n = 1$. Hence the weight may be taken as linear in r, and we obtain

$$\int_0^\infty (\Phi - \Phi_{10})\, r\, dr = \text{const.}\left(3 - \frac{2Z}{a_0}\rho_0\right),$$

which vanishes for

$$\rho_0 = \tfrac{3}{2}\frac{a_0}{Z};$$

that is, for exactly the value $\bar{r}$ as given by equation (4). It is probable that the explicit consideration of further cases would lead to similar conclusions. The ξ values corresponding to $r = \bar{r}$ are shown in fig. 2.

In the following discussion we shall use m_i to denote the principal quantum number of the ith shell, *i.e.*, instead of n. We shall introduce for convenience the numerical factor γ_i, such that

$$\bar{r} = \gamma_i \frac{a_0 m_i^2}{Z}. \tag{5}$$

From equations (4) and (5) we accordingly obtain for an electron with the quantum numbers m_i and l_i the expression

$$\gamma_i = 1 + \tfrac{1}{2}\left\{1 - \frac{l_i(l_i+1)}{m_i^2}\right\}. \tag{6}$$

It has been found that no significant error is introduced by combining the subgroups of an entire shell, using an average value of γ for the entire K, L, M, ... shell. With the Stoner distribution of electrons among the levels, this average value is

$$\gamma(m_i) = 1 + \frac{1}{2m_i} + \frac{(m_i-1)^2}{4m_i^2} \tag{7A}$$

for completed shells,

$$\gamma(m_i) = \tfrac{3}{2} - \frac{3}{4m_i^2} \tag{7B}$$

for eight-shells (octets), and

$$\gamma(m_i) = \tfrac{3}{2} - \frac{2}{m_i^2} \tag{7C}$$

for eighteen-shells.

It might be thought that these values of γ are not correct because of the fact that the electron shells actually do not consist of hydrogen-like electrons, but rather themselves of "penetrating" electrons. However, as Z increases the "penetrating orbits" become more and more hydrogen-like; and these values of γ can accordingly be used in our later treatment, which postulates that Z is large, the error introduced being quadratic in z/Z, and so negligible.

III.—*The Quantisation of Penetrating Orbits.*

Let us now consider an electron orbit n_k (in which $k = k_1$, in the X-ray nomenclature of Sommerfeld), which penetrates a number of electron shells. We shall determine the orbit with the methods of classical mechanics, quantising with the rules of the old quantum theory; values of the azimuthal quantum number k will later be chosen in such a way as to cause our formulas to approximate as closely as possible to the quantum mechanics. In accordance with the previous discussion, the ith electron shell is idealised as a homogeneous surface charge of amount $-z_i e$ on a sphere of radius $\rho_i = \bar{r}_i$. We shall let $Z_i e$ be the effective nuclear charge in the ith region, which is the region between the radii ρ_{i-1} and ρ_i; accordingly $Z_{i+1} = Z_i - z_i$, and $Z_1 = Z - z$, in which Z is the atomic number of the atom and z the number of electrons entirely within the orbit under consideration. With the use of Newtonian dynamics, *i.e.*, neglecting the relativistic effect and the perturbations due to the spinning electron, the motion of the electron is described by the Hamiltonian equation

$$\frac{1}{2m}\left(p_r^2 + \frac{p_\phi^2}{r^2}\right) + \mathrm{V}(r) = \mathrm{W}, \tag{8}$$

in which W is the energy constant and

$$\mathrm{V}(r) = \mathrm{V}_i(r) = -\frac{Z_i e^2}{r} - \frac{z_i e^2}{\rho_i} - \frac{z_{i+1}e^2}{\rho_{i+1}} - \quad \ldots \tag{9}$$

in the ith region. Since ϕ is cyclic, the quantum rules require

$$p_\phi = \frac{kh}{2\pi}.$$

Let us now define for the ith region a radial quantum number n_i', which we shall call the *segmentary* radial quantum number, by means of the equation

$$n_i'h = \oint \sqrt{2m\{\mathrm{W} - \mathrm{V}_i(r)\} - \frac{k^2h^2}{4\pi^2}\cdot\frac{1}{r^2}}\, dr. \tag{10}$$

n_i' is thus the radial quantum number which would characterise the orbit if the ith region were large enough to include the entire orbit. The true radial quantum number, on the other hand, is given by the equation

$$n'h = \sum_{i=1}^{j} \int_{i\text{th region}} \sqrt{2m\{\mathrm{W} - \mathrm{V}(r)\} - \frac{k^2h^2}{4\pi^2}\cdot\frac{1}{r^2}}\, dr. \tag{11}$$

From equations (8), (9) and (10) it is evident that the path of the electron in the ith region is a segment of the Kepler ellipse defined by the segmentary radial and the azimuthal quantum numbers n_i' and k, so that it can be described by the known equations

$$r = \frac{a_0 k^2}{Z_i} \cdot \frac{1}{(1 - \varepsilon_i \cos \phi)} = \frac{a_0 n_i^2}{Z_i}(1 + \varepsilon_i \cos u)$$

$$t = \frac{n_i^3}{4\pi R Z_i^2}(u + \varepsilon_i \sin u).$$

In these equations ϕ and u are the segmentary true anomaly and excentric anomaly, respectively, measured from aphelion; while n_i and ε_i are the segmentary principal quantum number and excentricity, given by the equations

$$n_i = n_i' + k, \qquad \varepsilon_i = \sqrt{1 - \frac{k^2}{n_i^2}}.$$

To evaluate the segmentary quantum numbers we observe from a comparison of equations (9) and (10) with the corresponding ones for a hydrogen-like orbit that

$$W = -\frac{e^2}{2a_0} \cdot \frac{Z_i^2}{n_i^2} + \frac{z_i e^2}{\rho_i} + \frac{z_{i+1} e^2}{\rho_{i+1}} + \ldots = -\frac{e^2}{2a_0} \cdot \frac{Z_{i+1}^2}{n_{i+1}^2} + \frac{z_{i+1} e^2}{\rho_{i+1}} + \ldots = \text{const.} \tag{12}$$

From this there is obtained, neglecting powers of z_i/Z higher than the first, the expression

$$n_{i+1} = n_i\left(1 + \frac{z_i}{Z} \cdot \beta_i\right), \quad \text{with} \quad \beta_i = \frac{n^2}{\gamma_i m_i^2} - 1. \tag{13}$$

On carrying out the integrations in equation (11), it becomes

$$n' = n_1\{F(\pi) - F(u_1)\} + n_2\{F(u_2') - F(u_2)\} + \ldots + n_j\{F(u_j') - F(0)\}, \tag{14}$$

in which

$$F(u_i) = \frac{1}{\pi}\left[u_i - \varepsilon_i \sin u_i - \sqrt{1 - \varepsilon_i^2} \arcsin\left\{\frac{\sqrt{1 - \varepsilon_i^2} \sin u_i}{1 + \varepsilon_i \cos u_i}\right\} - \pi\left(1 - \sqrt{1 - \varepsilon_i^2}\right)\right], \tag{15}$$

the initial and final values u_i and u_i' of the excentric anomaly in the ith region being given by the equations

$$1 + \varepsilon_i \cos u_i = \frac{\rho_i Z_i}{a_0 n_i^2}, \qquad 1 + \varepsilon_{i+1} \cos u'_{i+1} = \frac{\rho_i Z_{i+1}}{a_0 n_{i+1}^2}. \tag{16}$$

From this, with the use of equation (13), and again neglecting powers of z_i/Z

higher than the first, there is derived the following relation between n_1 and the true quantum number n :

$$n_1 = n\left[1 - \sum_{i=1}^{j} \cdot \frac{1}{\pi} \cdot \frac{z_i}{Z}\{\beta_i u_i + (1+\beta_i)\,\varepsilon \sin u_i\}\right]. \tag{17}$$

The equation connecting ε_i and ε is easily obtained from the definition of ε_i with the use of equations (13) and (17).

In order to approximate as closely as possible to the quantum mechanics we shall use throughout for k^2 the quantity $l\,(l+1)$; for often in the quantum mechanics $l\,(l+1)$ occupies the place formerly given to k^2, as we have seen in the case of $\bar{r}$.

The use of these expressions describing the penetrating orbit in predicting the physical properties of many-electron atoms will be exemplified in the following sections.

IV.—*The Theoretical Determination of the Mole Refraction.*

A simple consideration involving a slow mechanical transformation* shows that if the energy quantity corresponding to the second-order Stark effect of a system is

$$\Delta E = -\tfrac{1}{2}\alpha\, F^2, \tag{18}$$

then the electric moment induced in the system is

$$\bar{\mu} = \alpha\, F. \tag{19}$$

The polarisation in unit volume can be expressed in terms of the index of refraction n as

$$P = \frac{N}{V}\bar{\mu} = \frac{N}{V}\ \alpha\ F = \frac{3}{4\pi}\frac{n^2-1}{n^2+2}\cdot F \tag{20}$$

in which N is Avogadro's number and V the volume occupied by one mole of the molecules under consideration, α referring to one molecule. The mole refraction R is defined by the equation

$$R = V\cdot\frac{n^2-1}{n^2+2} = \frac{4\pi N}{3}\cdot\alpha. \tag{21}$$

Wentzel,† Waller‡ and Epstein§ have derived a formula for the second-order

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[*] Jones, 'Roy. Soc. Proc.,' A, vol. 105, p. 650 (1924). The first attempt to calculate the mole refraction from the quadratic Stark effect formula was made by Lennard-Jones (Jones), with the old quantum theory.

[†] 'Z. f. Physik,' vol. 38, p. 518 (1926).

[‡] 'Z. f. Physik,' vol. 38, p. 635 (1926).

[§] Epstein, 'Nature,' vol. 118, p. 444 (1926), 'Phys. Rev.,' vol. 28, p. 695 (1926).

Stark effect of a hydrogen-like atom, using the Schrödinger wave mechanics. Their equation, obtained independently and by different methods, is

$$\Delta E = -\frac{h^6}{16\,(2\pi)^6\, m^3 e^6 Z^4}\, n^4\,(17n^2 - 3m^2 - 9n_3^2 + 19)\,.\,F^2, \tag{22}$$

which gives

$$R = \frac{N\,.\,h^6}{12\,(2\pi)^5\, m^3 e^6 Z^4}\, n^4\,(17n^2 - 3m^2 - 9n_3^2 + 19), \tag{23A}$$

or, introducing for the physical constants their accepted values,

$$R \underset{\bullet}{=} \frac{0{\cdot}0470}{Z^4}\, n^4\,(17n^2 - 3m^2 - 9n_3^2 + 19). \tag{23B}$$

Here n is the principal quantum number, and m and n_3 are given by the equations

$$m = n_2 - n_1, \qquad n_3 = n - 1 - n_1 - n_2.$$

The quantum numbers n_1 and n_2 have the integral values

$$0 \leqq n_1 \leqq n - 1, \qquad 0 \leqq n_2 \leqq n - 1.$$

These conditions suffice to determine the possible values of m and n_3. As was shown by Pauli,* they are compatible with the experimental evidence, and explain many previously difficultly explicable facts involving the exclusion of certain quantum states.†

The electrons within the atom are actually not quantised in parabolic co-ordinates, but instead, on account of the central field of the atom core, in polar co-ordinates. It would, then, not be logical to attempt to select favoured values of m and n_3. Instead, we shall calculate the quantity

$$n^4\,(17n^2 - 3m^2 - 9n_3^2 + 19)$$

for each set of values of the quantum numbers, and then average the result. This procedure is justified to a considerable extent by the fact that the polarisation does not depend largely on the subsidiary quantum numbers, but is a function mainly of the principal quantum number, which is not changed by quantisation in a central field. On averaging over all values of m^2 and n_3^2,

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* 'Z. f. Physik,' vol. 36, p. 336 (1926).

† Equation 22 differs from that derived by Epstein with the old quantum theory only in the inclusion of the number 19, and in the values given to n_3 (previously $n_3 = n - n_1 - n_2$). Wentzel and Waller have shown that the new equation is in somewhat better agreement with the best experimental data than the old one.

assigning equal weight to each set of values of n_1 and n_2, there is obtained the result $\overline{m^2} = \overline{n_3{}^2} = \frac{1}{6}(n^2 - 1)$, which on substitution in equation (23) gives

$$\mathrm{R} = 0 \cdot 0470 \,.\, n^4 (15n^2 + 21) \,.\, \sum_{\kappa} \frac{1}{(\mathrm{Z} - \mathrm{S}_{\mathrm{R}_\kappa})^4}, \tag{24}$$

in which the summation is to be taken over all electrons in the nth shell.* $\mathrm{S_R}$ is called the mole refraction screening constant.

We shall now predict values of $\mathrm{S_R}$ for ions for which z_i/Z is small, *i.e.*, for Z large. If this screening constant is constant, and does not depend on Z, these values hold for all atoms and ions with the structures considered. The nature of the agreement between the theoretical and the experimental values of R or of $\mathrm{S_R}$ will show to what extent this is true.

From equation (24) it is seen that, except for a small additive term in $n^4\mathrm{Z}^{-4}$, the mole refraction of a hydrogen-like electron is proportional to $n^6\mathrm{Z}^{-4}$. Now most of the polarisation occurs in the outermost part of the orbit, for here the externally applied field has its greatest value relative to the nuclear field. Accordingly we shall assume that the polarisation produced in a penetrating orbit is equal to that produced in a hydrogen-like orbit having the same parameters as those effective in the outermost (jth) region. This assumption is reasonable in view of the fact that in every case nearly the entire outer half of the orbit lies in this region. We accordingly write

$$\mathrm{R} = \text{const.}\ n_j{}^6\, \mathrm{Z}_j{}^{-4} = \text{const.}\ n^6 (\mathrm{Z} - \mathrm{S_R})^{-4}, \tag{25}$$

and from this determine $\mathrm{S_R}$.

For generality let us consider a property proportional to $n^r\mathrm{Z}^{-t}$, so that we have

$$\text{const.}\ n_j{}^r\, \mathrm{Z}_j{}^{-t} = \text{const.}\ n^r (\mathrm{Z} - \mathrm{S})^{-t}.$$

On expanding the left hand expression in powers of z_i/Z, using equations (13) and (17), and comparing the first term of the expansion with the corresponding term in the expansion of the right-hand expression in powers of S/Z, it is found that

$$\mathrm{S} = z + \sum_i z_i - \frac{r}{t} \sum_i z_i \mathrm{D}_i, \tag{26A}$$

in which D_i, which we shall call the unit screening defect for an electron in the ith shell, is given by the equation

$$\mathrm{D}_i = \frac{1}{\pi}\ \beta_i u_i + (1 + \beta_i)\, \varepsilon \sin u_i \} - \beta_i \tag{26B}$$

with
$$1 + \varepsilon \cos u_i = \frac{\gamma_i m_i{}^2}{n^2}. \tag{27}$$

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* This equation is, of course, rigorously true for H, He^+, etc., for which $\mathrm{S_R}$ is zero.

Internal shells are thus seen to screen completely, and the screening effects of penetrated shells are additive. Moreover, it is seen that for properties proportional to different powers of n and Z the total screening defect varies directly with r/t.

For the mole refraction screening constant we accordingly have

$$S_{\mathbf{R}\infty} = z + \sum_i z_i - \tfrac{3}{2}\sum_i z_i D_i. \tag{28}$$

Table I.—The Mole Refraction Screening Constant.

	Z_0		$S_{R\infty}$.	S_{R_0}.	$S_{R_0} - S_{R\infty}$.	ΔS_R.
He	2	K	0·391	0·397		0
Ne	10	L_{11}	4·45	4·31	−0·14	0
		L_{21} L_{22}	5·64	5·50		
Ar	18	M_{11}	9·70	11·11	1·41	0·05
		M_{21} M_{22}	10·99	12·40		
Kr	36	N_{11}	21·28	26·69	5·41	0·19
		N_{21} N_{22}	22·92	28·33		
Xe	54	O_{11}	34·29	42·26	7·97	0·29
		O_{21} O_{22}	36·63	44·60		
$[Cu^+]_0$	28	M_{11}	14·4	14·9	0·5	0·02
		M_{21} M_{22}	16·1	16·6		
		M_{32} M_{33}	19·5	20·0		
$[Ag^+]_0$	46	N_{11}	25·7	32·15	6·5	0·23
		N_{21} N_{22}	27·5	33·95		
		N_{32} N_{33}	31·1	37·55		
$[Au^+]_0$	78	O_{11}	46·0	59·9	13·9	0·50
		O_{21} O_{22}	48·1	62·0		
		O_{32} O_{33}	52·4	66·3		

In column 4 of Table I are given the values of S_{R_∞} obtained by the application of this equation to the structures included. (We have written S_{R_∞} because the values are derived for very large values of Z.) The symbols $[Cu^+]_0$, $[Ag^+]_0$, and $[Au^+]_0$ denote atoms with the corresponding structures and the atomic numbers 28, 46, and 78. In column 5 are given values of S_R obtained from the experimental values of R (for light of infinite wave-length) shown in Table II by the following procedure. It is assumed that the differences in S_R for different sub-levels within a shell are those given by the theory; the solution of equation (24), with R given its experimental values, then gives the "experimental" values, S_{R_0}.

Table II.—Experimental Values of the Mole Refraction.*

—	R.	—	R.
He	0·513	Zn^{++}	0·72
Ne	0·995	Cd^{++}	2·74
Ar	4·132	Hg^{++}	3·14
Kr	6·25	Ag^{+}	4·33
Xe	10·16		

* The experimental values for the rare gases are those of C. and M. Cuthbertson ('Roy. Soc. Proc.,' A, vol. 84, p. 13 (1911)) extrapolated to infinite wave-length by Born and Heisenberg ('Z. f. Physik,' vol. 23, p. 388 (1924)). The silver ion value is obtained from the solution value given by Heydweiller ('Phys. Z.,' vol. 26, p. 526 (1925)) by taking 2·17 for the potassium ion. The cadmium ion value was calculated from this by the methods in the text, and the zinc and mercury ion values obtained from Heydweiller's by correcting by the difference between his cadmium value and ours; this procedure being adopted to correct for the effect of hydration of these highly charged ions.

The agreement between the theoretical and the experimental values of S_R is most encouraging. It is seen that for elements with only a few electrons the agreement is complete, and that it becomes less satisfactory as the electron number of the structure increases, the difference $S_{R_0} - S_{R_\infty}$ showing a uniform increase. We can hence draw the conclusions that for light atoms all of the assumptions involved in the derivation of equations (24) and (28) are justified, that for these atoms the theoretical treatment of the electron orbits proposed in this paper is in general acceptable, and that it is permissible, in addition, to suppose the screening constants to be constant, and not to vary with Z. For heavier atoms the theoretical derivation of screening constants (valid for Z large) is only approximate, and the assumption that the screening constants are independent of Z is only approximately true, for they approach the theoretical values as Z becomes large. Evidence tending to show the fundamental correctness of our theoretical procedure, other than the good agreement of theory and experiment for light atoms, is provided by the regularity in the increase of $S_{R_0} - S_{R_\infty}$ as the electron number of the structure increases, and by the similarity in the values of $S_{R_0} - S_{R_\infty}$ for corresponding eight-shell and eighteen-shell structures.

It is of interest to note that on introducing the theoretical value of S_{R_∞} for helium in equation (24), the result $R = 0{\cdot}506$ is obtained. The experimental data of C. and M. Cuthbertson were extrapolated to 0·513 for light of infinite wave-length by Born and Heisenberg, and to 0·518 by Heydweiller; so that our *entirely theoretically derived* value agrees with experiment within the limit of error of the extrapolation.

By introducing in equation (24) the values of S_{R_0} given in Table I we obtain tentative predicted values for the mole refraction of univalent ions with the structures considered (Table III). These values apply only to free ions in the gaseous state. It is difficult to say *a priori* whether measurements made on alkali halide crystals or those made on dilute aqueous solutions of the alkali halides would give mole refraction values in the better agreement with those holding for the gaseous ions. Previous investigators, in attempting to derive values of the polarisabilities of gaseous ions from experimental data for salts, have decided differently; Born and Heisenberg* chose to use crystals, while Fajans and Joos† and Heydweiller‡ used dilute aqueous solutions. One fact showing that the perturbing effects in crystals are large is the large deviation from additivity exhibited by their mole refraction, amounting to as much as 1·5 units for the alkali halides.§ Our predicted values for gaseous ions show that ions in solution are indeed more similar to gaseous ions than are ions in crystals, as far as the mole refraction is concerned. In column 3 of Table III are given experimental values of R for ions in dilute solution, obtained from Heydweiller's tables by assuming the value 2·17 for potassium ion to be correct; and in column 4 values of R for the ions in the alkali halide crystals, calculated from the data given by Born and Heisenberg by again assuming the same value for potassium ion. Only the sodium, fluoride, and chloride ions can be compared

Table III.—Mole Refraction of Univalent Ions.

Ion.	R predicted.	R solution.	R crystal.
Na^+	0·457	0·11	0·04 to −0·55
K^+	2·17	(2·17)	(2·17)
Rb^+	3·88	3·56	3·77 to 4·10
Cs^+	6·82	6·17	6·23 to 6·42
F^-	2·65	2·71	2·96
Cl^-	8·92	8·76	8·04 to 8·48
Br^-	10·75	12·14	11·06 to 11·80
I^-	15·71	18·07	16·24 to 17·02

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* Born and Heisenberg, 'Z. f. Physik,' vol. 23, p. 388 (1924); for criticism of their derivation of polarisabilities from spectral term values see Hartree, 'Proc. Camb. Phil. Soc.,' vol. 22, p. 409 (1924); 'Roy. Soc. Proc.,' A, vol. 106, p. 552 (1924); and Schrödinger 'Ann. d. Physik,' (4), vol. 77, p. 43 (1925).

† Fajans and Joos, 'Z. f. Physik,' vol. 23, p. 1 (1924). These authors also discussed the data for crystals, and showed that the mole refraction values for ions in solution are usually only slightly different from those for gaseous ions.

‡ Heydweiller, 'Phys. Z.,' vol. 26, p. 526 (1925); for a discussion of the experimental and previous theoretical work on mole refraction see the two preceding papers.

§ Fajans and Joos; also Spangenberg, 'Z. f. Krist.,' vol. 53, p. 499 (1923).

with the theoretical results, for only in these cases have we shown S_R to be practically independent of Z. In each of these three cases the solution results agree better with the theoretical values than do the crystal results, so that the conclusion can be safely drawn that in general ions in solution resemble gaseous ions more closely than do ions in crystals. The agreement between the solution values and the theoretical ones is good for the fluoride and chloride ions; the solution value for the sodium ion is low, without doubt on account of the action of this very small ion on the surrounding water molecules, which has previously been estimated by Fajans and Joos to cause a decrease of about 0·3 in R.

We are now led to introduce a second empirical correction into our calculations. The theoretical values for the rubidium, cæsium, bromide, and iodide ions in Table III resulted from the assumption that S_R is independent of Z, which is known not to be true for these structures, on account of the difference between S_{R_0} and S_{R_∞}. The solution values of R, which we may assume to hold also for gaseous ions in these cases, also show that the screening constant for the negative ions should be larger and for the positive ions smaller than that used; that is, as Z increases S_R decreases, presumably approaching our theoretical values for Z large. We shall assume that S_R is a linear function of Z in this region, and evaluate the parameters of the function with the use of the solution values for the bromide and iodide ions. If we write

$$S_R = S_{R_0} - (Z - Z_0)\,\Delta S_R, \tag{29}$$

within a range of values of Z not too far removed from Z_0 (the electron number of the structure), then ΔS_R is found to be 0·19 and 0·29 for the krypton and xenon structures respectively. These values are approximately proportional to $S_{R_0} - S_{R_\infty}$; hence we may safely accept 0·23 and 0·50 for the silver and aurous ion structures, respectively; and for consistency the corresponding values 0·05 and 0·02 will be used for the argon and cuprous ion structures also.

In Table IV are given values* of the mole refraction of gaseous ions calculated from equations (24) and (29) with the use of the values found above for S_{R_0} and ΔS_R. Values for hydrogen-like atoms and ions are also included; these are, of course, accurate, since no screening constant is needed. Table IV is

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* Throughout we have considered only the portion of the mole refraction produced in the outermost shell. In the case of xenon one finds by our methods that as much as 4 per cent. of the total mole refraction is due to the N shell; accordingly our values of S_R for the O electrons would be decreased by about 0·1 on making this correction. The values of R for ions would in most cases not be changed materially by the explicit consideration of the polarisation of inner shells, and so the less complicated treatment of this paper has been adopted.

Table IV.—The Mole Refraction and Diamagnetic Susceptibility of Atoms and Ions.

				H	He^+	Li^{++}						
$R =$				1·691	0·1058	0·0209						
$-\chi \cdot 10^6 =$				2·415	0·604	0·268						
				H^-	He	Li^+	Be^{+2}	B^{+3}	C^{+4}	N^{+5}		
$R =$				25·65	0·513	0·074	0·020	0·0076	0·0034	0·0018		
$-\chi \cdot 10^6 =$				8	1·54	0·63	0·34	0·21	0·15	0·11		
	C^{-4}	N^{-3}	O^{-2}	F^-	Ne	Na^+	Mg^{+2}	Al^{+3}	Si^{+4}	P^{+5}	S^{+6}	Cl^{+7}
$R =$	5400	72·6	9·88	2·65	0·995	0·457	0·238	0·136	0·084	0·054	0·036	0·025
$-\chi \cdot 10^6 =$	50	22	12·6	8·1	5·7	4·2	3·2	2·5	2·1	1·7	1·4	1·2
	Si^{-4}	P^{-3}	S^{-2}	Cl^-	Ar	K^+	Ca^{+2}	Sc^{+3}	Ti^{+4}	V^{+5}	Cr^{+6}	Mn^{+7}
$R =$	950	105	26·0	9·30	4·13	2·12	1·19	0·73	0·47	0·31	0·22	0·16
$-\chi \cdot 10^6 =$	110	65	40	29	21·5	16·7	13·3	10·9	9·0	7·7	6·6	5·7
						Cu^+	Zn^{+2}	Ga^{+3}	Ge^{+4}	As^{+5}	Se^{+6}	Br^{+7}
					$R =$	1·08	0·72	0·50	0·36	0·26	0·19	0·15
					$-\chi \cdot 10^6 =$	13	11	9·5	8·5	7·5	6·5	6·0
	Ge^{-4}	As^{-3}	Se^{-2}	Br^-	Kr	Rb^+	Sr^{+2}	Y^{+3}	Zr^{+4}	Nb^{+5}	Mo^{+6}	
$R =$	276	72·6	26·8	12·14	6·26	3·57	2·18	1·41	0·95	0·66	0·48	
$-\chi \cdot 10^6 =$	140	95	70	54	42	35	28	24	20	17	15	
						Ag^+	Cd^{+2}	In^{+3}	Sn^{+4}	Sb^{+5}	Te^{+6}	I^{+7}
					$R =$	4·33	2·74	1·84	1·26	0·91	0·66	0·49
					$-\chi \cdot 10^6 =$	44	37	32	28	24	20	17
	Sn^{-4}	Sb^{-3}	Te^{-2}	I^-	Xe	Cs^+	Ba^{+2}	La^{+3}	Ce^{+4}			
$R =$	228	80·6	35·6	18·07	10·16	6·15	3·94	2·64	1·86			
$-\chi \cdot 10^6 =$	180	130	105	80	66	55	46	38	33			
						Au^+	Hg^{+2}	Tl^{+3}	Pb^{+4}	Bi^{+5}		
					$R =$	4·75	3·14	2·19	1·56	1·15		
					$-\chi \cdot 10^6 =$	65	55	48	42	37		

made complete because it is often desirable to have even approximate values of R for ions, even for those which are not capable of existence in solution. Thus, for example, they may be compared with core polarisabilities deduced from the energy levels of non-penetrating alkali-like electron states in order to test the spectral theory used in the deduction. Moreover, the deviation of the observed mole refraction from the calculated value for a crystal or complex ion can be considered as a measure of the deformation experienced by the individual ions composing the crystal or ion, as was especially emphasised by Fajans and Joos. For example, they give for $PO_4^{\equiv}$, $SO_4^{=}$, and ClO_4^- the values 16·3, 14·6, and 13·3 respectively; from Table IV we obtain 39·5 in each case, assuming the complex ion to consist of undeformed monatomic ions. They give also for $CO_3^{=}$ 12·3 and for NO_3^- 11·0; our values are 29·6 in each case.* The reasonable conclusion can hence be drawn that in each series the deforming influence of the central ion increases with its electrical charge.†

No extensive comparison with experiment to test the values in Table IV will be made. The close agreement between the purely theoretical and the experimental results in the case of helium and neon allows one to place confidence in the R values for ions with these structures; and the same remark applies with less force in the case of the argon structure, where only a small empirical correction was introduced. It is interesting to note that the theoretical values 3·57 and 6·15 for the rubidium and the cæsium ion agree very well with the experimental ones, 3·56 and 6·17 (Table III), which were not used at all in the evaluation of the empirical corrections for these structures. Finally, we may mention that our values agree in general with those of Fajans and Wulff,‡ obtained by them from the experimental R values for salt solutions by the application of only the simplest theoretical considerations.

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* The experimental values are for the sodium D-lines, but are only slightly changed on extrapolation to infinite wave-length.

† For other uses of the ionic polarisability reference may be made to its rôle in the theoretical discussion of the structures of molecules (Heisenberg, 'Z. f. Physik,' vol. 26, p. 196 (1924); Kornfeld, *ibid.*, vol. 26, p. 205 (1924); Hund, *ibid.*, vol. 31, p. 81 (1925); vol. 32, p. 1 (1925); and in simple thermodynamic quantities such as the heat of vaporisation of crystals (Born and Heisenberg), and the heat of ionisation (into H^+ and X^-) of the hydrogen halides (Kemble, 'Journ. Opt. Soc. Am.,' vol. 12, p. 1 (1926)).

‡ Fajans and Wulff, not yet published. Their ionic refraction values for light of infinite wave-length are found by the methods applied by Fajans and Joos to the refraction for the sodium D-lines.

V.—*Diamagnetic Susceptibility.*

According to the classical theory, the effect of a magnetic field on a system composed of electrons in motion about a fixed nucleus is equivalent to the first order of approximation to the imposition on the system of a uniform rotation about the field direction (the Larmor precession) with the angular velocity $2\pi\omega_{\mathrm{H}} = \mathrm{H}e/2mc$. This rotation of electrons produces a magnetic moment opposed to the field, such that the molal diamagnetic susceptibility is

$$\chi = -\frac{\mathrm{N}e^2}{4mc^2}\cdot\sum_{\kappa}\overline{r_\kappa^2 \sin^2 \vartheta_\kappa},$$

in which $r_\kappa \sin \vartheta_\kappa$ is the projection normal to the field direction of the distance r_κ of the κth electron from the nucleus; $\overline{r_\kappa^2 \sin^2 \vartheta_\kappa}$ denotes the time average of $r_\kappa^2 \sin^2 \vartheta_\kappa$. For S states and for completed groups and sub-groups the new quantum mechanics gives $\overline{r_\kappa^2 \sin^2 \vartheta_\kappa} = \frac{2}{3}\overline{r_\kappa^2}$, so that we obtain

$$\chi = -\frac{\mathrm{N}e^2}{6mc^2}\cdot\sum_{\kappa}\overline{r_\kappa^2}. \tag{30}$$

Adhering to our general method of treatment, we shall now evaluate a screening constant $\mathrm{S_M}$ valid in the case of Z large. Taking the time average of r^2 in the various regions traversed, we write

$$\overline{r^2} = \frac{\sum\limits_{i=1}^{j}\int\limits_{i\text{th region}} r^2\,dt}{\sum\limits_{i=1}^{j}\int\limits_{i\text{th region}} dt},$$

which gives, on evaluating the integrals,

$$\overline{r^2} = a_0^2\,\frac{\sum\limits_{i=1}^{j} n_i^7 \mathrm{Z}_i^{-4}\{\mathrm{U}(u_i') - \mathrm{U}(u_i)\}}{\sum\limits_{i=1}^{j} n_i^3 \mathrm{Z}_i^{-2}\{(u_i' + \varepsilon_i \sin u_i') - (u_i + \varepsilon_i \sin u_i)\}},$$

in which

$$\mathrm{U}(u_i) = u_i(1 + \tfrac{3}{2}\varepsilon_i^2) + 3\varepsilon_i \sin u_i + \tfrac{3}{2}\varepsilon_i^2 \sin u_i \cos u_i + \varepsilon_i^3 \sin u_i - \tfrac{1}{3}\varepsilon_i^3 \sin^3 u_i,$$

and u_i and u_i' are given by equation (16). On expanding this in powers of z_i/Z, with the use of equations (13) and (17) and neglecting terms other than linear, and comparing the expansion with that of

$$\overline{r^2} = a_0^2\,\frac{n^4}{(\mathrm{Z} - \mathrm{S_{M\infty}})^2}(1 + \tfrac{3}{2}\varepsilon^2), \tag{31}$$

in powers of S_{M_∞}/Z, there is obtained for S_{M_∞} the value

$$S_{M\infty} = z + \sum_i S_{Mi} = z + \sum_i z_i - \sum_i D_{Mi} \tag{32A}$$

with
$$S_{Mi} = \frac{z_i}{\pi}\left\{u_i + \frac{\varepsilon \sin u_i \left(\frac{3}{4} - \frac{7}{4}\varepsilon^2 - \varepsilon \cos u_i + \frac{1}{12}\varepsilon^2 \sin^2 u_i\right)}{\left(1 + \frac{3}{2}\varepsilon^2\right)\left(1 + \varepsilon \cos u_i\right)}\right\} \tag{32B}$$

with u_i as given in equation (27).

In column 4 of Table V are given values of S_{M_∞} calculated by means of equation (32). The mole refraction results show that we may expect the

Table V.—The Diamagnetism Screening Constant.

Z_0.			S_{M_∞}.	S_{M_0}.	ΔS_M.
He	2	K	0·228	0·228	0
Ne	10	L_{11} L_{21} L_{22}	3·26 4·11	3·26 4·11	0
Ar	18	M_{11} M_{21} M_{22}	7·57 8·68	9·40 10·63	0·07
Kr	36	N_{11} N_{21} N_{22}	17·19 18·94	24·21 26·13	0·25
Xe	54	O_{11} O_{21} O_{22}	27·34 29·38	38·28 40·87	0·39
$[Cu^+]_0$	28	M_{11} M_{21} M_{22} M_{32} M_{33}	10·8 12·2 14·4	11·45 12·9 15·25	0·03
$[Ag^+]_0$	46	N_{11} N_{21} N_{22} N_{32} N_{33}	20·0 21·8 25·0	28·35 30·35 34·3	0·31
$[Au^+]_0$	78	O_{11} O_{21} O_{22} O_{32} O_{33}	36·7 39·1 43·3	54·8 57·35 62·35	0·65

theoretical values to be correct in the case of the helium and neon structures, and to show an increasing error with increasing electron number for the other structures. The form of equation (26), which gives the screening constant for a property proportional to $n^r Z^{-t}$, immediately suggests a method for correction by means of the empirical changes introduced in the mole refraction screening constant S_R; namely, with the assumption that the various screening constants (for various physical properties) of an atom or ion deviate from their values calculated for Z large in such a way as to keep constant the ratios of the corresponding screening defects of the penetrated shells. Thus we would assume that D_M/D_R for argon, krypton, etc., has the values holding for Z large;

and from this ratio and the empirical D_R values D_M and hence S_{M_0} and ΔS_M can be found. The results are given in Table V, which accordingly contains theoretical values of the diamagnetism screening constant, corrected for all structures but helium and neon by the empirical mole refraction data. For each ion S_M is obtained by an equation of the form of equation (29).

The quantum mechanics treatment of diamagnetism has not been published.* It seems probable, however, that Larmor's theorem will be retained essentially, in view of the marked similarity between the results of the quantum mechanics and those of the classical theory in related problems, such as the polarisation due to permanent electric dipoles and the paramagnetic susceptibility.† Thus we are led to use equation (30), introducing for $\overline{r_\kappa^2}$ the quantum mechanics value

$$\overline{r^2}_{nlm} = \int r^2 \Psi^*_{nlm} \overline{\Psi}_{nlm}\, dV = a_0^2 \cdot \frac{n^4}{(Z - S_M)^2}\left[1 + \tfrac{3}{2}\left\{1 - \frac{l(l+1) - \frac{1}{3}}{n^2}\right\}\right], \quad (33)$$

differing from the value of the old quantum theory in the number $\frac{1}{3}$, and in having $l(l+1)$ instead of k^2. Substituting this in equation (30), and introducing the numerical values of the physical constants, there results

$$\chi = -2{\cdot}010 . 10^{-6} . \sum_\kappa \frac{n_\kappa^4}{(Z - S_{M_\kappa})^2}\left[1 - \frac{\{3l_\kappa(l_\kappa + 1) - 1\}}{5n_\kappa^2}\right], \quad (34)$$

in which the summation over κ denotes over all the electrons in the atom.

The molal diamagnetic susceptibilities of rare gas atoms and a number of monatomic ions obtained by the use of equation (34) are given in Table IV. The values for the hydrogen-like atoms and ions are accurate, since here the screening constant is zero. It was found necessary to take into consideration in all cases except the neon (and helium) structure not only the outermost electron shell but also the next inner shell, whose contribution is for argon 5 per cent., for krypton 12 per cent., and for xenon 20 per cent. of the total.

The available experimental data, because of their paucity and their inaccuracy, do not permit the extensive testing of these figures. The directly determined susceptibilities for helium, neon, and argon are in gratifying agreement with the theoretical ones (Table VI). From the mole refraction results we may expect ions in solution to have values of χ near those for gaseous ions. Koenigsberger‡ has made determinations of χ for seven alkali halides in aqueous solution, in

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* Schrödinger (IV) has tentatively advanced a form of the wave equation in which magnetic fields are considered.

† Mensing and Pauli, 'Phys. Z.,' vol. 27, p. 509 (1926); Van Vleck, 'Nature,' vol. 118, p. 226 (1926).

‡ Koenigsberger, quoted in Landolt-Börnstein.

Table VI.—Diamagnetic Susceptibilities of the Rare Gases.

——	$-\chi\,.\,10^6$ Calculated.	Observed.*	From salt solutions.
He	1·54	1·88	1·8
Ne	5·7	6·7	9
Ar	21·5	18·1, 20·3	18
Kr	42		37
Xe	66		59

* The three numbers in the first column are from Hector, 'Phys. Rev.,' vol. 24, p. 418 (1924); the second value for argon is from Lehrer, 'Ann. d. Physik, vol. 81, p. 229 (1926).

each case obtaining a specific susceptibility of $-0{\cdot}45\,.\,10^{-6}$ units per gram. Assuming this rule to hold in general, one obtains the rare gas susceptibilities given in the last column of Table VI, in satisfactory agreement with those calculated. He also gives for the halides of calcium, barium, and strontium specific susceptibilities somewhat lower, about $-0{\cdot}41\,.\,10^{-6}$, corresponding satisfactorily with the decrease observed in Table IV on going from a univalent to the adjoining divalent cation.

The experimental specific susceptibilities of solid salts obtained by different investigators (quoted in Landolt-Börnstein) show wide variations, but in general agree roughly with those from solutions. Thus for sodium chloride five investigators report five values, varying from $-0{\cdot}38$ to $-0{\cdot}58\,.\,10^{-6}$. Of these the most trustworthy seems to be that of Ishiwara, $-0{\cdot}498\,.\,10^{-6}$. This corresponds to $\chi = -29{\cdot}2\,.\,10^{-6}$, in satisfactory agreement with our value $-33\,.\,10^{-6}$. Pascal has also made extensive experimental investigations, from which he deduced a set of atomic susceptibilities,* choosing them in such a way as to give agreement with those for the elementary substances in a number of cases. These values are of little use to us because of lack of information regarding the nature of the compounds studied.† Pascal‡ has later reported the susceptibilities of several salts of each of the alkali and alkali earth metals, from which ionic susceptibilities can be derived after the choice of one as a starting point. We shall take for $-\chi\,.\,10^6$ for sodium ion 5·2 and for potassium ion 14·5 (compatible values), which are 4 smaller than those chosen by Pascal; in this way the "experimental" values in Table VII are obtained. For helium-, neon- and argon-like ions, as well as for the cuprous ion, the agreement with our

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* 'C. R.,' vol. 158, p. 1895 (1914).

† Despite the improbability that these atomic susceptibilities correspond at all with true ionic susceptibilities, they have been made the basis of a theoretical discussion by Cabrera, 'Journ. de physique et le radium,' VI, vol. 6, p. 241 (1925).

‡ 'C. R.,' vol. 158, p. 37 (1914); vol. 159, p. 429 (1914); vol. 173, p. 144 (1921).

Table VII.—Ionic Susceptibilities, from Pascal.

——	$-\chi . 10^6$ Experiment.	Theory.	——	$-\chi . 10^6$ Experiment.	Theory.
Li^+	0·2	0·6			
Na^+	5·2	4·2	F^-	10·3	8·1
K^+	14·5	16·7	Cl^-	24·1	29
Rb^+	23·2	35	Br^-	34·6	54
Cs^+	37·0	55	I^-	48·6	80
Be^{++}	0·2	0·3	$CO_3^=$	30·2	38
Mg^{++}	3·3	3·2	NO_3^-	18·2	38
Ca^{++}	7·8	13·3	$PO_4^{\equiv}$	47·1	52
Sr^{++}	16·5	28	$SO_4^=$	41·6	51
Ba^{++}	29·8	46	OH^-	11·5	12·6
Cu^+	ca. 14	13			
Ag^+	27	44			

predicted values is satisfactory ; but for the more complicated ions the experimental values are low. It is impossible to give with certainty the explanation of this difference. The experimental values from solutions indicate that our predicted values are at least approximately correct for isolated ions, so that probably the differences are real, and are to be attributed to the mutual action of the ions in crystals. In regard to this effect of mutual action it is significant that the crystals show deviations from additivity (as in the case of the mole refraction), amounting, however, to only a few per cent.

We can draw conclusions regarding deformation of ions from observations of the diamagnetic susceptibility just as from those of the mole refraction. Thus in the series $CO_3^=$, NO_3^- and $PO_4^{\equiv}$, $SO_4^=$ the experimental values of χ show successively greater deviations from the theoretical ones (assuming undeformed $O^=$ ions) with increasing electrical charge of the central ion.*

We may accordingly conclude that our theoretical values of the diamagnetic susceptibility of atoms and ions are not incompatible with the experimental data.

VI.—*The Electron Distribution in Atoms and Ions. Atomic Sizes.*

According to the discussion in Section II, the quantity $\Psi\bar{\Psi}$ represents the electron density about the nucleus in a hydrogen-like atom. The electron

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* Larmor's Theorem is, of course, valid only for systems of electrons and one nucleus, so that complexes of atoms presumably do not permit the usual treatment. It seems probable, however, that the introduction of a hydrogen nucleus into an ion would cause a diminution in the susceptibility (in absolute value). The value of $-\chi . 10^6$ for water, 13·0, suggests that 12·6 for O is low, in agreement with the fact that the value 5·7 for neon is smaller than Hector's 6·7.

density corresponding to a " penetrating orbit " could be found by the solution of the boundary problem resulting on giving the potential energy V in the wave equation the value shown in equation (4). An approximation to this result is obtained by the introduction of a screening constant S_S, which we shall call the size screening constant, the shape of the distribution curve being considered to remain unaltered.

To evaluate this screening constant, we observe that in the penetrating orbits of the old quantum theory the electron remains for most of its period in the outer half of its orbit, *i.e.*, in the outermost or *j*th region. Hence we may consider that the entire orbit corresponds to one characterised by the segmentary quantum number n_j of the outermost region. It is desirable to evaluate S_S in such a way as to give the correct value to $\bar{r}$, the average distance of the electron from the nucleus. This distance is given by equation (4) Omitting for simplicity the factor $1+\frac{1}{2}\left\{1-\frac{l(l+1)}{n^2}\right\}$, which is of little significance in the result obtained, we then write

$$a_0 \cdot \frac{n_j^2}{Z_j} = a_0 \cdot \frac{n^2}{(Z - S_{S_\infty})} \, .$$

The value of the size screening constant S_{S_∞} is accordingly given by equation (26), r/t being replaced by 2.

As before, we may expect the values of S_{S_∞} calculated for Z large to be valid for actual ions with the helium and neon structures. For the other structures we introduce the empirical corrections based upon those used for the mole refraction screening constant, with the aid of the principle of the constancy of the ratios of corresponding screening defects, already used for the diamagnetism screening constant. In this way the values of S_{S_0} and ΔS_S given in Table VIII are obtained. An equation similar to equation (29) is to be used to find individual values of S_S.

The most instructive method of representing the electron distribution is by a graph showing it as a function of the distance r from the nucleus ; that is, by the use of $D = 4\pi r^2 \rho$, where ρ is the electron density. Such a graph is shown in fig. 3, in which is represented the total value of D for the sodium ion and the chloride ion, the D values being calculated as in Section II, but with the use of the appropriate effective atomic numbers $Z - S_S$. The vertical line for each shell is drawn at the average position $\bar{r}$ of the electrons in that shell, and its height gives the contribution of these electrons to D at this point. The distribution curves of the individual shells are those of fig. 2, with the scale

Table VIII.—The Size Screening Constant.

Z_0			S_{S_0}	ΔS_S
He	2	K	0·188	0
Ne	10	L_{11} L_{21} L_{22}	2·84 4·52	0
Ar	18	M_{11} M_{21} M_{22}	9·15 10·87	0·07
Kr	36	N_{11} N_{21} N_{22}	23·91 26·83	0·25
Xe	54	O_{11} O_{21} O_{22}	38·68 41·80	0·49
$[Cu^+]_0$	28	M_{11} M_{21} M_{22} M_{32} M_{33}	10·9 13·15 17·7	0·03
$[Ag^+]_0$	46	N_{11} N_{21} N_{22} N_{32} N_{33}	27·9 30·3 35·1	0·31
$[Au^+]_0$	78	O_{11} O_{21} O_{22} O_{32} O_{33}	54·2 57·0 62·7	0·67

varied as indicated by the positions and heights of the corresponding vertical lines.*

We are thus led to the following picture of atoms and ions containing only completed sub-groups of electrons ; the chloride ion, for example. The electron distribution about the nucleus is spherically symmetrical. The two K electrons in the chloride ion form a ball about the nucleus extending to the radius of about 0·1 Å, the electron density ρ decreasing monotonically as r increases. (This meaning will be implied by the word " ball." See fig. 1, in which the ordinates are proportional to $\pm\sqrt{\rho}$, to find the electron density.) The two L_{11} electrons provide a small ball extending to 0·07 Å, and then a thick shell, of maximum density at a distance of about 0·15 Å. The six L_{21} L_{22} electrons form one shell only, its density increasing from zero at $r = 0$ to a maximum at $r = 0·1$ Å, and then decreasing. A small portion (1 per cent.) of the two M_{11} electrons forms a ball about the nucleus, extending to 0·13 Å ; from this distance to 0·48 Å extends a shell containing about 10 per cent. of

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* In fig. 3 L_1 represents L_{11}, L_2 represents L_{21} L_{22}, &c. Through a mistake the L_1 and L_2 vertical lines for the chloride ion are drawn to the wrong heights ; the L_2 line should have the height shown for the L_1 line, and *vice versa.*

the two electrons, of maximum density at about 0·2 , and the remainder forms still another shell of maximum density at 0·8 Å. The six M_{21} M_{22} electrons

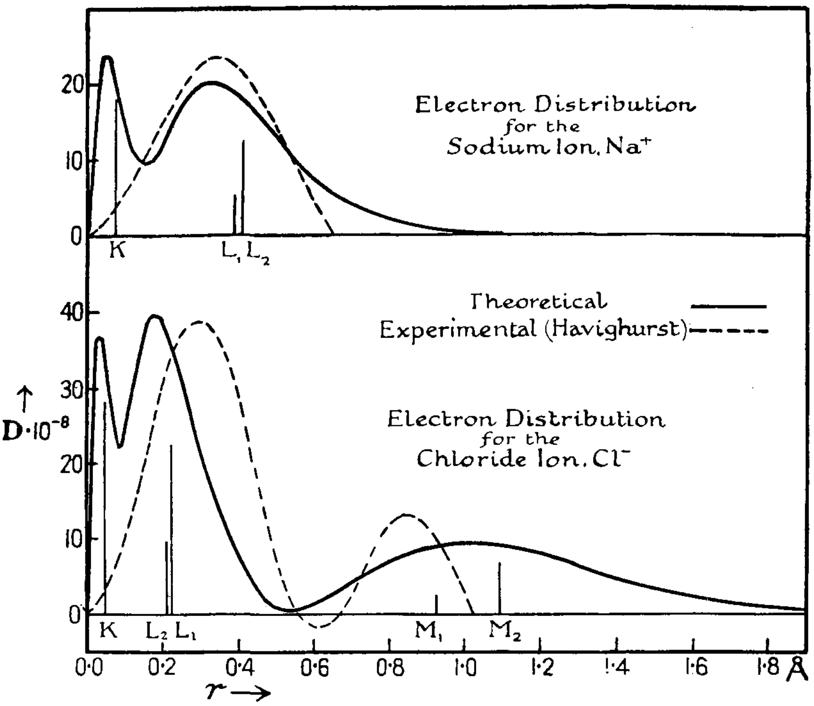

Fig. 3.—The theoretical and the experimental electron distribution (as a function of the distance from the nucleus) for the sodium and the chloride ion.

form two shells, one, containing about 10 per cent. of the electrons, having its maximum density at 0·13 Å, and the other with maximum density at 0·9 Å.*

We may accordingly say that an atom is composed of a nucleus embedded in a ball of electricity (the two K electrons with small contributions from other shells), which in turn is surrounded by more or less distinctly demarcated thick concentric shells, containing essentially the L, M, N, etc., electrons.†

Of particular interest is the result that for a radius of around 0·55 Å the electron density in the chloride ion falls nearly to zero ; for this conclusion has

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* The details of this description would be changed slightly, but not essentially, by the introduction of the spinning electron into the theory.

† The experiments of Davisson and Kunsman, 'Phys. Rev.,' vol. 22, p. 242 (1923), on the distribution in angle of electrons scattered by metals provide some experimental verification of this layer structure of atoms ; for the investigators remark that their results are explicable by the atomic model involving the surface layer idealisation of electron shells.

been previously drawn from the experimental intensities of reflection of X-rays from sodium chloride crystals. It was remarked by Duane* that if the distribution of diffracting power (the electron density) within a crystal be represented by a triple Fourier series, then the intensity of reflection of X-rays from the plane (*hkl*) of the crystal† is proportional to the square of the coefficient of the corresponding term in the series ; which for a crystal such as sodium chloride has the form,

$$\rho(x, y, z) \sim \sum_h \sum_k \sum_l \mathrm{A}_{hkl} \cos 2\pi h \frac{x}{a} \cos 2\pi k \frac{y}{a} \cos 2\pi l \frac{z}{a}. \qquad (35)$$

The quantity A^2_{hkl} can be obtained from the measured intensities of reflection of X-rays by making various corrections (for dependence on angle of reflection, extinction of the beam of X-rays, etc.). With the aid of a reasonable assumption regarding the sign of A_{hkl}, Havighurst‡ has in this way obtained the Fourier series representation of the distribution of refracting power in sodium chloride, using planes as complex as (10.0.0). From this he calculated the electron distribution D as a function of r for the sodium and the chloride ion, obtaining the curves§ shown in fig. 3. On comparing the curve for sodium ion with the theoretical curve it is seen that except for the maximum made by the K electrons there is satisfactory agreement. The experimental chloride ion curve also does not show the maximum due to K electrons, and, moreover, the ratio of the area of the M to that of the L hump is smaller than the theoretical one. It is gratifying, however, to observe the experimental verification of the existence of the M shell, and of the minimum in the electron density in the region at 0·6 Å from the nucleus. In explanation of the small size of the M hump found by Havighurst we observe that the densities ρ in this region as given by equation (35) are very small, not much larger than the random fluctuations shown by the series, so that this portion of the curve may be in considerable error. The non-appearance of the K maxima may be attributed to several co-operating causes. In order for the Fourier series to be sensitive enough to show such sharp maxima, accurate values of the coefficients A_{hkl} for a large number of planes with indices of the order of 15 would be required. Furthermore, it is probable that

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* ‘ Proc. Nat. Acad. Amer.,’ vol. 11, p. 489 (1925).

† (*hkl*) represents here the Miller indices multiplied by the order of reflection.

‡ ‘ Proc. Nat. Acad. Amer.,’ vol. 11, p. 502 (1925). Havighurst used the intensity measurements of W. L. Bragg, James, and Bosanquet, ‘ Phil. Mag.,’ vol. 41, p. 309 (1921) ; vol. 42, p. 1 (1921).

§ A somewhat similar but not identical electron distribution for these ions has been derived by A. H. Compton, ‘ Phys. Rev.,’ vol. 27, p. 510 (1926), from the same experimental data.

thermal motion of the ions in the crystal at ordinary temperatures would smooth the curve somewhat, and displace it towards larger values of r. It is also possible that for the tightly bound K electrons the reflecting power and the electron density are no longer proportional. The careful determination of many coefficients A_{hkl} for sodium chloride and other crystals will no doubt provide much valuable information regarding the electron distribution in atoms, permitting a decision to be reached concerning the validity of Schrödinger's interpretation of his eigenfunctions, and incidentally testing the procedure of this paper for evaluating the screening constants.

The theoretically obtained electron densities of ions may be used for the calculation of the so-called F curves, which give the effective reflecting power of the ion as a function of the angle of reflection and the wave-length of X-rays, and which are of use in the determination of crystal structures. It may be mentioned that the high maximum value of the electron density at the nucleus given by our calculations provides considerable justification for the method* of determining crystal structures with the aid of the relative intensities of Laue spots produced by crystal planes with complicated indices.

VII.—*Interatomic Distances.*

Schrödinger's ideas lead to a simple explanation of the forces between atoms, in particular of the previously difficultly understandable repulsive force.† As an illustration we shall calculate the internuclear distances for the hydrogen halides.

For simplicity we shall assume the fluoride ion to consist of the nucleus, two K electrons very close to it, and eight L_{21} L_{22} electrons; for as can be seen from the representation of the sodium ion in fig. 3 the L_{11} electrons show nearly the same distribution along r as the L_{21} L_{22} electrons. The potential energy of a hydrogen nucleus at the distance R from the fluorine nucleus is then

$$\Phi = \frac{7e^2}{R} - 8e^2\left\{\int_0^R X_{21}^2(r)\frac{r^2}{R}\,dr + \int_R^\infty X_{21}^2(r)\frac{r^2}{r}\,dr\right\}, \qquad (36)$$

assuming that the fluoride ion is not deformed by the hydrogen ion. The first term in Φ is due to the nucleus and the K electrons, with a charge of $7e$, and the second term to the eight L electrons. For equilibrium we have the condition

$$\left(\frac{d\Phi}{dR}\right)_{R=R_0} = -\frac{7e^2}{R_0^2} + \frac{8e^2}{R_0^2}\int_0^{R_0} X_{21}^2(r)\,r^2\,dr = 0, \qquad (37)$$

---

* Used principally in the United States, by Wyckoff, Dickinson, etc.

† This was remarked by Unsöld, ' Dissertation,' Munich, 1927.

with the simple interpretation that the number of electrons within the radius R_0 is Z, so that the repulsive force of the nucleus on the hydrogen ion just balances the attractive force of an equivalent number of electrons.

The solution of this equation is $R_0 = 0 \cdot 91$ Å, in deceptively good agreement with the band spectra value given in Table IX. For there are two important considerations which must be introduced in the more detailed treatment of interatomic forces, and which in this case apparently effectively neutralise each other. Our evaluation of the electron distribution provides only an approximation to that corresponding to a "penetrating orbit," so that the average electron-nucleus distance $\bar{r}$ is correctly given, but for large values of r the electron density is given a smaller value than the actual one. This effect, if taken into consideration, would increase the repulsive force at large values of R, and would tend to give a larger value of R_0. But the deforming action of the hydrogen ion on the fluoride ion must also be taken into account. This can be thought of as the polarisation of the fluoride ion in the field of the positive ion, resulting in an attractive force between the two ions of amount $2\alpha e^2/R_0^5$, if the polarisability α be assumed constant. The potential of this term, introduced in equation (37), would tend to decrease the value of R_0. The higher order effects, induced quadrupole, etc., moments, also in reality are of importance.

Table IX.—Internuclear Distances in the Hydrogen Halides.

——	Theoretical.	Experimental.*
	Å	Å
HF	0·91	0·92
HCl	1·55	1·265, 1·28
HBr	2·12	1·407

* The experimental figures, with one exception, were obtained from oscillation-rotation spectra with the use of integral rotational quantum numbers by Kratzer, 'Z. f. Physik,' vol. 3, p. 289 (1920). The second figure for hydrogen chloride was calculated by Colby, 'Astrophys. Journ.,' vol. 58, p. 303 (1923), from the same data, with the use of half quantum numbers, and by Czerny, 'Z. f. Physik,' vol. 34, p. 227 (1925), from pure rotation spectra with half quantum numbers.

The values of R_0 similarly calculated for hydrogen chloride and hydrogen bromide, with the substitution of $X_{31}(r)$ and $X_{41}(r)$ for $X_{21}(r)$ in equation (37), are somewhat larger than the experimental ones. This indicates that the deforming effect of the hydrogen ion on the halide ions is of greater relative importance for these ions than for the fluoride ion.

A similar procedure can be used in predicting interatomic distances in ionic crystals, by evaluating the potential energy of a three-dimensional array of undeformed ions, and determining the condition that this be a minimum. Such a procedure leads to interatomic distances of the order of magnitude of the actual ones ; because of the approximate nature of our determination of the electron distribution it is not worth while to carry out accurately the lengthy calculations involved.

VIII.—*Conclusion.*

The general method followed in this paper is capable of refinements which should make possible the accurate prediction of the properties of any atom or ion. The most obvious one is the use of the wave mechanics in determining the state of an electron under the influence of a positive nucleus and several idealised electron shells. Explicit expressions for the properties of an electron in such a state may then be derived, eliminating the necessity of the more or less inaccurate adaptation of the equations obtained for hydrogen-like atoms. Further progress may also be made in approximating an electron shell more closely than is possible with a spherical surface charge. All of these refinements will greatly complicate the treatment, however ; and while without doubt they will sooner or later be introduced, the relatively simple, if less exact, procedure which we have used suffices to show the general applicability of the method, and to provide approximate values of the physical properties of ions which may not exist under conditions permitting experimental investigation. The usefulness of these values in the consideration of the structure of molecules and of crystals will be illustrated elsewhere.

I wish to express my sincere thanks to Prof. A. Sommerfeld, from whose Seminar much of the inspiration for this research was obtained. I am also indebted to the John Simon Guggenheim Memorial Foundation and to the California Institute of Technology for providing the opportunity for its prosecution.

[*Added February* 10, 1927.—J. H. Van Vleck in ' Proc. Nat. Acad. America,' vol. 12, p. 662 (December, 1926), has discussed the mole refraction and the diamagnetic susceptibility of hydrogen-like atoms with the use of the wave mechanics, obtaining results identical with our equations (24) and (34). He also considered the effect of the relativity corrections (which is equivalent to the effect of a central field) and concluded that equation (24), derived by the use of parabolic instead of spherical co-ordinates, is not invalidated.]

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Screening Constants for Many-electron Atoms. The Calculation and Interpretation of X-ray Term Values, and the Calculation of Atomic Scattering Factors

By

Linus Pauling and J. Sherman

With 10 figures

1932
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Screening Constants for Many-electron Atoms. The Calculation and Interpretation of X-ray Term Values, and the Calculation of Atomic Scattering Factors.

By

Linus Pauling and **J. Sherman** in Pasadena.

(With 10 figures.)

The problem of the theoretical discussion of the properties of many-electron atoms and ions is a troublesome one, for it involves in every case a decision as to the extent to which rigor and accuracy are to be sacrificed to convenience. An accurate treatment of some properties of light atoms can be carried through. Thus Hylleraas[1]) has evaluated the energy of normal helium with great accuracy, and of other states with somewhat less accuracy, and the calculation of the polarizability of helium has also been reported[2]). But the methods used cannot be extended to heavy atoms because of the labor involved. The Thomas-Fermi[3]) atom is so simplified that it often does not give sufficient accuracy. Hartree's theory of the selfconsistent field[4]) gives the best values we have for electron distributions in heavy atoms; but this treatment is also very laborious, so that in the four years which have elapsed since it was originated only a few atoms have been treated, and, moreover, the discussion of every new property requires carrying out numerical or graphical calculations.

Moseley[5]), in his paper on the high-frequency spectra of the elements, expressed the frequencies of the K-lines which he had measured by the approximate equation

$$\nu = \frac{3}{4} R (Z - 1)^2 = (Z - 1)^2 R \left(\frac{1}{1^2} - \frac{1}{2^2}\right).$$

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1) E. A. Hylleraas, Z. Physik **54**, 347. 1930; **65**, 209. 1930.

2) H. R. Hassé, Pr. Cambridge Phil. Soc. **26**, 542. 1930; J. C. Slater and J. G. Kirkwood, Physic. Rev. **37**, 682. 1931.

3) L. H. Thomas, Pr. Cambridge Phil. Soc. **23**, 542. 1927; E. Fermi, Z. Physik **48**, 73. 1928.

4) D. R. Hartree, Pr. Cambridge Phil. Soc. **24**, 89, 111. 1928.

5) H. G. J. Moseley, Phil. Mag. **26**, 1024. 1913.

In this equation, closely resembling the equation giving the frequencies of spectral lines of hydrogen-like atoms, the presence in the atom of electrons other than the emitting electron is taken into account by the use of a screening constant, here given the value 1. In further developing the theory of X-ray spectra Sommerfeld made continued use of the same procedure. He showed that the separations of the spin doublets were very well represented by his relativistic fine-structure equation for hydrogen-like atoms when suitable screening constants σ_2, independent of the atomic number, were introduced, and also pointed out that the main energy term could be similarly expressed, although the corresponding screening constants are not independent of the atomic number. A similar procedure was applied in the optical region with great success by Millikan and Bowen in their study of stripped atom spectra.

The simplicity of the calculation of the value of a physical property of a many-electron atom by this method is a strong argument in its favor. The theoretical discussion of most atomic phenomena is usually carried through first for hydrogen-like atoms, and often it is very difficult to extend the equations rigorously to atoms containing more than one electron. It would be pleasant if we could construct a single set of screening constants which on introduction in the appropriate hydrogen-like equation would deliver approximately correct values for any physical property of a many-electron atom. This possibility was eliminated, however, by Sommerfeld's early discovery[1]) that different screening constants must be used for different properties.

Five years ago one of us developed an approximate method for calculating screening constants, which was found to give values of the spin-doublet screening constant σ_2 in quite good agreement with those observed[2]). This led to the application of the same treatment in the discussion of other physical properties, the mole refraction, diamagnetic susceptibility, and sizes of a large number of atoms and ions[3]). It was found that the calculated screening constants for K and L electrons agreed well with experiment, but that for the succeeding shells there were increasingly large discrepancies arising from the approximations introduced in the theory. Of much greater importance than the calculation of individual screening constants was the discovery of a simple relation among the screening constants for various physical properties. This makes possible the construction of a single set of standard screening con-

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[1]) A. Sommerfeld, Ann. Physik **51**, 125. 1916.

[2]) Linus Pauling, Z. Physik **40**, 344. 1926.

[3]) Linus Pauling, Pr. Roy. Soc. (A) **114**, 181. 1927.

stants, from which there can be easily obtained screening constants suitable for the discussion of any physical property of a large class, namely, those properties dependent mainly on the behaviour of the electrons in the outer parts of their orbits. In the following sections there is described such a standard set, obtained partially from theory, but mainly from empirical mole-refraction values and X-ray term values. It is shown that these constants lead to the complete interpretation of X-ray term values and optical ionization potentials. It is also found empirically that screening constants for an electron in a penetrating orbit are independent of the atomic number Z only as long as Z is so small as not to produce a large spin-relativity perturbation of the orbits of the electrons in the penetrated shells. The subsequent increase in their values is explained as resulting from the spin-relativity perturbation. In illustration of the use of the screening constants, a complete set of F-values, atomic scattering factors for X-rays, for atoms and ions is calculated with their aid.

There has recently been a recrudescence of interest in screening constants. Guillemin, Zener, and Eckart[1]) have applied variation methods to the wave equation to obtain approximate eigenfunctions for light atoms, in which screening constants occur as parameters, and Slater[2]) has suggested an empirical set of screening constants to be used in calculating various physical properties.

The Derivation of the Screening Constants.

The first set of screening constants was obtained from the discussion of the motion of an electron in the field of the nucleus and its surrounding electron shells, idealized as electrical charges uniformly distributed over spherical surfaces of suitably chosen radii. This idealization of electron shells was first used by Schrödinger[3]), and later by Heisenberg[4]) and Unsöld[5]), who pointed out that it is justified to a considerable extent by the quantum mechanics. The radius of a shell of electrons with principal quantum number n_i is taken as

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1) V. Guillemin and C. Zener, Z. Physik **61**, 199. 1930; C. Zener, Physic. Rev. **36**, 50. 1930; C. Eckart, ibid. **36**, 878. 1930.

2) J. C. Slater, ibid. **36**, 57. 1930.

3) E. Schrödinger, Z. Physik **4**, 347. 1921.

4) W. Heisenberg, Z. Physik **39**, 499. 1926.

5) A. Unsöld, Ann. Physik **82**, 355. 1927.

$$\bar{r} = \int r\,\Psi\Psi^* d\tau = \gamma_i\,\frac{a_0 n_i^2}{Z} \tag{1}$$

with

$$\gamma_i = 1 + \frac{1}{2}\left\{1 - \frac{l_i(l_i+1)}{n_i^2}\right\}. \tag{2}$$

According to the old quantum theory, the orbit of an electron moving in such a field consists of a number of elliptical segments. Each segment can be characterized by a segmentary quantum number n_i, in addition to the azimuthal quantum number k, which is the same for all segments. In all cases it is found that about half of the entire orbit lies in the outermost (${}_j{}^{\mathrm{th}}$) region.

Now many physical properties depend mainly on the behaviour of the electron in the outer part of its orbit. As an example we may mention the mole refraction or polarizability of an atom, which arises from deformation of the orbit in an external field. This deformation is greatest where the ratio of external field strength to atomic field strength is greatest; that is, in the outer part of the orbit. Let us consider such a property which for hydrogen-like atoms is found to vary with $n^r Z^{-t}$. Then a screening constant for this property would be such that

$$\text{const.}\ n_j^r Z_j^{-t} = \text{const.}\ n^r (Z - S)^{-t}.$$

It was found on expansion in powers of $\frac{z_i}{Z}$1), neglecting all terms beyond the first, that

$$S = \sum_i z_i - \frac{r}{t}\sum_i z_i D_i \tag{3}$$

in which D_i, which is called the unit screening defect for an electron in the i^{th} shell, is given by the equation

$$D_i = \frac{1}{\pi}\{\beta_i u_i + (1+\beta_i)\,\varepsilon \sin u_i\} - \beta_i \tag{4}$$

with

$$1 + \varepsilon \cos u_i = \frac{\gamma_i n_i^2}{n^2},$$

and

$$\beta_i = \frac{n^2}{\gamma_i n_i^2} - 1.$$

From equation 3 it is seen that the total screening defect, that is, the difference between the number of screening electrons (those with principal quantum number equal to or less than that of the electron under consideration) and the screening constant, is proportional to $\frac{r}{t}$. For

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1) z_i is the number of electrons in the i^{th} shell.

example, for a $1s$ electron screened by another $1s$ electron D_i is equal to 0.406. Now the energy of a penetrating electron is $Rh\,\frac{z_j^2}{n_j^2} = \frac{Rh(Z-S_E)^2}{n^2}$, so that S_E is given by equation (3) with $\frac{r}{t} = 1$. Hence S_E for a $1s$ electron is 0.594. The mole refraction is dependent essentially on n^6/Z^4, so that $\frac{r}{t} = 3/2$, and $S_R = 0.391$. The value of $\bar{r}$, that is, the size of the orbit, varies with n^2/Z, so that S_s, the size screening constant, is equal to 0.188. This shows how great the range of variation of screening constants for various properties is. It is probable that the relation found among the various screening constants holds with considerable accuracy even when the expression found for D_i is no longer accurate.

In the previous publication it was shown that the calculated screening constants for K and L electrons are in good agreement with the observed mole refraction values for helium and neon, so that in these cases the theory may be accepted as accurate. This result is not surprising. The idealization of electron shells as spherical surface charges is a reasonably good one for the inner electrons, as can be seen from their electron distribution functions, and the quantization of the orbit of the penetrating electron by the rules of the old quantum theory with the substitution of $\sqrt{l(l+1)}$ in place of the azimuthal quantum number k is also expected to give results closely approximating those which would be obtained from the quantum mechanics. For M, N, and O electrons the calculated screening constants are found on comparison with experiment to be too small, the error increasing in this order. This probably is due largely to the fact that the spherical-shell model is too strongly idealized for the outer electrons, whose distribution function does not show the rather sharp maximum of the inner shells. Accordingly for these electrons recourse must be made to empirical screening constants in constructing a standard set. The procedure followed is described in the next section.

The Screening Constants and their Use.

In fig. 1 and table I there are given size screening constants (with $\frac{r}{t}$ in equation 3 equal to 2) for all electrons in all neutral atoms. For K and L electrons the values given are the theoretical ones[1]. For M. N, and O electrons in atoms with rare-gas configurations the values given are those obtained from the measured mole refraction of argon, krypton,

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[1] A small numerical error in the values for $2s$ is corrected.

Table I.
Size Screening Constants[1]).

		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	6s	6p	6d	7s
H	1	0																
He	2	0.19																
Li	3		1.25															
B	5			2.50														
Ne	10		3.10	4.57														
Na	11				6.6													
Al	13					8.7												
Ar	18				9.1	10.9												
K	19							13.4										
Ca	20				9.1	10.9		13.9										
Sc	21						14.7											
Zn	30				10.9	13.2	17.7	21.5										
Ga	31								24.4									
Kr	36							24.2	26.6									
Rb	37											30.4						
Sr	38							24.2	26.6			30.8						
Y	39									31.8		31.3						
Cd	48							25.6	28.4	34.0		37.0						
In	49												39.4					
Xe	54											38.8	41.8					
Cs	55														47			
Ba	56											38.8	41.8		47.4			
La	57							25.6	28.4	34.0				48.6	48			
Ce	58										43.0							
Lu	71							29.4	32.8	39.6	49.8	47.8	51.4	59	62			
Hg	80											50	54	62	66			
Tl	81															71.0		
Rn	86														67	72		
—	87																	80
Ac	89																81.0	
U	92	0.19	3.10	4.57	10.9	13.2	17.7	29.4	32.8	39.6	49.8	50	54	62	68	73	82	82.4

and xenon with the use of the calculated *s*-*p* separations, as described in the previous paper[2]). These values are extrapolated to smaller values of *Z*, for incomplete 8-shells, with the aid of the theoretical values. For 3*s*, 3*p*, and 3*d* in completed 18-shells the values obtained from the mole refraction of Zn^{++} with the calculated separations are retained. For 4*s*, 4*p*, 4*d* and 5*s*, 5*p*, 5*d* in 18-shells it was found from X-ray term

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[1]) Screening constants for an atom not included in the table are to be obtained by linear interpolation. Thus S_s for a 2*p* electron for *C*, $Z = 6$, is $2.50 + \frac{1}{5}$ (4.57—2.50) = 2.91. [2]) See note 3, p. 2.

Table Ia.

Electron Configurations of Atoms.

		1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*	4*d*	4*f*	5*s*	5*p*	5*d*	6*s*	6*p*	6*d*	7*s*
H	1	1																
He	2	2																
Li	3		1															
B	5		2	1														
Ne	10		2	6														
Na	11				1													
Al	13				2	1												
Ar	18				2	6												
K	19				2	6		1										
Ca	20				2	6		2										
Sc	21				2	6	1	2										
Zn	30				2	6	10	2										
Ga	31							2	1									
Kr	36							2	6									
Rb	37							2	6			1						
Sr	38							2	6			2						
Y	39							2	6	1		2						
Cd	48							2	6	10		2						
In	49							2	6	10		2	1					
Xe	54							2	6	10		2	6					
Cs	55							2	6	10		2	6		1			
Ba	56							2	6	10		2	6		2			
La	57							2	6	10		2	6	1	2			
Ce	58							2	6	10	1	2	6	1	2			
Lu	71							2	6	10	14	2	6	1	2			
Hg	80											2	6	10	2			
Tl	81														2	1		
Rn	86														2	6		
—	87														2	6		1
Ra	88														2	6		2
Ac	89														2	6	1	2
U	92	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	4	2

values (next section) that the calculated separations were somewhat too small, and so revised values are used, which, however, are in pretty good agreement with the observed mole refractions of 18-shell ions. The values given for 4*s*, 4*p*, 4*d*, and 4*f* in the completed shell are from X-ray term values, while those for 6*s*, 6*p*, 6*d*, and 7*s* are estimated. The electron configurations assumed (which differ slightly in some cases from those for the normal states of the neutral atoms) are given in table I a.

The screening constants for neutral atoms are constant so long as no additional screening electrons are introduced, as is strikingly shown by the energy screening constant for X-ray term values. But this constancy results in part from contributions of external electrons. It was found in the discussion of mole refraction of 8-shell atoms and ions that in an iso-electronic sequence the screening constant is in general a function of the atomic number, so that it can be written

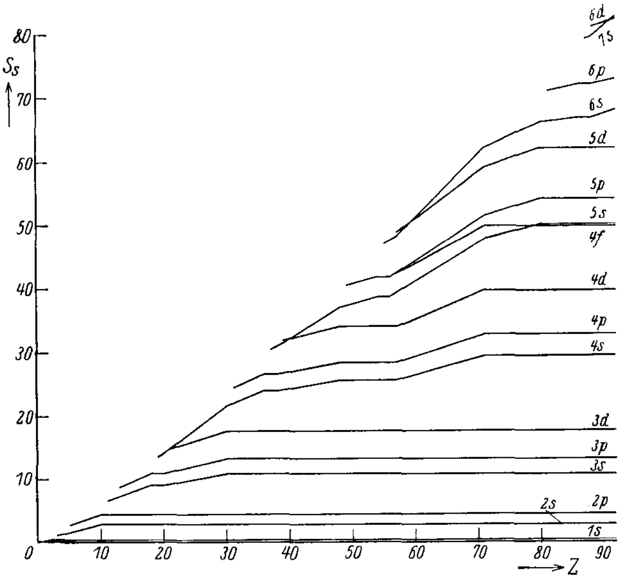

Fig. 1. Size screening constants S_S as functions of the atomic number Z.

$$S = S_0 - (Z - Z_0)\Delta S \tag{5}$$

in which S_0 is the value for the neutral atom with this configuration (and the atomic number Z_0), and ΔS has the values given in table II (for the size screening constant). This expression is to be

Table II.

The Size Screening Constant Correction for Ions.

Ion-type	Shell	Z_0		Ion-type	Z_0	Shell	
Ne	*L*	10	0.00				
Ar	*M*	18	0.07	Cu^+	28	*M*	0.07
Kr	*N*	36	0.25	Ag^+	46	*N*	0.30
Xe	*O*	54	0.50	Au^+	78	*O*	0.60
Rn	*P*	86	0.60				

used in obtaining screening constants for the outer electrons in ions. It is evident that it cannot hold when $Z—Z_0$ becomes very large, but is probably valid for actually occurring ions.

From this set of standard size screening constants it is possible to obtain screening constants for any atom or ion for any property dependent mainly on the behaviour of the electrons in the outer parts of their orbits. The constants can probably be trusted to be accurate to within about 10% of the quantum defect, for example, S_s values for M levels to within ± 1. In case that empirical data are available for some atoms or ions of a sequence it is well to use them to correct the screening constants.

Ionization Potentials and X-ray Term Values.

The energy of removal of an electron from an atom can be expressed in two ways by means of screening constants, either by taking the difference of $\sum_{i=1}^{n} \frac{(Z-S_i)^2}{n_i^2}$ for the neutral atom and $\sum_{i=1}^{n-1} \frac{(Z-S_i)^2}{n_i^2}$ for the ion, or by simply writing $I = \frac{(Z-S_E)^2}{n^2}$. The first of these methods, involving more arbitrary parameters, can be made more accurate, and, indeed, it seems in general to provide somewhat better values for the energy of removal of outer electrons than the second method. The two treatments give the same result for inner electrons, and for outer electrons in highly charged ions, in which cases the energy of rearrangement of the remaining electrons is negligible.

The energy of removal of an outer electron in a penetrating orbit is found with our treatment to be

$$I = \frac{(Z-S_E)^2}{n^2} \tag{6}$$

in Rydberg units of 13.53 Volt-electrons, in which S_E is given by equation 3 with $\frac{r}{t} = 1$. In table III there are given the experimental values of S_E for the removal of L electrons for various electron configurations of the atoms from Li to Si, together with the calculated values of S_E. Values of $Z—S_E$ are also plotted in figure 2. It is seen that in almost every sequence the empirical values approach the theoretical one asymptotically. This is strikingly shown by the six lithium-like ions and the five neon-like ions. Furthermore, for initial configurations with from one to five L electrons the empirical values are all in good agreement with the theoretical Moseley straight lines, but for more electrons there is pronounced deviation

Table III.
Values of the Energy Screening Constant S_E from Ionization Potentials.

Type of Ionization	Atom												Theoretical Values of S_E
	Li	*Be*	*B*	*C*	*N*	*O*	*F*	*Ne*	*Na*	*Mg*	*Al*	*Si*	
2s from $1s^2\,2s$	1.740	1.684	1.658	1.644	1.637	1.633							1.626
2s from $1s^2\,2s^2$		2.323	2.327	2.334									2.319
2p from $1s^2\,2s^2\,2p$			3.43	3.32	3.26	3.23							3.244
2p from $1s^2\,2s^2\,2p^2$				4.17	4.04	3.97							3.952
2p from $1s^2\,2s^2\,2p^3$					4.93	4.78							4.660
2p from $1s^2\,2s^2\,2p^4$						6.00	5.91						5.368
2p from $1s^2\,2s^2\,2p^5$							6.76	6.52					6.076
2p from $1s^2\,2s^2\,2p^6$								7.48	7.27	7.10	7.00	6.92	6.784

except for large *Z*. This deviation is to be attributed to the effect of the resultant spin as determined by Pauli's principle; when one electron is removed from a configuration with more than five *L* electrons, the multiplicity is increased instead of decreased.

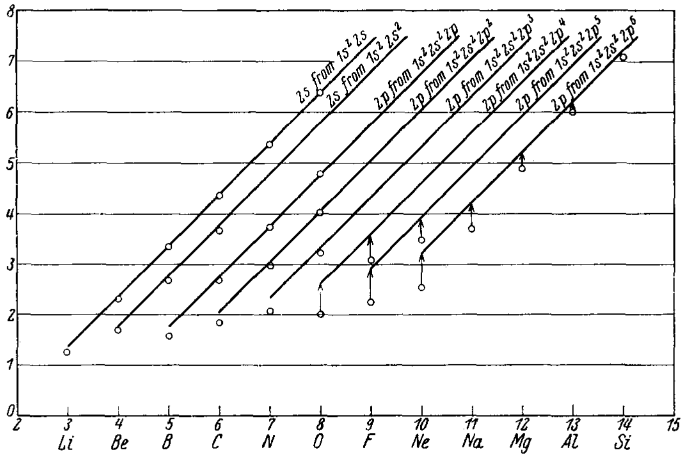

Fig. 2. Moseley diagrams for the energy of removal of an outer 2s or 2p electron. The straight lines give the theoretical values for large *Z*, the circles experimental values.

It has been shown[1]) that a similar treatment can be applied in the interpretation of X-ray term values by correcting for external screening with the aid of size screening constants. After correcting for the spin

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1) L. Pauling and S. Goudsmit, "The Structure of Line Spectra". McGraw-Hill Book Co., New York, **1930**, pp. 187—191.

and relativity effects, the energy of removal of an inner electron from an atom may be written as

$$W = \frac{Rhc(Z-\sigma_1)^2}{n^2} = \frac{Rhc(Z-\sigma_0)^2}{n^2} - \sum_i \frac{z_i e^2}{\varrho_i a_0}, \tag{7}$$

in which σ_0 is equal to the energy screening constant S_E and the indicated summation is over the outer shells of electrons, each involving z_i electrons at an averate distance from the nucleus of ϱa_0. The customarily tabulated screening constant σ_1 is related to σ_0 by the equation

$$(Z-\sigma_1)^2 = (Z-\sigma_0)^2 - 2n^2 \sum_i \frac{z_i}{\varrho_i}. \tag{8}$$

$\varrho_i a_0$ is to be chosen in such a way as to give the right average value to $\frac{1}{r_i}$; that is

$$\frac{1}{\varrho_i a_0} = \overline{\left(\frac{1}{r_i}\right)}.$$

For hydrogen-like states we have

$$\overline{\left(\frac{1}{r}\right)} = \frac{Z}{a_0 n^2},$$

so that from equation (3) we must place

$$\varrho_i = \frac{n_i^2}{Z - S_{S_i}}, \tag{9}$$

in which S_{s_i} is the size screening constant. Using the values of S_s given earlier, it was shown that the correction for external screening converts the empirical values of σ_1 which vary rapidly with Z into values of σ_0 which are effectively independent of Z.

But the relation between S_E and S_S given by equation (3) makes it possible to evaluate a complete set of screening constants from X-ray and optical term values alone. In view of the accuracy with which these term values can be measured and the completeness of the information they provide relative to all the electrons in all atoms, this method of obtaining screening constants must be considered as particularly valuable. The method of deriving the set is the following, illustrated with xenon. From the ionization potentials values of S_E for $5s$ and $5p$ are calculated by equation (6), and from them values of S_S. These are used in calculating S_E $(=\sigma_0)$ for $4s$, $4p$, and $4d$ from the empirical values of σ_1 given by the X-ray data for the N levels, using equations (8) and (9). The process is then repeated for the M, L, and K shells successively.

This treatment has not been systematically applied in constructing table I because of the lack of completeness of the X-ray term tables. It was accordingly necessary to assume a set of screening constants and test it by subsequent comparison of assumed and empirical S_E values. The empirical values of σ_1 are given in a figure on p. 460 of Sommerfeld's "Atombau und Spektrallinien," 4th edition. Their behaviour with changing Z is such as to make it absurd to call them screening constants. When the correction for external screening is made with the S_S values of table I, there result values of σ_0 which are practically independent of Z except when additional electrons are being introduced into inner shells. These σ_0 values are, moreover, in excellent general agreement with the S_E values obtained from table I by the use of equation (3), as is seen from figure 3.

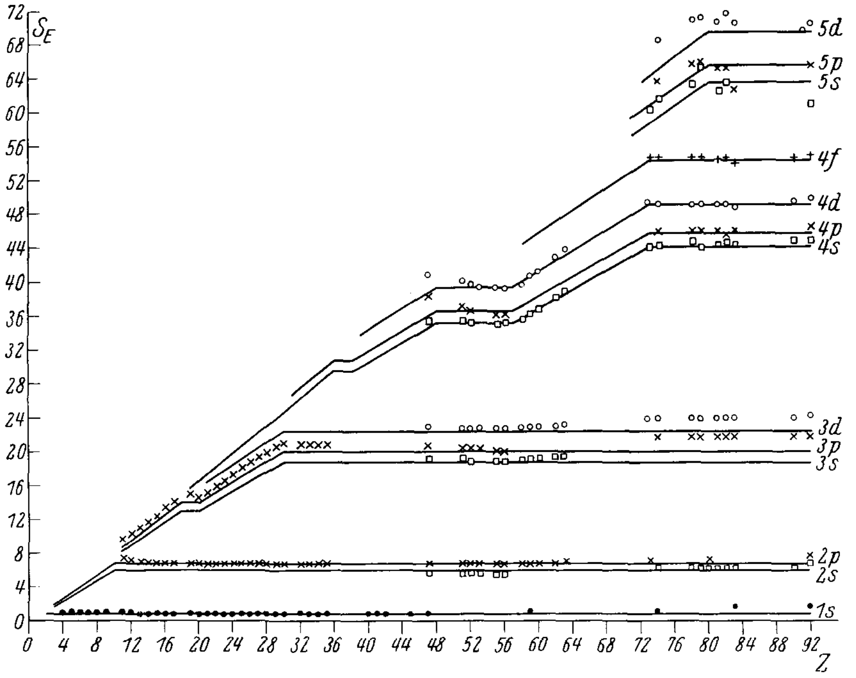

Fig. 3. Energy screening constants S_E as functions of the atomic number Z, compared with σ_0 values calculated from X-ray term values.

In this calculation use was made of the reduced X-ray term values given by Wentzel[1]) for elements above silver, and of the K, L, and M term values for light elements given by Mukherjee and Ray[2]), corrected

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[1]) G. Wentzel, Z. Physik 16, 46. 1923.

[2]) B. C. Mukherjee and B. B. Ray, Z. Physik 57, 345. 1929.

for fine structure with the use of the Sommerfeld equation. For K levels the fine-structure correction was made by inserting the value $\sigma_2 = 0.167$ in the expanded equation, using three terms for the heavier atoms.

It will be noticed from figure 3 and figure 4, in which σ_0 values for the $1s$ level are shown on a larger scale, that the σ_0 values agree well with S_E for light elements, but show an increasing deviation as the atomic number increases. This trend is found to be such that $\sigma_0 - S_E$ increases approximately with Z^3 or Z^4. This suggests at once that the spin-relativity correction has not been properly made; but on investigation it is found that this correction cannot be in error by an amount large enough to eliminate the trend in σ_0. Nor can the trend be due to error in the external screening correction, for even replacing the size screening constant S_S by the fine-structure screening constant σ_2, which is necessarily a safe lower limit for it, does not suffice to remove the trend. The explanation of the phenomenon is provided by the spin-relativity perturbations of the electron orbits, which cause all screening constants to be constants only for small values of Z, and then to increase with Z. The spin-relativity effect is for all electrons largest in the neighbourhood of the nucleus. As a result of this effect we expect an unusually large increase of the electron-density function $\psi\psi^*$ in the neighbourhood of the nucleus as Z increases, producing an extra ball of electricity near the nucleus, and hence increasing the screening constants for all electrons by about the same amount; and this increase should vary with Z^4. This expectation is

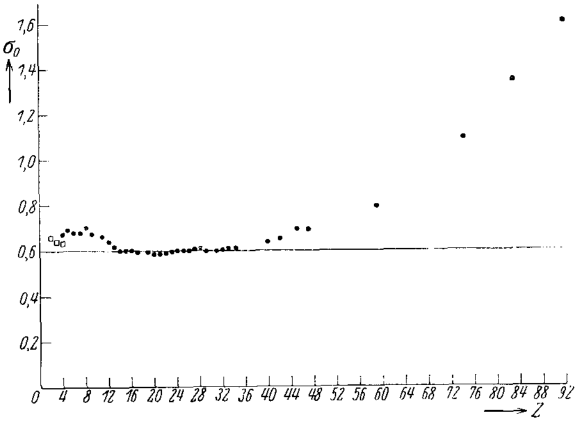

Fig. 4. Experimental σ_0 values. The circles are obtained from X-ray term values corrected for the spin-relativity effect and external screening, the squares from optical ionization potentials.

substantiated by the calculation of the electron distributions for 1*s* and 2*s* electrons according to Dirac's theory of the electron, using

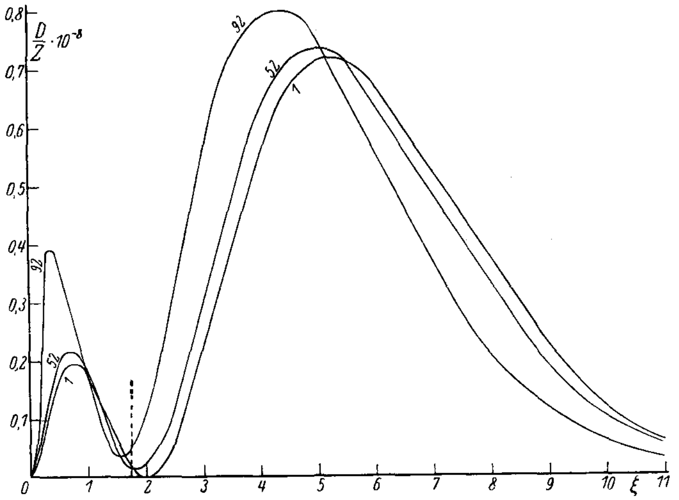

Fig. 5. The electron distribution function for a Dirac 2*s* electron in atoms with the indicated atomic numbers. The vertical broken line shows the position of $\bar{r}$ for a 1*s* electron.

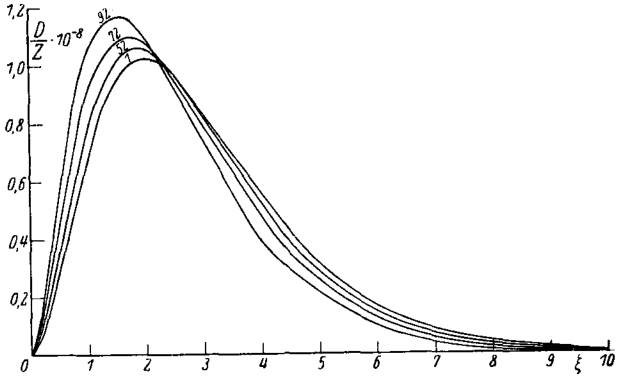

Fig. 6. The electron distribution function for a Dirac 1*s* electron in atoms with the indicated atomic numbers.

Gordon's complete solution¹) of Dirac's equations. It is seen from figures 5 and 6 that the spin-relativity effect brings the electrons closer to the nucleus. The effect is particularly pronounced for 2*s* electrons,

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1) W. Gordon, Z. Physik 48, 11. 1928. We are indebted to Mr. Sidney Weinbaum for the construction of figures 5 and 6.

in which case the small ball of electricity included within the first node of Schrödinger's eigenfunction is increased by about one-twentieth of an electron for $Z = 92$. This increase lies within the mean radius for $1s$ electrons, and so should be effective in increasing the $1s$ screening constants. It is probable that a similar and only slightly smaller concentration near the nucleus is shown also by the electrons in outer shells, so that the aggregate increase in the screening constant for $1s$ electrons may well reach the value 1 found empirically (increase from 0.6 to 1.6 for uranium). The effect should not be so pronounced for outer orbits, since these are already completely screened by certain inner shells, whose further concentration can have no influence.

This increase should be observed for all screening constants, and in particular for the Sommerfeld fine-structure screening constants. The constancy of s reported for the L-doublet throughout the periodic system ($s = 3.50 \pm 0.08$ from $Z = 41$ to $Z = 92$, Sommerfeld, "Atombau" pp. 447, 462) seems to contradict this. But actually this constancy proves the point. For s has been calculated with the complete formula,

$$\Delta\nu = R\left\{\frac{\alpha^2(Z-\sigma_2)^4}{2^4} + \frac{5\alpha^4(Z-\sigma_3)^6}{2^7} + \frac{53\alpha^6(Z-\sigma_4)^8}{2^{11}} + \dots\right\}, \qquad (10)$$

by giving σ_2, σ_3, σ_4, ... the same value s. But σ_3, σ_4, ..., which should have such values as to make $(Z - \sigma_3)^6$ equal to the mean value of $Z^6_{\text{effective}}$, are necessarily smaller than σ_2, since with increasing exponent the maximum values of $Z_{\text{effective}}$ become increasingly important. These higher terms are of considerable significance; for uranium $\frac{\Delta\nu_L}{R}$ is equal to 278, of which 75 is due to the higher terms. Accordingly Sommerfeld's values of s are actually mean values of σ_2 and σ_3, σ_4 ..., all of which are smaller than σ_2, and so decrease the mean. The values $\sigma_0 = 6.79$ and $\sigma_2 = 3.50$ suggest that σ_3, σ_4, ... are probably of the order of magnitude of 2. Assuming this value for uranium, it is found that the doublet separation leads to $\sigma_2 = 4.4$ instead of 3.5. Hence σ_2 also shows the spin-relativity increase, and the constancy of Sommerfeld's s is to be attributed to the fortuitous cancellation of this increase by the decrease produced by the inclusion in s of contributions by the smaller constants.

It is worthy of mention that the screening constants of table I and all those which can be derived from them satisfy an interval relation similar to that suggested for s by Sommerfeld; for a given total quantum number the intervals s—p, p—d, and d—f are in the ratios 1 : 2 : 3.

This relation is supported by the X-ray data as well as the theoretical calculations[1]).

F-Values for Hydrogen-like Eigenfunctions.

The scattering power of an electron distribution ϱ for the effective interplaner distance D given by the equation

$$\lambda = 2\,D \sin\,\Theta \tag{11}$$

or

$$D = \frac{d_{hkl}}{n} \tag{12}$$

is

$$F = \int\limits_0^\infty \int\limits_0^\pi \int\limits_0^{2\pi} \varrho\, e^{2\pi i \frac{r}{D} \cos\Theta}\, r^2\, dr \sin\Theta\, d\Theta\, d\Phi\,, \tag{13}$$

in which r, Θ, and Φ are polar coordinates. We wish to evaluate F when ϱ is the electron distribution corresponding to the Schrödinger eigenfunctions for a hydrogen-like atom: i. e., for

$$\varrho_{nlm} = \Psi_{nlm}\, \Psi^*_{nlm}. \tag{14}$$

Instead of evaluating F_{nlm} for the individual eigenfunctions, let us average over the eigenfunctions corresponding to a subgroup; namely, over the $2\,l + 1$ states with given n and l, and with $m = -l, -l+1, \ldots l-1, +l$. Since $\sum\limits_m \Psi_{nlm}\, \Psi^*_{nlm}$ is independent of Θ and Φ, the electron distribution for a completed subgroup has spherical symmetry. With $\varrho = \varrho\,(r)$, equation (13) can at once be integrated over Φ and Θ, giving

$$F_{nl} = 2\,D \int\limits_0^\infty \varrho_{nl}\,(r) \sin \frac{2\pi r}{D}\, r\, d\,r. \tag{15}$$

The averaged squared eigenfunction for a completed subgroup is

$$[\Psi_{nl}\,(r)]^2 = \frac{1}{2l+1} \sum_{m=-l}^{+l} \Psi_{nlm}\,(r, \Theta, \Phi)\, \Psi^*_{nml}\,(r, \Theta, \Phi)\,, \tag{16}$$

---

[1]) It may be mentioned that the neglect to take such an interval relation into consideration is the most pronounced defect of Slater's empirical set of screening constants (just as the arbitrary equating of the corresponding constant δ for $2\,s$ and $2\,p$ eigenfunctions is the most unsatisfactory part of Zener's variation treatment of the wave equation for light atoms). Thus Slater's screening constants for $3\,s$, $3\,p$, and $3\,d$ for an atom with completed K, L, and M shells are 11.6, 11.6, and 18, which may be compared with our values of 10.9, 13.2, and 17.7; the corresponding interval ratios p—s, d—p are 0:6.4 and 2.3:4.5. The effects of this unsatisfactory treatment of the *spdf* sequence can be observed throughout Slater's discussion of applications of his screening constants.

with the value

$$\overline{\Psi}_{nl}(r) = \frac{1}{\sqrt{2\pi}}\left\{\frac{(2\gamma)^{l+1}}{(n+l)!}\left(\frac{\gamma(n-l-1)!}{n(n+l)!}\right)^{\frac{1}{2}}\right\} e^{-\gamma r} r^{l} L_{n+l}^{2l+1}(2\gamma r), \tag{17}$$

in which

$$\gamma = \frac{4\pi^2 \mu e^2 Z}{n^2 h^2} = \frac{Z}{n a_0}, \tag{18}$$

with $a_0 = 0.529$ Å. The symbols are the customary ones (μ mass of electron, etc.).

$L_{n+l}^{2l+1}(2\gamma r)$ is an associated Laguerre polynomial, defined by the identity[1])

$$\sum_{\beta=0}^{\infty} \frac{L_{\alpha+\beta}^{\alpha}(\xi)}{(\alpha+\beta)!} u^{\beta} \equiv (-)^{\alpha} \frac{e^{\frac{-\xi u}{1-u}}}{(1-u)^{\alpha+1}}. \tag{19}$$

We are interested in integrating equation (15) with $\varrho_{nl}(r) = [\overline{\Psi}_{nl}(r)]^2$. It is convenient, however, to consider a more general class of integrals, in which

$$\varrho(r) = \varrho_{n_1 n_2 l}(r) = \overline{\Psi}_{n_1 l}(r)\,\overline{\Psi}_{n_2 l}(r). \tag{20}$$

Substituting this in equation (15), we obtain

$$F_{n_1 n_2 l} = \frac{D^{\frac{1}{2}}}{2}\left\{(2\gamma_1)^{l+1}\left(\frac{\gamma_1(n_1-l-1)!}{n_1(n_1+l)!}\right)^{\frac{1}{2}}\right\} \left\{(2\gamma_2)^{l+1}\left(\frac{\gamma_2(n_2-l-1)!}{n_2(n_2+l)!}\right)^{\frac{1}{2}}\right\} I_{n_1 n_2 l}(D), \tag{21}$$

in which γ_1 and γ_2 are given by equation (18) with $n = n_1$ and n_2 respectively, and $I_{n_1 n_2 l}(D)$ is the integral

$$I_{n_1 n_2 l}(D) = \int_0^{\infty} e^{-(\gamma_1+\gamma_2)r} \frac{L_{n_1+l}^{2l+1}(2\gamma_1 r)}{(n_1+l)!} \frac{L_{n_2+l}^{2l+1}(2\gamma_2 r)}{(n_2+l)!} J_{\frac{1}{2}}\left(\frac{2\pi r}{D}\right) r^{2l+\frac{3}{2}} dr. \tag{22}$$

In deriving this expression the factor $\sin\frac{2\pi r}{D}$ has been converted into a Bessel function of order $\frac{1}{2}$ by the known relation

$$\sin x = \sqrt{\frac{\pi x}{2}}\, J_{\frac{1}{2}}(x). \tag{23}$$

In order to evaluate the integrals $I_{n_1 n_2 l}(D)$ let us consider a function G defined by the identity

$$G = G_l(D, u, v) = \sum_{n_1=l+1}^{\infty} \sum_{n_2=l+1}^{\infty} I_{n_1 n_2 l}(D)\, u^{n_1-l-1} v^{n_2-l-1} \tag{24}$$

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1) E. Schrödinger, Ann. Physik 80, 484. 1926.

G is then a generating function for these integrals, which occur as coefficients in its expansion in powers of u and v; and it can be evaluated with the use of the generating function for the associated Laguerre polynomials, given in equation (19). Thus we have

$$G = \int_0^\infty e^{-(\gamma_1+\gamma_2)r} \sum_{n_1=l+1}^{\infty} \frac{L_{n_1+l}^{2l+1}(2\gamma_1 r)}{(n_1+l)!} u^{n_1-l-1} \sum_{n_2=l+1}^{\infty} \frac{L_{n_2+l}^{2l+1}(2\gamma_2 r)}{(n_2+l)!} v^{n_2-l-1}$$

$$\cdot J_{\frac{1}{2}}\left(\frac{2\pi r}{D}\right) r^{2l+\frac{3}{2}} dr = \int_0^\infty e^{-(\gamma_1+\gamma_2)r} \frac{(-)^{2l+1} e^{\frac{-2\gamma_1 r u}{1-u}}}{(1-u)^{2l+2}} \frac{(-)^{2l+1} e^{\frac{-2\gamma_2 r v}{1-v}}}{(1-v)^{2l+2}}$$

$$J_{\frac{1}{2}}\left(\frac{2\pi r}{D}\right) r^{2l+\frac{2}{3}} dr, \tag{25}$$

or, introducing the new variable

$$\zeta = \frac{Z}{a_0} r, \tag{26}$$

$$G = [(1-u)(1-v)]^{-2l-2} \left(\frac{a_0}{Z}\right)^{2l+\frac{5}{2}} \int_0^\infty e^{-\zeta\left[\frac{1}{n_1}\left(\frac{1+u}{1-u}\right)+\frac{1}{n_2}\left(\frac{1+v}{1-v}\right)\right]}$$

$$J_{\frac{1}{2}}\left(\frac{2\pi a_0}{ZD}\zeta\right) \zeta^{2l+\frac{3}{2}} d\zeta. \tag{27}$$

This last integral is a special case of a more general integral which has before been found useful in quantum mechanical problems[1]. It was shown by Hankel and Gegenbauer that

$$\int_0^\infty e^{-a\zeta} J_\nu(z\zeta)\, \zeta^{\mu-1} d\zeta = \frac{\left(\frac{z}{2a}\right)^\nu \Gamma(\mu+\nu)}{a^\mu \Gamma(\nu+1)}$$

$$F\left(\frac{\mu+\nu}{2}, \frac{\mu+\nu+1}{2}; \nu+1; -\frac{z^2}{a^2}\right), \tag{28}$$

where F denotes the hypergeometric function. Putting

$$a = \frac{1}{n_1}\left(\frac{1+u}{1-u}\right) + \frac{1}{n_2}\left(\frac{1+v}{1-v}\right), \quad \nu = \tfrac{1}{2}, \quad z = \frac{2\pi a_0}{ZD}, \quad \text{and } \mu = 2l + \tfrac{5}{2},$$

this gives

$$G = [(1-u)(1-v)]^{-2l-2} \left(\frac{a_0}{Z}\right)^{2l+\frac{5}{2}} \frac{z^{\frac{1}{2}} \Gamma(2l+3)}{2^{\frac{1}{2}} \Gamma(\frac{3}{2})\, a^{2l+3}} F\left(l+\tfrac{3}{2}, l+2; \tfrac{3}{2}; -\frac{z^2}{a^2}\right) \tag{29}$$

---

[1] B. Podolsky and Linus Pauling, Physic. Rev. **34**, 109. 1929.

the abbrevations z and a being retained for convenience. The hypergeometric series can be evaluated by the following method

$$\left.\begin{aligned} F\left(l+\tfrac{3}{2},\, l+2;\, \tfrac{3}{2};\, \frac{-z^2}{a^2}\right) &= 1-\frac{(l+\frac{3}{2})\,(l+2)}{1\cdot\frac{3}{2}}\,\frac{z^2}{a^2} \\ &\quad+\frac{(l+\frac{3}{2})\,(l+\frac{5}{2})\,(l+2)\,(l+3)}{1\cdot 2\cdot\frac{3}{2}\cdot\frac{5}{2}}\,\frac{z^4}{a^4}+\cdots \\ &= \sum_{t=0,2,4}^{\infty}\frac{(2l+2+t)!}{(2l+2)!\,(t+1)!}\left(\frac{iz}{a}\right)^t \\ &= \left(\frac{a}{iz}\right)\sum_{k=1,3,5,\ldots}^{\infty}\frac{(2l+2+k-1)!}{(2l+2)!\,k!}\left(\frac{iz}{a}\right)^k. \end{aligned}\right\} \tag{30}$$

Now the series given consists of just the alternate terms (the imaginary terms) in the expansion of $\left(1-\frac{iz}{a}\right)^{-2l-2}$. Hence we write

$$F\left(l+\tfrac{3}{2},\, l+2;\, \tfrac{3}{2};\, \frac{-z^2}{a^2}\right)=\frac{a}{z}\,\mathfrak{Im}\left[\left(1-\frac{iz}{a}\right)^{-2l-2}\right], \tag{31}$$

in which the symbol $\mathfrak{Im}$ means that only the imaginary part of the expression which follows it is to be retained. This leads to

$$G=\frac{D^{\frac{1}{2}}\,(2l+1)!}{\pi}\left(\frac{a_0}{Z}\right)^{2l+2}$$
$$\mathfrak{Im}\left[\left(\frac{(1+u)\,(1-v)}{n_1}+\frac{(1-u)\,(1+v)}{n_2}-iz\,(1-u)\,(1-v)\right)^{-2l-2}\right]. \tag{32}$$

The problem is now solved. To find the F-value for the electron distribution of equation (20) with given n_1, n_2, and l, it is necessary to expand the bracketed expression in equation (32), to collect the imaginary terms, and multiply the coefficient of $u^{n_1-l-1}\, v^{n_2-l-1}$ by the factors given in equations (32) and (21).

The easiest way to obtain the coefficient of $u^{n_1-l-1}\, v^{n_2-l-1}$ is to differentiate n_1-l-1 times with respect to u, and n_2-l-1 times with respect to v. This causes all terms of lower degree in each auxiliary variable to vanish. Then by placing u and v equal to zero all terms of higher degree vanish, and the desired coefficient remains, multiplied by $(n_1-l-1)!\;(n_2-l-1)!$.

We are interested in the terms with $n_1=n_2=n$. With the introduction of the new variable

$$x=\frac{n\pi a_0}{ZD}, \tag{33}$$

Equations (21) and (32) lead to

$$
\begin{aligned}
F_{n,l}(x) = {} & \frac{(2l+1)!}{2n(n+l)!\,(n-l-1)!} \\
& x^{-1}\,\mathfrak{Im}\left[\frac{\partial^{2n-2l-2}}{\partial u^{n-l-1}\,\partial v^{\cdot\, n-l-1}}\{1-uv-ix(1-u)(1-v)\}^{-2l-2}\right] \\
& u=0,\ v=0. \qquad (34)
\end{aligned}
$$

Carrying out the indicated operations, there is obtained

$$
\begin{aligned}
F_{n,l}(x) = {} & \frac{1}{(n-l-1)!\,2n\,(1+x^2)^{2n}}\,(C_1^{n-l-1}(1+x^2)^{n-l-1} \\
& - C_2^{n-l-1}(n+l+1)(1+x^2)^{n-l-2}x^2 \\
& + C_3^{n-l-1}(n+l+1)(n+l+2)(1+x^2)^{n-l-3}x^4 \ldots \qquad (35) \\
& \ldots + (-1)^{n-l-1}C_{n-l}^{n-l-1}(n+l+1)\ldots\ldots(2n-1)\,x^{2(n-l-1)}) \\
& \cdot x^{-1}\,\mathfrak{Im}\,(1+ix)^{2n},
\end{aligned}
$$

in which the coefficients C_r^{n-l-1} are numbers discussed later. The expression $(1+ix)^{2n}$ can now be expanded into a finite series and its imaginary part taken, with the result

$$
\begin{aligned}
x^{-1}\,\mathfrak{Im}\,(1+ix)^{2n} = {} & \binom{2n}{1} - \binom{2n}{3}x^2 + \binom{2n}{5}x^4 - \binom{2n}{7}x^6 + \ldots \\
& + (-)^{n+1}\binom{2n}{2n-1}x^{2n-2}, \qquad (36)
\end{aligned}
$$

in which $\binom{2n}{1}$ etc. are binomial coefficients.

We can accordingly write

$$
\begin{aligned}
F_{n,l}(x) = {} & \frac{1}{(n-l-1)!}\{C_1^{n-l-1}(1+x^2)^{n-l-1} \\
& - C_2^{n-l-1}(n+l+1)(1+x^2)^{n-l-2}x^2 \\
& + C_3^{n-l-1}(n+l+1)(n+l+2)(1+x^2)^{n-l-3}x^4 - \ldots \qquad (37) \\
& \ldots (-)^{n-l-1}C_{n-l}^{n-l-1}(n+l+1)\ldots(2n-1)\,x^{2(n-l-1)}\}\,F_{n,\,n-1}(x),
\end{aligned}
$$

in which

$$
\begin{aligned}
F_{n,n-1}(x) = {} & \frac{1}{2n\,(1+x^2)^{2n}}\left\{\binom{2n}{1} - \binom{2n}{3}x^2 + \ldots\right. \\
& \left. + (-)^{n+1}\binom{2n}{2n-1}x^{2n-2}\right\}. \qquad (37)
\end{aligned}
$$

A table of binomial coefficients is given below (table IV). The numbers C_r^{n-l-1}, resulting from the successive partial differentiations, are given in table V, which can easily be extended with the use of the recursion formula

$$C_r^{n-l-1} = C_{r-1}^{n-l-2} + (2r-1)\, C_r^{n-l-2} + r^2\, C_{r+1}^{n-l-2} \tag{38}$$

or by the expression

$$C_r^{n-l-1} = \left\{\frac{(n-l-1)!}{(r-1)!}\right\}^2 \cdot \frac{1}{(n-l-r-1)!}. \tag{39}$$

We are indebted to Professor R. T. Birge of the Physics Department of the University of California for the discovery of the last expression.

Table IV.

Binomial Coefficients $\binom{2n}{\nu}$.

	$\nu = 1$	3	5	7	9	11	13
$2n = 0$	1						
$2n = 2$	2						
$2n = 4$	4	4					
$2n = 6$	6	20	6				
$2n = 8$	8	56	56	8			
$2n = 10$	10	120	252	120	10		
$2n = 12$	12	220	792	792	220	12	
$2n = 14$	14	364	2002	3432	2002	364	14

Table V.

Coefficients C_r^{n-l-1}.

	$r = 1$	2	3	4	5	6	7	8	9
$n - l - 1 = 0$	1								
1	1	1							
2	2	4	1						
3	6	18	9	1					
4	24	96	72	16	1				
5	120	600	600	200	25	1			
6	720	4320	5400	2400	450	36	1		
7	5040	35280	52920	29400	7350	882	49	1	
8	40320	322560	564480	376320	117600	18816	1568	64	1

The Calculation of Atomic Scattering Factors.

Atomic scattering factors can now be calculated for any atom or ion by introducing in equation (37) the size screening constant for each electron as given in table I and summing over all electrons in the atom. Substitution of numerical values for the quantum numbers n and l in equation (37) gives the individual formulas of table VI. The seventeen functions corresponding to the eigenfunctions occupied in normal atoms were plotted on semi-log paper, with values of F as ordinates and of $\frac{1}{(Z-S_s)D}$ as logarithmic abscissae. This plot is reproduced in figure 7.

An inverse logarithmic scale was also constructed along the horizontal axis.

Table VI.

Formulas for F-values for hydrogen-like eigenfunctions

$$F_{1s} = \frac{1}{(1+x^2)^2}, \text{ with } x = \frac{n\pi a_0}{(Z-S_s)D}$$

$$F_{2p} = \frac{1-x^2}{(1+x^2)^4}. \quad F_{2s} = (1-2x^2)F_{2p}$$

$$F_{3d} = \frac{(1-3x^2)(3-x^2)}{3(1+x^2)^6}. \quad F_{3p} = (1-4x^2)F_{3d}. \quad F_{3s} = (1-6x^2+3x^4)F_{3d}$$

$$F_{4f} = \frac{(1-x^2)(1-6x^2+x^4)}{(1+x^2)^8}. \; F_{4d} = (1-6x^2)F_{4f}. \; F_{4p} = (1-10x^2+10x^4)F_{4f}$$

$$F_{4s} = (1-12x^2+18x^4-4x^6)F_{4f}$$

$$F_{5g} = \frac{(5-60x^2+126x^4-60x^6+5x^8)}{5(1+x^2)^{10}} \qquad F_{5f} = (1-8x^2)F_{5g}$$

$$F_{5d} = (1-14x^2+21x^4)F_{5g}$$

$$F_{5p} = (1-18x^2+45x^4-20x^6)F_{5g}$$

$$F_{5s} = (1-20x^2+60x^4-40x^6+5x^8)F_{5g}$$

$$F_{6h} = \frac{(1-x^2)(3-52x^2+146x^4-52x^6+3x^8)}{3(1+x^2)^{12}}$$

$$F_{6d} = (1-24x^2+84x^4-56x^6)F_{6h}$$

$$F_{6p} = (1-28x^2+126x^4-140x^6+35x^8)F_{6h}$$

$$F_{6s} = (1-30x^2+150x^4-200x^6+75x^8-6x^{10})F_{6h}$$

$$F_{7j} = \frac{(7-182x^2+1001x^4-1716x^6+1001x^8-182x^{10}+7x^{12})}{7(1+x^2)^{14}}$$

$$F_{7s} = (1-42x^2+315x^4-700x^6+525x^8-126x^{10}+7x^{12})F_{7j}$$

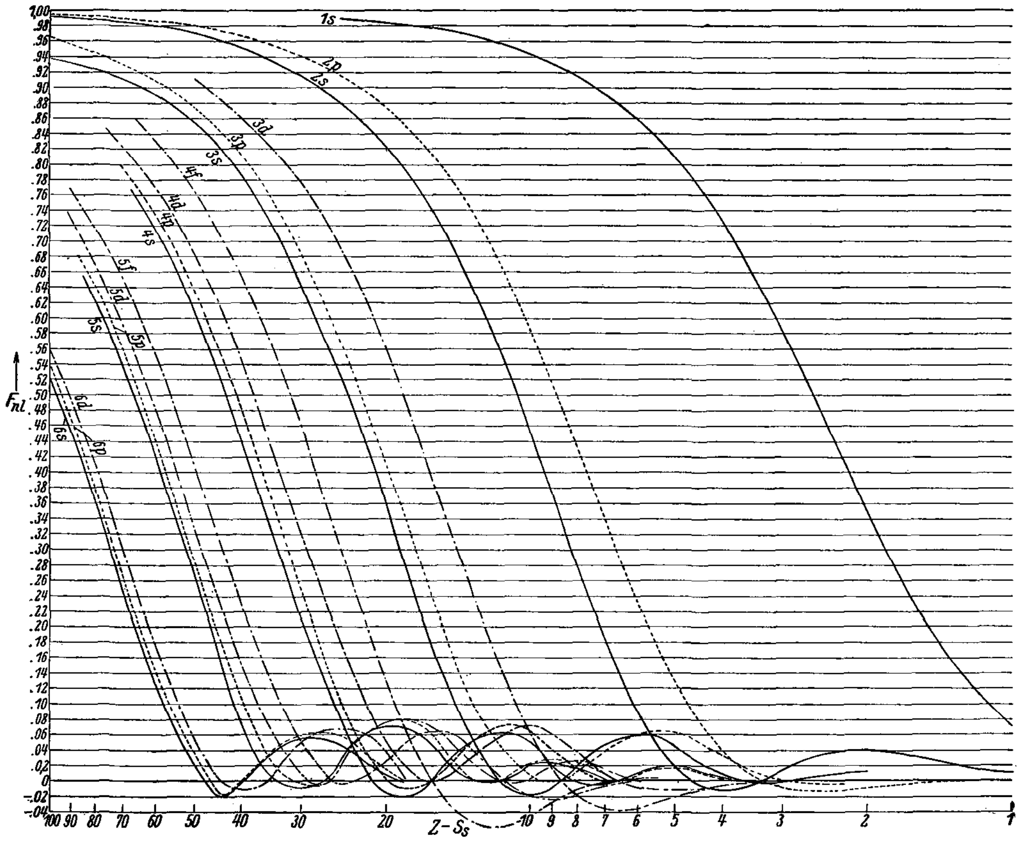

Fig. 7. F-values for hydrogen-like eigenfunctions.

With the aid of a movable template reproducing the horizontal scales, the values of F on a given curve for a given value of $Z—S_S$ and a series of values of D or of $\frac{\sin\Theta}{\lambda} = \frac{1}{2D}$ can be read from a single setting of the template, as is seen from the relation

$$\log\left(\frac{1}{(Z-S_s)D}\right) = -\log(Z-S_S) - \log D$$

$$= -\log(Z-S_S) + \log\frac{2\sin\Theta}{\lambda}. \tag{40}$$

If the template is used as an inverse logarithmic scale, and is set at a given value of $Z—S_S$ on the inverse scale of the graph, then values of D on the template give the abscissae of the corresponding values of $\frac{1}{(Z-S_s)D}$.

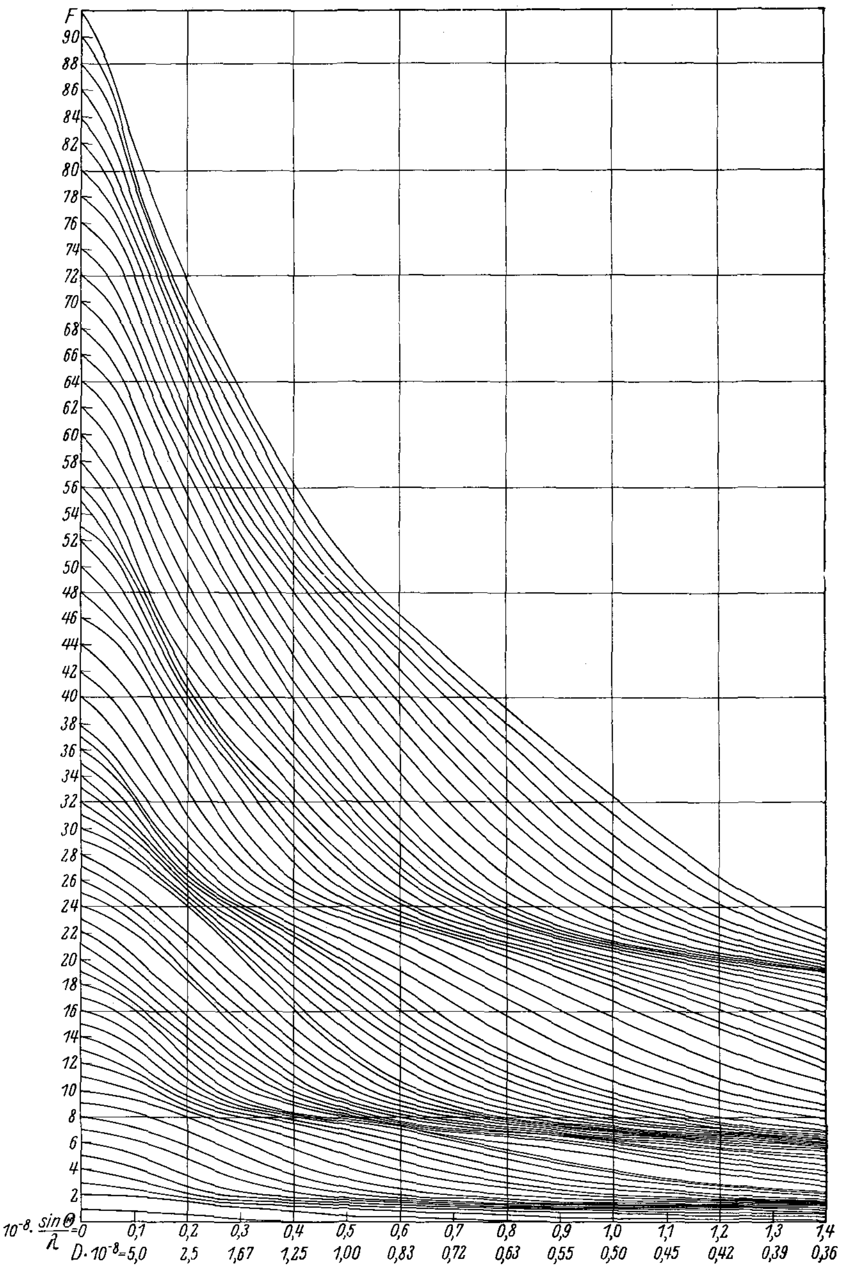

Fig. 8. F-values for neutral atoms.

If the template is used as a normal scale, and is set at a given value of Z—S_S on the inverse scale of the graph, then values of $\frac{2 \sin \Theta}{\lambda}$ on the template give the abscissae of the corresponding values of $\frac{1}{(Z - S_s) D}$.

Using the S_S values of table I, values of F for each electron in every atom from hydrogen to strontium and in every atom of even atomic number from strontium to uranium were obtained by this method for $10^8 \frac{\sin \Theta}{\lambda} = 0.0,\ 0.1,\ \ldots$ Atomic scattering factors were then found by taking the algebraic sum of the F-values for all electrons in the atom. These values are given in table VII, and are shown graphically in figure 8. Values of F similarly calculated for a number of ions are given in table VIII and figure 9.

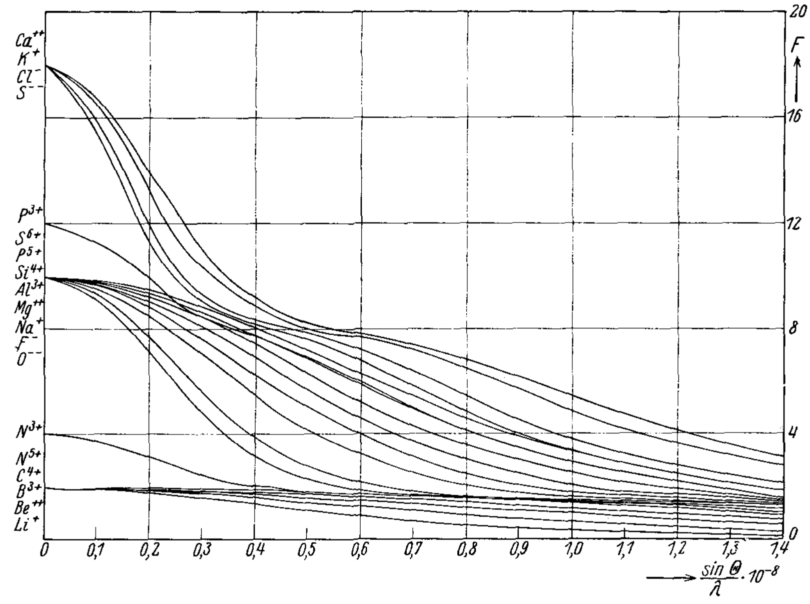

Fig. 9. F-values for ions.

These F-values are not so reliable as those calculated by Hartree's method. On the other hand, they are obtained with much less labor, Hartree's calculations having so far been carried out for only a small number of atoms. In figure 10 F-curves are shown for Li^+, Na^+, K^+, and Rb^+ as obtained by the method described in this paper, by Hartree's method and by the Thomas-Fermi method. It is seen that for all

Table VII. Scattering factors for atoms.

$\frac{\sin\theta}{\lambda}\cdot 10^{-8}$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4
H	1	0.81	0.48	0.25	0.13	0.07	0.04	0.03	0.02	0.01	0.01	0.00	0.00	0.00	0.00
He	2	1.86	1.55	1.17	0.84	0.54	0.40	0.29	0.21	0.15	0.12	0.09	0.07	0.05	0.04
Li	3	2.27	1.77	1.60	1.37	1.13	0.90	0.72	0.55	0.44	0.36	0.29	0.23	0.19	0.13
Be	4	3.19	2.10	1.73	1.61	1.48	1.31	1.13	0.94	0.82	0.68	0.57	0.48	0.41	0.34
B	5	4.16	2.73	1.96	1.69	1.59	1.49	1.39	1.26	1.11	0.97	0.87	0.75	0.65	0.57
C	6	5.21	3.62	2.42	1.86	1.66	1.57	1.51	1.42	1.32	1.21	1.10	0.99	0.89	0.79
N	7	6.32	4.76	3.26	2.33	1.86	1.65	1.55	1.50	1.43	1.36	1.27	1.17	1.09	0.99
O	8	7.36	5.82	4.14	2.90	2.19	1.80	1.63	1.54	1.49	1.44	1.38	1.31	1.23	1.15
F	9	8.42	6.95	5.17	3.66	2.69	2.10	1.77	1.61	1.51	1.47	1.43	1.38	1.35	1.28
Ne	10	9.47	8.09	6.29	4.62	3.37	2.57	2.05	1.77	1.60	1.51	1.47	1.43	1.39	1.35
Na	11	10.06	8.53	7.10	5.56	4.22	3.22	2.54	2.09	1.80	1.64	1.53	1.47	1.44	1.40
Mg	12	10.80	8.94	7.66	6.37	5.12	3.95	3.10	2.53	2.12	1.85	1.68	1.56	1.48	1.44
Al	13	11.50	9.32	8.11	7.05	5.89	4.72	3.74	3.04	2.54	2.15	1.87	1.70	1.60	1.51
Si	14	12.31	9.72	8.41	7.58	6.51	5.45	4.42	3.59	2.98	2.53	2.17	1.91	1.74	1.61
P	15	13.20	10.22	8.67	7.91	7.10	6.13	5.10	4.19	3.46	2.93	2.50	2.19	1.95	1.76
S	16	14.10	10.80	8.96	8.16	7.52	6.67	5.73	4.80	4.00	3.36	2.88	2.49	2.20	1.96
Cl	17	15.16	11.59	9.06	8.35	7.84	7.16	6.29	5.41	4.54	3.83	3.28	2.83	2.49	2.20
A	18	16.17	12.36	9.60	8.37	7.85	7.28	6.51	5.66	4.81	4.04	3.43	2.96	2.56	2.27
K	19	16.56	13.28	10.30	8.84	7.99	7.69	7.15	6.45	5.69	4.92	4.22	3.63	3.16	2.78
Ca	20	17.24	13.93	11.13	9.21	8.28	7.85	7.39	6.80	6.16	5.47	4.76	4.12	3.60	3.16
Sc	21	18.11	14.75	11.83	9.58	8.50	7.95	7.56	7.07	6.49	5.89	5.24	4.56	4.02	3.53
Ti	22	19.29	15.68	12.59	10.03	8.74	8.03	7.66	7.27	6.75	6.21	5.64	5.04	4.41	3.90
V	23	20.35	16.70	13.48	10.64	9.06	8.20	7.74	7.40	7.00	6.50	6.01	5.45	4.90	4.34
Cr	24	21.97	18.35	14.53	11.32	9.38	8.33	7.74	7.44	7.15	6.72	6.27	5.77	5.27	4.70
Mn	25	22.88	18.84	15.31	12.09	9.81	8.64	7.91	7.54	7.23	6.90	6.48	6.05	5.58	5.07
Fe	26	23.63	20.00	16.32	12.99	10.40	9.02	8.13	7.62	7.34	7.05	6.75	6.34	5.92	5.47
Co	27	24.60	21.05	17.37	13.87	10.98	9.33	8.33	7.70	7.37	7.11	6.84	6.49	6.11	5.69
Ni	28	25.55	22.16	18.50	14.85	11.79	9.77	8.60	7.87	7.44	7.20	6.97	6.68	6.34	5.97
Cu	29	27.28	24.03	20.09	16.08	12.80	10.29	8.89	7.97	7.41	7.14	6.93	6.71	6.42	6.07
Zn	30	27.90	24.36	20.76	16.88	13.53	10.84	9.26	8.26	7.61	7.22	7.02	6.79	6.55	6.25
Ga	31	28.50	24.84	21.58	17.89	14.57	11.81	9.85	8.67	7.87	7.34	7.04	6.83	6.61	6.36
Ge	32	29.20	25.24	22.30	18.84	15.52	12.70	10.51	9.16	8.22	7.57	7.12	6.88	6.69	6.45
As	33	29.87	25.61	22.90	19.75	16.44	13.59	11.30	9.72	8.64	7.87	7.33	6.96	6.74	6.55
Se	34	30.43	26.04	23.25	20.40	17.31	14.42	11.97	10.22	9.02	8.15	7.51	7.13	6.81	6.57
Br	35	31.20	26.40	23.72	21.24	18.24	15.23	12.81	10.89	9.54	8.57	7.82	7.26	6.88	6.59
Kr	36	32.48	26.87	24.04	21.86	19.03	16.09	13.53	11.54	10.04	9.00	8.16	7.54	7.07	6.72
Rb	37	32.70	27.49	24.23	22.20	19.71	16.89	14.22	12.15	10.47	9.34	8.44	8.16	7.47	7.15
Sr	38	33.36	28.34	24.64	22.58	20.37	17.70	15.13	12.89	11.11	9.77	8.85	8.11	7.53	7.08
Zr	40	35.15	29.61	25.54	23.27	21.36	19.07	16.62	14.36	12.34	10.77	9.56	8.72	8.03	7.49
Mo	42	37.67	31.06	26.35	24.04	22.25	20.22	17.96	15.66	13.66	11.83	10.48	9.37	8.59	7.95
Ru	44	39.90	32.89	27.46	24.62	22.95	21.23	19.17	17.03	14.98	13.12	11.47	10.18	9.21	8.46
Pd	46	42.52	35.22	28.77	25.17	23.46	22.07	20.34	18.32	16.21	14.25	12.53	11.06	9.89	8.99
Cd	48	43.89	36.60	30.36	25.98	23.85	22.52	21.18	19.42	17.43	15.52	13.75	12.16	10.84	9.77

Table VII (continuation).

$\frac{\sin\theta}{\lambda}\cdot 10^{-8}$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4
Sn	50	44.90	38.29	32.15	27.32	24.39	22.78	21.57	20.28	18.60	16.87	15.05	13.36	11.89	10.67
Te	52	46.62	37.44	34.06	28.82	25.33	23.22	21.94	20.75	19.45	17.87	16.30	14.65	13.05	11.69
I	53	47.42	39.83	34.70	29.60	25.85	23.56	22.13	20.97	19.77	18.39	16.84	15.28	13.66	12.27
Cs	55	49.00	40.87	35.91	31.22	26.99	24.19	22.43	21.28	20.19	18.96	17.62	16.22	14.81	13.34
Ba	56	49.42	41.58	35.54	32.08	27.73	24.66	22.78	21.56	20.48	19.38	18.11	16.69	15.31	13.92
Ce	58	50.98	43.11	37.75	33.29	29.03	25.52	23.31	21.87	20.83	19.82	18.72	17.49	16.14	14.76
Nd	60	53.27	45.20	39.28	34.66	30.22	26.40	23.81	22.15	21.11	20.14	19.20	18.09	16.95	15.68
Sa	62	55.38	47.10	40.64	35.63	31.00	27.06	24.29	22.58	21.47	20.59	19.67	18.71	17.66	16.43
Gd	64	57.58	49.11	42.16	36.78	31.97	27.78	24.78	22.88	21.66	20.83	20.00	19.16	18.16	17.10
Dy	66	58.40	51.33	44.11	38.24	33.22	28.81	25.45	23.32	21.91	21.04	20.29	19.53	18.66	17.72
Er	68	61.93	53.45	46.66	39.70	34.45	29.83	26.17	23.79	22.26	21.29	20.60	19.88	19.12	18.22
Yb	70	64.06	55.71	47.78	41.30	35.81	30.93	26.94	24.23	22.49	21.40	20.75	20.06	19.43	18.59
Hf	72	66.05	57.58	49.71	43.16	37.62	32.45	28.25	25.10	22.96	21.67	20.81	20.16	19.60	18.98
W	74	67.81	58.84	51.06	44.96	39.33	34.24	29.77	26.33	23.80	22.10	20.95	20.23	19.62	18.97
Os	76	69.64	60.33	52.33	46.67	41.26	36.12	31.51	27.73	24.86	22.76	21.42	20.41	19.73	19.17
Pt	78	72.27	61.92	53.43	48.12	43.01	38.00	33.13	29.12	26.06	23.72	22.07	20.81	19.96	19.36
Hg	80	73.84	63.48	54.68	49.25	44.49	39.50	34.93	30.68	27.22	24.89	22.75	21.34	20.28	19.45
Pb	82	74.93	65.08	56.10	50.02	45.61	40.93	36.39	32.25	28.51	25.57	23.47	21.84	20.66	19.82
Po	84	76.14	66.58	57.74	51.16	46.61	42.16	37.90	33.81	29.97	26.78	24.30	22.51	21.13	20.11
Rn	86	77.64	67.86	59.43	52.19	47.55	43.38	39.28	35.37	31.53	28.12	25.30	23.19	21.67	20.48
Ra	88	78.80	68.77	60.85	53.47	48.23	44.46	40.43	36.72	33.06	29.59	26.58	24.11	22.30	20.96
Th	90	79.73	69.77	62.19	55.04	49.31	45.49	41.63	37.99	34.56	31.09	27.99	25.26	23.11	21.51
U	92	80.75	71.38	63.36	56.46	50.42	46.16	42.69	39.07	35.72	32.47	29.30	26.41	23.96	22.21

Table VIII. Scattering factors for ions.

$\frac{\sin\theta}{\lambda}\cdot 10^{-8}$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4
Li^+	2.00	1.94	1.78	1.58	1.33	1.09	0.88	0.70	0.54	0.43	0.35	0.28	0.23	0.18	0.13
Be^{++}	2.00	1.97	1.88	1.75	1.59	1.41	1.23	1.06	0.91	0.77	0.65	0.54	0.46	0.39	0.33
B^{3+}	2.00	1.98	1.92	1.84	1.72	1.60	1.45	1.32	1.18	1.04	0.92	0.81	0.70	0.61	0.54
C^{4+}	2.00	1.99	1.95	1.88	1.80	1.70	1.60	1.49	1.37	1.25	1.13	1.03	0.92	0.83	0.74
N^{5+}	2.00	1.99	1.96	1.91	1.85	1.78	1.69	1.60	1.51	1.41	1.31	1.21	1.11	1.02	0.93
N^{3+}	4.00	3.73	3.12	2.47	2.02	1.79	1.66	1.59	1.54	1.46	1.38	1.29	1.19	1.09	1.00
$O^=$	10.00	9.15	7.07	4.84	3.22	2.32	1.83	1.61	1.51	1.46	1.42	1.37	1.29	1.22	1.14
F^-	10.00	9.33	7.65	5.61	3.90	2.80	2.14	1.78	1.60	1.50	1.46	1.42	1.37	1.34	1.27
Na^+	10.00	9.60	8.54	7.06	5.49	4.19	3.25	2.54	2.09	1.79	1.63	1.53	1.46	1.43	1.39
Mg^{++}	10.00	9.70	8.86	7.65	6.26	5.02	3.92	3.10	2.53	2.12	1.84	1.66	1.55	1.46	1.42
Al^{3+}	10.00	9.77	9.08	8.10	6.90	5.72	4.63	3.71	3.04	2.54	2.15	1.87	1.69	1.58	1.49
Si^{4+}	10.00	9.81	9.25	8.42	7.41	6.28	5.27	4.31	3.57	2.98	2.55	2.18	1.91	1.73	1.59
P^{5+}	10.00	9.85	9.37	8.67	7.79	6.82	5.84	4.93	4.11	3.44	2.94	2.52	2.21	1.95	1.76
P^{3+}	12.00	11.30	9.85	8.68	7.79	6.91	5.97	5.01	4.15	3.45	2.93	2.51	2.21	1.96	1.77
S^{6+}	10.00	9.88	9.47	8.86	8.09	7.22	6.31	5.44	4.64	3.92	3.34	2.89	2.51	2.22	1.98
$S^=$	18.00	15.50	11.20	8.97	8.21	7.64	6.79	5.81	4.84	4.02	3.37	2.87	2.49	2.19	1.96

Table VIII (continuation).

$\frac{\sin\theta}{\lambda}\cdot 10^{-8}$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4
Cl^-	18.00	15.90	11.90	9.31	8.36	7.89	7.22	6.35	5.44	4.56	3.84	3.28	2.83	2.49	2.20
K^+	18.00	16.50	13.20	10.30	8.80	7.98	7.69	7.15	6.45	5.69	4.92	4.22	3,63	3.16	2.78
Ca^{++}	18.00	16.80	13.90	11.00	9.22	8.26	7.81	7.37	6.79	6.16	5.47	4.76	4.12	3.60	3.16
Rb^+	36.00	32.64	27.44	24.22	22.19	19.71	16.89	14.22	12.15	10.47	9.34	8,44	8.16	7.47	7.15

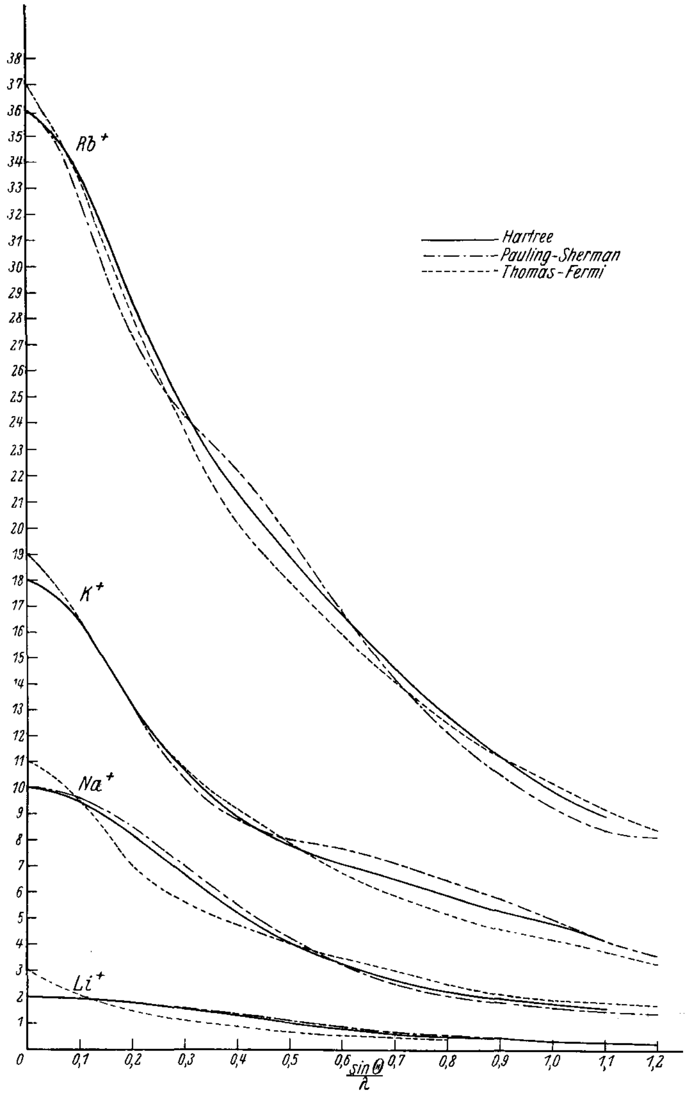

Fig. 10. Comparison of Hartree, Pauling-Sherman, and Thomas-Fermi F-values for Li^+, Na^+, K^+, and Rb^+. (Thomas-Fermi values are for neutral atoms.)

atoms there is good agreement between the values of this paper and those of Hartree, the maximum difference being 0.3 for Na^+ and 1.2 for Rb^+. The agreement between the Thomas-Fermi values and Hartree's is nearly as good for heavy atoms, but not good for light ones, on account of the approximations involved in the Thomas-Fermi statistical treatment. It is of interest to note the effect of the completed *K*, *L*, *M* etc. shells in causing the Pauling-Sherman curves to vary from one side to the other of the Thomas-Fermi curves. The Hartree curves behave in the same way, but the waves are not so pronounced, inasmuch as the nodes in the eigenfunctions, neglected completely in the Thomas-Fermi treatment, have been over-emphasized in using hydrogen-like eigenfunctions. For this reason the Hartree curves usually lie between the Thomas-Fermi and Pauling-Sherman curves, and for heavy atoms the mean of the Thomas-Fermi and Pauling-Sherman values is probably somewhat better than either set alone.

The effect of the *K*, *L*, and *M* shells in successive atoms is strikingly shown in figures 9 and 10 by the concentration of the curves in certain regions.

Summary.

After a discussion of screening constants and their uses, in which the relation between screening constants for various physical properties is presented, it is pointed out that a complete set of screening constants could be obtained from X-ray term values and ionization potentials alone. In default of complete knowledge of term values and ionization potentials of heavy atoms, a table of size screening constants for all electrons in all atoms has been prepared partially from theoretical calculations and partially from term values. It is shown that this table of screening constants permits a satisfactory detailed interpretation of energy levels of atoms. The screening constants for inner electrons are found not to be constant but to increase rapidly for large values of the atomic number. The phenomenon is interpreted as a spin-relativity effect with the aid of Dirac's theory of the electron.

A general expression for the scattering factor for X-rays of a hydrogen-like eigenfunction has been obtained. By substituting screening constants in it, *F*-values for atoms and ions have been obtained which show good agreement with those calculated by Hartree's method.

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The van der Waals Interaction of Hydrogen Atoms

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The van der Waals interaction energy of two hydrogen atoms at large internuclear distances is discussed by the use of a linear variation function. By including in the variation function, in addition to the unperturbed wave function, 26 terms for the dipole-dipole interaction, 17 for the dipole-quadrupole interaction, and 26 for the quadrupole-quadrupole interaction, the interaction energy is evaluated as

$$W''=-\frac{6.49903\,e^2}{a_0\,\rho^6}-\frac{124.399\,e^2}{a_0\,\rho^8}-\frac{1135.21\,e^2}{a_0\,\rho^{10}}-\cdots,$$

in which $\rho=R/a_0$, with R the internuclear distance. Some properties of the functions $F_{\nu\lambda\mu}(\xi,\vartheta,\varphi)$, which are orthogonal for the volume element $\xi d\xi\sin\theta d\theta d\varphi$, are discussed, and their usefulness in atomic problems is pointed out.

INTRODUCTION

AN approximate second-order perturbation treatment of the inverse sixth power interaction energy of two hydrogen atoms a large distance apart (corresponding to the so-called dipole-dipole van der Waals attraction) was given in 1930 by Eisenschitz and London.[1] This treatment led to the result $W''=-e^2A/a_0\rho^6$, with $\rho=r_{AB}/a_0$ (r_{AB} being the internuclear distance for the two atoms), A being evaluated as 6.47. Applications of the variation method by Hassé[2] and by Slater and Kirkwood[3] verified this result essentially, the constant A being shown to be equal to or greater than 6.4976.

As early as 1927 this problem had been attacked by Wang,[4] using the method developed by Epstein[5] for the treatment of the Stark effect. Wang claimed to have obtained an exact solution; it was, however, pointed out by Eisenschitz and London that Wang's result is necessarily in error. It seemed to us possible that Wang's work might have contained only a numerical error, and that the method might actually be capable of giving an exact solution. Because of the usefulness which a method of exact solution of problems of this sort would have, we thought it worth while to study the problem thoroughly. We have found that the method used by Wang does not give an exact solution,[6] but that it can be extended to give as closely approximate a solution as is desired. The results of the treatment are communicated in this paper.

A rough treatment of the dipole-quadrupole and quadrupole-quadrupole interactions of two hydrogen atoms has been published by Mar-

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[1] R. Eisenschitz and F. London, Zeits. f. Physik **60**, 491 (1930).

[2] H. R. Hassé, Proc. Camb. Phil. Soc. **27**, 66 (1931).

[3] J. C. Slater and J. G. Kirkwood, Phys. Rev. **37**, 682 (1931).

[4] S. C. Wang, Physik. Zeits. **28**, 663 (1927).

[5] P. S. Epstein, Phys. Rev. **28**, 695 (1926).

[6] Wang does not present the final steps in his calculation in detail, but states that he set up a sixth degree secular equation from which he obtained an accurate value for the energy. We believe that the error in his treatment occurs at this point.

genau.[7] We have applied our method to obtain reasonably accurate expressions for these interactions also.

Formulation of the Problem

In the wave equation for two hydrogen atoms $H\psi = W\psi$ let us put $H = H^0 + H'$, H^0 being the part of the Hamiltonian corresponding to two isolated hydrogen atoms and H' representing the interaction of the two hydrogen atoms. In order to do this we neglect the resonance phenomenon (which is unimportant at large distances), taking as the unperturbed wave function the product function $\psi_{100}(A1)\ \psi_{100}(B2)$; that is, we consider electron 1 to be attached to nucleus A and electron 2 to nucleus B. We also write $W = W^0 + W''$ (W', the first-order perturbation energy, being equal to zero). We shall consider only the interaction of two normal hydrogen atoms, so that W^0 is equal to $-e^2/a_0$. Making the substitutions $\xi_1 = 2r_{A1}/a_0$ and $\xi_2 = 2r_{B2}/a_0$, the wave equation becomes

$$\left(\nabla_1^2 + \frac{1}{\xi_1} - \frac{1}{4}\right)\psi + \left(\nabla_2^2 + \frac{1}{\xi_2} - \frac{1}{4}\right)\psi - \frac{a_0}{2e^2}H'\psi = \lambda\psi, \quad (1)$$

in which $\lambda = -W''a_0/2e^2$.

The interaction H' is equal to

$$-e^2/r_{A2} - e^2/r_{B1} + e^2/r_{AB} + e^2/r_{12}.$$

If $R(=r_{AB})$ is large, this can be expanded[7] in inverse powers of R to give the expression

$$\begin{aligned} H' = {} & (e^2/R^3)(x_1x_2 + y_1y_2 - 2z_1z_2) \\ & + (3/2)(e^2/R^4)\{r_1^2 z_2 - r_2^2 z_1 \\ & + (2x_1x_2 + 2y_1y_2 - 3z_1z_2)(z_1 - z_2)\} \\ & + \tfrac{3}{4}(e^2/R^5)\{r_1^2 r_2^2 - 5r_2^2 z_1^2 - 5r_1^2 z_2^2 \\ & - 15z_1^2 z_2^2 + 2(x_1x_2 + y_1y_2 + 4z_1z_2)^2\} + \cdots. \quad (2) \end{aligned}$$

In this expression $x_1y_1z_1$ are Cartesian coordinates of electron 1 relative to nucleus A, and $x_2y_2z_2$ those of electron 2 relative to nucleus B, the z axis for each being directed towards the other nucleus. The first term represents the mutual energy of two dipoles; this term alone is important for large values of R. The second and third terms represent the dipole-quadrupole and quadrupole-quadrupole interactions, respectively. It can be easily shown that in the calculation of the second-order perturbation energy the terms can be considered separately, their contributions being additive.

In the solution of the problem we shall make use of the functions $F_{\nu\lambda\mu}(\xi, \vartheta, \varphi)$ discussed in the appendix. Each of these functions can be made identical with a hydrogen-like wave function $\psi_{nlm}(r, \vartheta, \varphi)$ by choosing a suitable linear relation between r and ξ; the functions $F_{\nu\lambda\mu}$ all contain the same exponential function, in contradistinction to the functions ψ_{nlm}. We have defined ξ_1 and ξ_2 in such a way that $F_{100}(\xi_1, \vartheta_1, \varphi_1)$ and $F_{100}(\xi_2, \vartheta_2, \varphi_2)$ are identical with $\psi_{100}(r_1, \vartheta_1, \varphi_1)$ and $\psi_{100}(r_2, \vartheta_2, \varphi_2)$, respectively; that is, the unperturbed wave function can be written as $F_{100}(\xi_1)\ F_{100}(\xi_2)$. We now apply the variation method in treating the perturbed wave equation, using as the variation function a linear combination of the product functions $F_{\nu_1\lambda_1\mu_1}(\xi_1, \vartheta_1, \varphi_1)\ F_{\nu_2\lambda_2\mu_2}(\xi_2, \vartheta_2, \varphi_2)$, with arbitrary coefficients. It can be seen that the second-order perturbation energy for the perturbation function

$$\begin{aligned} H' = {} & -(2e^2/a_0)\{\alpha\xi_1\xi_2 \cos\vartheta_1 \cos\vartheta_2 \\ & + \beta\xi_1\xi_2^2 \cos\vartheta_1(3\cos^2\vartheta_2 - 1) \\ & + \gamma\xi_1^2\xi_2^2(3\cos^2\vartheta_1 - 1)(3\cos^2\vartheta_2 - 1) \\ & + \cdots\}, \quad (3) \end{aligned}$$

in which

$$\alpha = (6)^{\frac{1}{2}}a_0^3/8R^3, \quad \beta = (30)^{\frac{1}{2}}a_0^4/32R^4, \quad \text{and} \quad \gamma = (70)^{\frac{1}{2}}a_0^5/128R^5, \quad (4)$$

is identical with that for the function of Eq. (2), and, moreover, that to obtain the first-order perturbed wave function and the second-order perturbation energy, the variation function used need contain, in addition to the unperturbed part $F_{100}(\xi_1)\ F_{100}(\xi_2)$, only the terms $F_{\nu_1 10}(\xi_1, \vartheta_1)\ F_{\nu_2 10}(\xi_2, \vartheta_2)$ (for the dipole-dipole term in α), $F_{\nu_1 10}(\xi_1, \vartheta_1)\ F_{\nu_2 20}(\xi_2, \vartheta_2)$ (for the term in β), and $F_{\nu_1 20}(\xi_1, \vartheta_1).\ F_{\nu_2 20}(\xi_2, \vartheta_2)$ (for the term in γ).[8]

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[7] H. Margenau, Phys. Rev. **38**, 747 (1931).

[8] On application of the ordinary methods of perturbation theory, it is seen that the first-order perturbed wave function for a normal hydrogen atom with perturbation function $f(r)T(\vartheta, \varphi)$, where T is a tesseral harmonic, has the form $\Psi_{100}(r) + \Phi(r)T(\vartheta, \varphi)$, the perturbed part involving the same tesseral harmonic as the perturbation function. The statements in the text can be verified by an extension of this argument.

For a linear variation function $\sum_l a_l \Phi_l$ (where Φ_l represents the product functions $F_{\nu_1\lambda_1\mu_1}(\xi_1, \vartheta_1, \varphi_1)\, F_{\nu_2\lambda_2\mu_2}(\xi_2, \vartheta_2, \varphi_2)$) the secular equation corresponding to the wave equation (1) is the determinantal equation[9]

$$|\mathcal{H}_{jk}^0+\mathcal{H}_{jk}'-\Delta_{jk}\lambda|=0, \tag{5}$$

in which

$$\mathcal{H}_{jk}^0=\int\int\Phi_j^*(\nabla_1^2+(1/\xi_1)-\tfrac{1}{4}+\nabla_2^2+(1/\xi_2)-\tfrac{1}{4})\Phi_k d\tau_1 d\tau_2,$$

$$\mathcal{H}_{jk}'=\int\int\Phi_j^*(-(a_0/2e^2)H')\Phi_k d\tau_1 d\tau_2,$$

and

$$\Delta_{jk}=\int\int\Phi_j^*\Phi_k d\tau_1 d\tau_2,$$

$d\tau_1$ being equal to $\xi_1^2 \sin\theta_1 d\xi_1 d\vartheta_1 d\varphi_1$ (with $d\tau_2$ differing only in the subscripts) and the integrals extending over the configuration space of the system. It is to be noted that the volume element $d\tau_1 d\tau_2$ is not such as to make the functions Φ mutually orthogonal. The integrals can be evaluated with the help of the relations given in the appendix. To obtain the second-order perturbation energy we need introduce the term in λ in the row and column corresponding to the wave function for the unperturbed system only.

THE DIPOLE-DIPOLE INTERACTION

The secular equation for the dipole-dipole interaction is

$$\begin{array}{c|cccccccccccc|l}
\nu_1\lambda_1\mu_1\nu_2\lambda_2\mu_2 & & & & & & & & & & & & \\
100100 & -4\lambda & 32\alpha & -16\alpha & -16\alpha & 8\alpha & 0 & 0 & 0 & 0 & 0 & \cdots & \\
210210 & 32\alpha & -8 & 2 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & \cdots & \\
210310 & -16\alpha & 2 & -14 & 0 & 4 & \surd(10) & 0 & 0 & 0 & 0 & \cdots & \\
310210 & -16\alpha & 2 & 0 & -14 & 4 & 0 & \surd(10) & 0 & 0 & 0 & \cdots & \\
310310 & 8\alpha & 0 & 4 & 4 & -24 & 0 & 0 & 2\surd(10) & 2\surd(10) & 0 & \cdots & \\
210410 & 0 & 0 & \surd(10) & 0 & 0 & -20 & 0 & 6 & 0 & 0 & \cdots & \\
410210 & 0 & 0 & 0 & \surd(10) & 0 & 0 & -20 & 0 & 6 & 0 & \cdots & =0, \quad (6) \\
310410 & 0 & 0 & 0 & 0 & 2\surd(10) & 6 & 0 & -34 & 0 & 3\surd(10) & \cdots & \\
410310 & 0 & 0 & 0 & 0 & 2\surd(10) & 0 & 6 & 0 & -34 & 3\surd(10) & \cdots & \\
410410 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 3\surd(10) & 3\surd(10) & -48 & \cdots & \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & & \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & & \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & &
\end{array}$$

the rows and columns corresponding to the values of $\nu_1\cdots\mu_2$ shown at the left. We obtain successive approximations to the solution of this equation by neglecting rows and columns beyond the nth. This process has been carried out for $n=2$, 5, 10, 17 and 26. Some simplification is achieved by combining rows (and columns) with ν_1 and ν_2 interchanged, the corresponding functions having the same coefficient. The results of the calculation are given in Table I, in terms of the constant A in the expression $W''=-Ae^2/a_0\rho^6$, with $\rho=R/a_0$ (A being equal to $3\lambda/16\alpha^2$).

TABLE I. *The dipole-dipole interaction constant A.*

Degree of approx.	Terms included		A
2	$\nu_1 \leq 2$,	$\nu_2 \leq 2$	6
5	3	3	6.4822
10	4	4	6.4984
17	5	5	6.49899
26	6	6	6.49903

TABLE II. *The dipole-quadrupole interaction constant B.*

Degree of approx.	Terms included		B
2	$\nu_1 \leq 2$,	$\nu_2 \leq 3$	115.7
5	3	4	124.10
10	4	5	124.386
17	5	6	124.399

TABLE III. *The quadrupole-quadrupole interaction constant C.*

Degree of approx.	Terms included		C
2	$\nu_1 \leq 3$,	$\nu_2 \leq 3$	1063.1
5	4	4	1132.6
10	5	5	1134.35
17	6	6	1135.12
26	7	7	1135.21

It is seen that the convergence is rapid, the final value of A, 6.49903, being trustworthy to within one unit in the last decimal place.

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[9] See, for example, L. Pauling and E. B. Wilson, Jr., *Introduction to Quantum Mechanics, with Applications to Chemistry*, McGraw-Hill Book Co., **1935**, Chap. VII.

THE DIPOLE-QUADRUPOLE INTERACTION

The secular equation for the dipole-quadrupole interaction is

$$\begin{array}{c|ccccccccccc|l}
\nu_1\lambda_1\mu_1\nu_2\lambda_2\mu_2 & & & & & & & & & & & & \\
100100 & -4\lambda & -192\sqrt{(3)}\beta & 96\sqrt{(3)}\beta & 96\sqrt{2}\beta & -48\sqrt{2}\beta & 0 & 0 & 0 & 0 & 0 & \cdots & \\
210320 & -192\sqrt{(3)}\beta & -14 & 4 & \sqrt{(6)} & 0 & 0 & 0 & 0 & 0 & 0 & \cdots & \\
310320 & 96\sqrt{(3)}\beta & 4 & -24 & 0 & 2\sqrt{(6)} & 2\sqrt{(10)} & 0 & 0 & 0 & 0 & \cdots & \\
210420 & 96\sqrt{2}\beta & \sqrt{(6)} & 0 & -20 & 6 & 0 & \sqrt{(14)} & 0 & 0 & 0 & \cdots & \\
310420 & -48\sqrt{2}\beta & 0 & 2\sqrt{(6)} & 6 & -34 & 0 & 0 & 3\sqrt{(10)} & 2\sqrt{(14)} & 0 & \cdots & \\
410320 & 0 & 0 & 2\sqrt{(10)} & 0 & 0 & -34 & 0 & 3\sqrt{(6)} & 0 & 0 & \cdots & \\
210520 & 0 & 0 & 0 & \sqrt{(14)} & 0 & 0 & -26 & 0 & 8 & 0 & \cdots & =0. \quad (7) \\
410420 & 0 & 0 & 0 & 0 & 3\sqrt{(10)} & 3\sqrt{(6)} & 0 & -48 & 0 & 3\sqrt{(14)} & \cdots & \\
310520 & 0 & 0 & 0 & 0 & 2\sqrt{(14)} & 0 & 8 & 0 & -44 & 4\sqrt{(10)} & \cdots & \\
410520 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 3\sqrt{(14)} & 4\sqrt{(10)} & -62 & \cdots & \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & &
\end{array}$$

We have solved this equation approximately, the results being given in Table II in terms of the constant B in the energy expression $-Be^2/a_0\rho^8$.

The error in the final value of B we estimate to be less than one unit in the last figure quoted.

THE QUADRUPOLE-QUADRUPOLE INTERACTION

The secular equation for the quadrupole-quadrupole interaction is

$$\begin{array}{c|ccccccccccc|l}
\nu_1\lambda_1\mu_1\nu_2\lambda_2\mu_2 & & & & & & & & & & & & \\
100100 & -4\lambda & 3456\gamma & -576\sqrt{(6)}\gamma & -576\sqrt{(6)}\gamma & 576\gamma & 0 & 0 & 0 & 0 & 0 & \cdots & \\
320320 & 3456\gamma & -24 & 2\sqrt{(6)} & 2\sqrt{(6)} & 0 & 0 & 0 & 0 & 0 & 0 & \cdots & \\
320420 & -576\sqrt{(6)}\gamma & 2\sqrt{(6)} & -34 & 0 & 3\sqrt{(6)} & 2\sqrt{(14)} & 0 & 0 & 0 & 0 & \cdots & \\
420320 & -576\sqrt{(6)}\gamma & 2\sqrt{(6)} & 0 & -34 & 3\sqrt{(6)} & 0 & 2\sqrt{(14)} & 0 & 0 & 0 & \cdots & \\
420420 & 576\gamma & 0 & 3\sqrt{(6)} & 3\sqrt{(6)} & -48 & 0 & 0 & 3\sqrt{(14)} & 3\sqrt{(14)} & 0 & \cdots & \\
320520 & 0 & 0 & 2\sqrt{(14)} & 0 & 0 & -44 & 0 & 4\sqrt{(6)} & 0 & 0 & \cdots & \\
520320 & 0 & 0 & 0 & 2\sqrt{(14)} & 0 & 0 & -44 & 0 & 4\sqrt{(6)} & 0 & \cdots & =0. \quad (8) \\
420520 & 0 & 0 & 0 & 0 & 3\sqrt{(14)} & 4\sqrt{(6)} & 0 & -62 & 0 & 4\sqrt{(14)} & \cdots & \\
520420 & 0 & 0 & 0 & 0 & 3\sqrt{(14)} & 0 & 4\sqrt{(6)} & 0 & -62 & 4\sqrt{(14)} & \cdots & \\
520520 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 4\sqrt{(14)} & 4\sqrt{(14)} & -80 & \cdots & \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & &
\end{array}$$

The results of the approximate solution of this equation, in terms of the constant C in the energy expression $-Ce^2/a_0\rho^{10}$, are given in Table III.

The final value, $C=1135.21$, is reliable except for the last figure.

DISCUSSION OF RESULTS

We have thus found for the interaction energy of two normal hydrogen atoms at the large distance $R=\rho a_0$ the expression

$$W''=-\frac{6.49903\, e^2}{a_0\rho^6}-\frac{124.399\, e^2}{a_0\rho^8}-\frac{1135.21\, e^2}{a_0\rho^{10}}-\cdots. \tag{9}$$

It is interesting to note that the value $A=6.4976$ found by Hassé for the dipole-dipole coefficient by the use of a variation function $\psi_{100}\,(r_1)\;\psi_{100}\,(r_2)\;\{1+H'(A+Br_1r_2+Cr_1^2r_2^2+Dr_1^3r_2^3)\}$ is very close to our value for $\nu_1\leq 4$, $\nu_2\leq 4$, which is based on a variation function involving all terms (unsymmetric as well as symmetric) out to $r_1^3r_2^3$. This indicates that the unsymmetric terms are of minor importance.

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[10] We use here shortened symbols, such as $F_{\nu_1}F_{\nu_2}$ for $F_{\nu_1\lambda_1\mu_1}(\xi_1,\vartheta_1,\varphi_1)F_{\nu_2\lambda_2\mu_2}(\xi_2,\vartheta_2,\varphi_2)$, etc.

The approximate second-order perturbation energy $W_0'' = (H_{00}')^2/W_0^0$, with $W_0^0 = -e^2/a_0$, leads to the values $A = 6$, $B = 135$, and $C = 1417.5$, the last two values being given by Margenau.[7] It is seen that the value of A is too low, and those of B and C are too high. This means that the dipole-dipole interaction is due more to excited states with negative energy (less than e^2/a_0 above the normal state of the system of two hydrogen atoms) than to excited states with positive energy, whereas the dipole-quadrupole and quadrupole-quadrupole interactions are due more to the latter than to the former states.

As has been pointed out by earlier authors, the van der Waals forces are more important than exchange forces for values of R greater than about $7a_0$. At this distance the dipole-quadrupole force is about one-half as large as the dipole-dipole force, and the quadrupole-quadrupole force is about one-eighth as large, the dipole-dipole attraction becoming relatively still more important at larger distances. This van der Waals calculation, based on product wave functions, is not significant for values of R much less than $7a_0$ because of neglect of the resonance phenomenon and because of failure of the expansion given in Eq. (2).

While our treatment has not led to an exact solution of our problem, the use of the functions $F_{\nu\lambda\mu}(\xi, \vartheta, \varphi)$ has permitted the reasonably accurate approximate solution to be made with considerable ease, and we feel that these functions may be found useful in the treatment of other problems of atomic and molecular structure.[11]

APPENDIX

The functions $F_{\nu\lambda\mu}(\xi, \vartheta, \varphi)$

We define

$$F_{\nu\lambda\mu}(\xi, \vartheta, \varphi) = \Lambda_{\nu\lambda}(\xi)\Theta_{\lambda\mu}(\vartheta)\Phi_\mu(\varphi),$$

with

$$\Lambda_{\nu\lambda}(\xi) = \{(\nu-\lambda-1)!/[(\nu+\lambda)!]^3\}^{\frac{1}{2}} e^{-\xi/2}\xi^\lambda L_{\nu+\lambda}{}^{2\lambda+1}(\xi),$$

L being an associated Laguerre polynomial,

$$\Theta_{\lambda\mu}(\vartheta) = \{[(2\lambda+1)(\lambda-\mu)!]/2(\lambda+\mu)!\}^{\frac{1}{2}} P_\lambda{}^{|\mu|}(\cos\vartheta),$$

P being an associated Legendre function, and

$$\Phi_\mu(\varphi) = (2\pi)^{-\frac{1}{2}} e^{i\mu\varphi}.$$

The functions are orthogonal and normalized for the weight function $\xi \sin\vartheta$, satisfying the equation

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} F'_{\nu'\lambda'\mu'}(\xi, \vartheta, \varphi) F_{\nu\lambda\mu}(\xi, \vartheta, \varphi)\xi \sin\vartheta d\varphi d\vartheta d\xi = \delta_{\nu'\nu}\delta_{\lambda'\lambda}\delta_{\mu'\mu}.$$

$F_{\nu\lambda\mu}(\xi, \vartheta, \varphi)$ satisfies the differential equation

$$(\nabla^2 + 1/\xi - \tfrac{1}{4})F_{\nu\lambda\mu} = -[(\nu-1)/\xi]F_{\nu\lambda\mu}.$$

The following relations involving the Λ's can be easily derived from the properties of the associated Laguerre polynomials:

$$\xi\Lambda_{\nu\lambda} = -\{(\nu-\lambda)(\nu+\lambda+1)\}^{\frac{1}{2}}\Lambda_{\nu+1,\,\lambda} + 2\nu\Lambda_{\nu\lambda} - \{(\nu+\lambda)(\nu-\lambda-1)\}^{\frac{1}{2}}\Lambda_{\nu-1,\,\lambda}.$$

$$\begin{aligned}\xi^2\Lambda_{\nu\lambda} = &-\{(\nu-\lambda)(\nu+\lambda+1)(\nu+\lambda+2)(\nu+\lambda+3)\}^{\frac{1}{2}}\Lambda_{\nu+2,\,\lambda+1} \\ &+2(2\nu-\lambda)\{(\nu+\lambda+1)(\nu+\lambda+2)\}^{\frac{1}{2}}\Lambda_{\nu+1,\,\lambda+1} - 6\nu\{(\nu+\lambda+1)(\nu-\lambda-1)\}^{\frac{1}{2}}\Lambda_{\nu,\,\lambda+1} \\ &+2(2\nu+\lambda)\{(\nu-\lambda-1)(\nu-\lambda-2)\}^{\frac{1}{2}}\Lambda_{\nu-1,\,\lambda+1} - \{(\nu+\lambda)(\nu-\lambda-1)(\nu-\lambda-2)(\nu-\lambda-3)\}^{\frac{1}{2}}\Lambda_{\nu-2,\,\lambda+1}.\end{aligned}$$

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[11] *Added in proof:* Professor J. H. Van Vleck has pointed out to us that the functions were used in the treatment of dispersion by hydrogen-like atoms by B. Podolsky, Proc. Nat. Acad. Sci. **14**, 253 (1928).

$$\begin{aligned}\xi^3\Lambda_{\nu\lambda}=&-\{(\nu-\lambda)(\nu+\lambda+1)(\nu+\lambda+2)(\nu+\lambda+3)(\nu+\lambda+4)(\nu+\lambda+5)\}^{\frac{1}{2}}\Lambda_{\nu+3,\ \lambda+2}\\&+2(3\nu-2\lambda)\{(\nu+\lambda+1)(\nu+\lambda+2)(\nu+\lambda+3)(\nu+\lambda+4)\}^{\frac{1}{2}}\Lambda_{\nu+2,\ \lambda+2}\\&-5(3\nu-\lambda)\{(\nu-\lambda-1)(\nu+\lambda+1)(\nu+\lambda+2)(\nu+\lambda+3)\}^{\frac{1}{2}}\Lambda_{\nu+1,\ \lambda+2}\\&+20\nu\{(\nu+\lambda+1)(\nu+\lambda+2)(\nu-\lambda-1)(\nu-\lambda-2)\}^{\frac{1}{2}}\Lambda_{\nu,\ \lambda+2}\\&-5(3\nu+\lambda)\{(\nu+\lambda+1)(\nu-\lambda-1)(\nu-\lambda-2)(\nu-\lambda-3)\}^{\frac{1}{2}}\Lambda_{\nu-1,\ \lambda+2}\\&+2(3\nu+2\lambda)\{(\nu-\lambda-1)(\nu-\lambda-2)(\nu-\lambda-3)(\nu-\lambda-4)\}^{\frac{1}{2}}\Lambda_{\nu-2,\ \lambda+2}\\&-\{(\nu+\lambda)(\nu-\lambda-1)(\nu-\lambda-2)(\nu-\lambda-3)(\nu-\lambda-4)(\nu-\lambda-5)\}^{\frac{1}{2}}\Lambda_{\nu-3,\ \lambda+2}.\end{aligned}$$

From these we obtain similar relations in the F's. The following special cases are needed in evaluating the matrix elements in Eqs. (6), (7) and (8):

$$\xi F_{100}=-\sqrt{2}F_{200}+2F_{100},$$

$$\xi^2\cos\vartheta F_{100}=-2\sqrt{2}F_{310}+4\sqrt{2}F_{210},$$

$$\xi^3(3\cos^2\vartheta-1)F_{100}=-24F_{420}+24\sqrt{(6)}F_{320}.$$

The evaluation of the matrix elements

In order to illustrate the method of construction of the matrices in Eqs. (6), (7) and (8), we shall evaluate some of the integrals. Let us first consider the integral[10]

$$\mathcal{H}^0{}_{\nu_1'\nu_2'\nu_1\nu_2}=\int\int F^*{}_{\nu_1'}F^*{}_{\nu_2'}\{\nabla_1{}^2+1/\xi_1-\tfrac{1}{4}+\nabla_2{}^2+1/\xi_2-\tfrac{1}{4}\}F_{\nu_1}F_{\nu_2}d\tau_1 d\tau_2.$$

By using the differential equation for $F_{\nu\lambda\mu}$ (ξ, ϑ, φ), the equation becomes

$$\begin{aligned}\mathcal{H}^0{}_{\nu_1'\nu_2'\nu_1\nu_2}&=\int\cdots\int F^*{}_{\nu_1'}F^*{}_{\nu_2'}\{-(\nu_1-1)/\xi_1-(\nu_2-1)/\xi_2\}F_{\nu_1}F_{\nu_2}\xi_1{}^2\xi_2{}^2\sin\vartheta_1\sin\vartheta_2 d\xi_1 d\vartheta_1 d\varphi_1 d\xi_2 d\vartheta_2 d\varphi_2\\&=\int\cdots\int F^*{}_{\nu_1'}F^*{}_{\nu_2'}\{-(\nu_1-1)\xi_2-(\nu_2-1)\xi_1\}F\nu_1 F_{\nu_2}\xi_1\xi_2\sin\theta_1\sin\theta_2 d\xi_1 d\vartheta_1 d\varphi_1 d\xi_2 d\vartheta_2 d\varphi_2.\end{aligned}$$

For Eq. (6) ($\lambda_1=\lambda_2=1$, $\mu_1=\mu_2=0$) this becomes

$$\begin{aligned}\mathcal{H}^0{}_{\nu_1'\nu_2'\nu_1\nu_2}=\int\cdots\int F^*{}_{\nu_1'}F^*{}_{\nu_2'}[&(\nu_2-1)\{(\nu_1-1)(\nu_1+2)\}^{\frac{1}{2}}F_{\nu_1+1}F_{\nu_2}+(\nu_1-1)\{(\nu_2-1)(\nu_2+2)\}^{\frac{1}{2}}F_{\nu_1}F_{\nu_2+1}\\&-2(2\nu_1\nu_2-\nu_1-\nu_2)F_{\nu_1}F_{\nu_2}+(\nu_2-1)\{(\nu_1+1)(\nu_1-2)\}^{\frac{1}{2}}F_{\nu_1-1}F_{\nu_2}\\&+(\nu_1-1)\{(\nu_2+1)(\nu_2-2)\}^{\frac{1}{2}}F_{\nu_1}F_{\nu_2-1}]\xi_1\xi_2\sin\vartheta_1\sin\vartheta_2 d\xi_1 d\vartheta_1 d\varphi_1 d\xi_2 d\vartheta_2 d\varphi_2,\end{aligned}$$

and hence we obtain

$$\mathcal{H}^0{}_{\nu_1+1,\ \nu_2,\ \nu_1,\ \nu_2}=(\nu_2-1)\{(\nu_1-1)(\nu_1+2)\}^{\frac{1}{2}},$$

$$\mathcal{H}^0{}_{\nu_1,\ \nu_2+1,\ \nu_1,\ \nu_2}=(\nu_1-1)\{(\nu_2-1)(\nu_2+2)\}^{\frac{1}{2}},$$

$$\mathcal{H}^0{}_{\nu_1-1,\ \nu_2,\ \nu_1,\ \nu_2}=(\nu_2-1)\{(\nu_1+1)(\nu_1-2)\}^{\frac{1}{2}},$$

$$\mathcal{H}^0{}_{\nu_1,\ \nu_2-1,\ \nu_1,\ \nu_2}=(\nu_1-1)\{(\nu_2+1)(\nu_2-2)\}^{\frac{1}{2}},$$

and

$$\mathcal{H}^0{}_{\nu_1,\ \nu_2,\ \nu_1,\ \nu_2}=-2(2\nu_1\nu_2-\nu_1-\nu_2),$$

all others being equal to zero.

In Eq. (7) we have

$$\mathcal{H}'_{\nu_1\nu_2,\,11}=\beta\int\cdots\int F_{\nu_1}{}^*F_{\nu_2}{}^*\xi_1\xi_2{}^2\cos\vartheta_1(3\cos^2\vartheta_2-1)F_1F_1\xi_1{}^2\xi_2{}^2\sin\vartheta_1\sin\vartheta_2 d\xi_1 d\vartheta_1 d\varphi_1 d\xi_2 d\vartheta_2 d\varphi_2$$

$$=\beta\int\cdots\int F_{\nu_1}{}^*F_{\nu_2}{}^*\{48\sqrt{2}F_{310}F_{420}-96\sqrt{(3)}F_{310}F_{320}-96\sqrt{2}F_{210}F_{420}$$
$$+192\sqrt{(3)}F_{210}F_{320}\}\xi_1\xi_2\sin\vartheta_1\sin\vartheta_2 d\xi_1 d\vartheta_1 d\varphi_1 d\xi_2 d\vartheta_2 d\varphi_2,$$

and hence

$$\mathcal{H}'_{23,11}=192\sqrt{(3)}\beta,\qquad \mathcal{H}'_{33,11}=-96\sqrt{(3)}\beta,\qquad \mathcal{H}'_{24,11}=-96\sqrt{2}\beta,$$

and $\mathcal{H}'_{34,\,11}=48\sqrt{2}\beta$, all others being equal to zero.

To illustrate the evaluation of the integral Δ let us consider $\Delta_{11,\,11}$:

$$\Delta_{11,\,11}=\int\cdots\int\{F_{100}(\xi_1)F_{100}(\xi_2)\}^2\xi_1{}^2\xi_2{}^2\sin\vartheta_1\sin\vartheta_2 d\xi_1 d\vartheta_1 d\varphi_1 d\xi_2 d\vartheta_2 d\varphi_2$$

$$=\int\cdots\int F_{100}(\xi_1)F_{100}(\xi_2)\{2F_{200}(\xi_1)F_{200}(\xi_2)-2\sqrt{2}F_{200}(\xi_1)F_{100}(\xi_2)-2\sqrt{2}F_{100}(\xi_1)F_{200}(\xi_2)$$
$$+4F_{100}(\xi_1)F_{100}(\xi_2)\}\xi_1\xi_2\sin\vartheta_1\sin\vartheta_2 d\xi_1 d\vartheta_1 d\varphi_1 d\xi_2 d\vartheta_2 d\varphi_2,$$

or, making use of the orthogonality and normalization of the F's, $\Delta_{11,\,11}=4$.

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The Diamagnetic Anisotropy of Aromatic Molecules

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(Received July 11, 1936)

Values of the diamagnetic anisotropy of benzene and other aromatic hydrocarbon molecules are calculated on the basis of the assumption that the p_z electrons (one per aromatic carbon atom) are free to move from carbon atom to adjacent carbon atom under the influence of the impressed fields. When combined with the assumed values for the contributions of the other electrons (-2.0×10^{-6} for hydrogen, -4.5×10^{-6} for aromatic carbon, -6.0×10^{-6} for aliphatic carbon) these lead to principal diamagnetic susceptibilities of molecules in approximate agreement with the available experimental data. The diamagnetic anisotropy of graphite is also discussed.

CERTAIN diamagnetic crystals, such as bismuth and graphite, show pronounced diamagnetic anisotropy, the susceptibility being of normal magnitude in the basal plane and abnormally large in the direction perpendicular to this plane. A similar phenomenon is shown by crystals of aromatic substances. It has been pointed out by Krishnan and his collaborators[1] that the magnitudes and orientations of the principal axes of the susceptibility ellipsoid of

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* Contribution No. 555.

[1] (a) K. S. Krishnan, Proc. Ind. Sci. Cong., Madras Session, January, 1929; (b) K. S. Krishnan, B. C. Guha and S. Banerjee, Phil. Trans. Roy. Soc. **A231**, 235 (1933); (c) K. S. Krishnan and S. Banerjee, ibid. **A234**, 265 (1935).

such a crystal are determined by the values of the principal susceptibilities of the molecules of the aromatic substance and by the orientations of the molecules relative to the crystal axes. The susceptibility ellipsoids of the aromatic molecules are found to be approximately prolate ellipsoids of revolution, with the long axis normal to the plane of the ring system. As a result of the valuable investigations of Krishnan and his collaborators this phenomenon has been made the basis of an important auxiliary method for determining the structure of crystals.[1, 2]

A qualitative explanation of these abnormally large diamagnetic susceptibilities as arising from the Larmor precession of electrons in orbits including many nuclei[3] has come to be generally accepted. With the aid of simple assumptions, I have now developed this idea into an approximate quantitative treatment, described below.

Benzene

The Hamiltonian function for an electron in a constant magnetic field of strength H parallel to the z axis is[4]

$$\mathcal{H} = \mathcal{H}^0 + \mathcal{H}' + \mathcal{H}'', \qquad (1)$$

in which $\mathcal{H}^0$ is the Hamiltonian function for zero field strength,

$$\mathcal{H}' = -(He/2mc)(xp_y - yp_x), \qquad (2)$$

and

$$\mathcal{H}'' = (H^2e^2/8mc^2)(x^2+y^2). \qquad (3)$$

The contribution of the electron to the diamagnetic susceptibility of the system can be calculated by the methods of quantum-mechanical perturbation theory, a second-order perturbation treatment being needed for the term in $\mathcal{H}'$ and a first-order treatment for that in $\mathcal{H}''$. In case that the potential function in $\mathcal{H}^0$ is cylindrically symmetrical about the z axis, the effect of $\mathcal{H}'$ vanishes, and the contribution of the electron to the susceptibility (per mole) is given by the Pauli expression, resulting from $\mathcal{H}''$,

$$\chi = -(Ne^2/4mc^2)(\rho^2)_{av}, \qquad (4)$$

in which $(\rho^2)_{av}$ is the mean square of the distance of the electron from the z axis. This expression is valid for atoms and monatomic ions, the z axis being passed through the nucleus. It is not applicable (without correction for the term in $\mathcal{H}'$) to molecules. For most molecules a satisfactory approximate treatment can be used which consists in assigning electrons to the nearest nucleus, Eq. (4) being applied to the electrons about each nucleus.

Of the forty-two electrons of the benzene molecule, twelve (the carbon K electrons) make no appreciable contribution to the magnetic susceptibility. Twenty-four of the L electrons (which may be considered to be involved in electron-pair bonds between adjacent atoms) are in orbitals which are symmetric with respect to reflection in the plane of the nuclei. It is probable that the contribution of these to the magnetic susceptibility is normal. The remaining six L electrons, which give to benzene its characteristic electronic structure and properties,[5] occupy orbital wave functions which are antisymmetric with respect to reflection in the plane of the nuclei. The probability distribution function for these electrons is large only in two ring-shaped regions, one above and one below the carbon hexagon. We may well expect that in these regions the potential function representing the interaction of an electron with the nuclei and other electrons in the molecule would be approximately cylindrically symmetrical with respect to the hexagonal axis of the molecule, the electron, some distance above or below the plane of the nuclei, passing almost imperceptibly from the field of one carbon atom to that of the next. Under these conditions the contribution of each of these six electrons to the susceptibility with the magnetic field normal to the plane of the nuclei would be given by Eq. (4), with ρ measured from the hexagonal axis of the molecule, and it would hence be very large. On the other hand, because of the nodal plane of the wave functions these electrons would make only a very small contribution to the susceptibility

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[2] S. Bhagavantam, Proc. Roy. Soc. **A124**, 545 (1929); S. Banerjee, Ind. J. Phys. **4**, 557 (1930); K. S. Krishnan, Nature **130**, 313, 698 (1932); K. S. Krishnan and S. Banerjee, ibid. **131**, 653 (1933); **132**, 968 (1933); Zeits. f. Krist. **91**, 173 (1935); K. Lonsdale, Nature **137**, 826 (1936); N. Ganguli, Zeits. f. Krist. **93**, 42 (1936).

[3] P. Ehrenfest, Physica **5**, 388 (1925); Zeits. f. Physik **58**, 719 (1929); C. V. Raman, Nature **123**, 945 (1929); **124**, 412 (1929); C. V. Raman and K. S. Krishnan, Proc. Roy. Soc. **A113**, 511 (1927).

[4] See, for example, J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford University Press, 1932).

[5] E. Hückel, Zeits. f. Physik **70**, 204; **72**, 310 (1931); L. Pauling and G. W. Wheland, J. Chem. Phys. **1**, 362 (1933).

with the field in the nuclear plane. There would thus arise a large diamagnetic anisotropy of the molecule. If we use for $(\rho^2)_{av}$ the value R^2, in which R is the distance from the axis to the carbon nuclei, 1.39A, the anisotropy is calculated to have the value $\Delta K = -49.2 \times 10^{-6}$, which is in reasonably good agreement with the experimental value for benzene,[1b] $\Delta K = -54 \times 10^{-6}$.

A more detailed consideration may be given this argument by evaluating the terms corresponding to $\mathcal{H}'$ and $\mathcal{H}''$ with the use of assumed expressions for the wave functions. Using hydrogen-like $2p_z$ wave functions, the term corresponding to $\mathcal{H}''$ (Eq. (4)) has the value -49.2×10^{-6} for large values of the effective nuclear charge, the absolute value increasing with decrease in the effective nuclear charge, as a result of the greater contribution of large radii to $(\rho^2)_{av}$. The term in $\mathcal{H}'$ can be represented by means of the approximate second-order perturbation theory[6] as

$$\chi' = [(xp_y - yp_x)^2]_{00} / ((W_m)_{av} - W_0), \qquad (5)$$

in which the numerator represents the diagonal matrix element for the normal state under consideration, W_0 the energy of this state, and $(W_m)_{av}$ an average energy for significant excited states. It is found on evaluating this expression that it is small for reasonable values of the effective nuclear charge. However, this expression as well as that of Eq. (1) are rather sensitive to changes in the assumed wave functions, and there is little prospect at present of carrying out an accurate theoretical calculation of the susceptibility.

Condensed aromatic ring systems

We may now calculate the magnetic anisotropy of other aromatic hydrocarbons in the same way as for benzene, making the assumption that the $2p_z$ electrons are free to move under the influence of the impressed fields from carbon atom to adjacent carbon atom. Our problem is equivalent to that of calculating the magnetic effect of the currents induced in a conducting network. In benzene we have assumed the induced current to flow from atom to atom along circular arcs. In large condensed ring systems, such as graphite, the current would be assumed to flow along straight lines between adjacent atoms. In order to simplify the calculation we shall first consider rectilinear hexagonal nets, and then make a small correction by replacing the outermost lines by circular arcs. We assume in all cases that the electrons are uniformly distributed along the segments of the network, the linear density of electrons being σ.

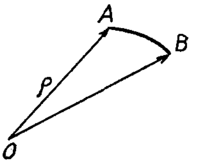

FIG. 1.

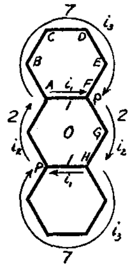

FIG. 2. Induced currents in anthracene.

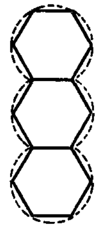

FIG. 3. Assumed path of induced currents in anthracene.

Let us consider anthracene as an example. One solution of Maxwell's equations corresponding to a magnetic field parallel to the z axis, with strength increasing linearly with the time, involves an electric field acting in a direction in the xy plane at right angles to the radius vector ρ measured from the z axis and with strength proportional to ρ. The integrated ponderomotive force for a segment AB of a conductor is accordingly proportional to the area swept out by the radius vector ρ, in this case OAB. Using as our unit the area of one-sixth of a carbon hexagon, the integrated ponderomotive forces for anthracene (Fig. 2) are $P_1 = 1$ (for the segment AF), $P_2 = 2$ (for FGH), and $P_3 = 7$ (for $ABCDEF$), with values for the other segments given by the center of symmetry of the molecule and field. In addition we must introduce an auxiliary potential at the junction F (relative to A) represented by the symbol p. The effective resistances of the circuits, arising from the inertia of the electrons, are proportional to the lengths of the segments, and have the values $R_1 = 1$, $R_2 = 2$, and $R_3 = 5$. We thus obtain the equations

$$i_1 = 1 - p,$$
$$2i_2 = 2 + p,$$
$$5i_3 = 7 - p$$

for the currents i_1, i_2, and i_3, together with the conservation equation

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[6] L. Pauling and E. B. Wilson, Jr., *Introduction to Quantum Mechanics*, Sec. 27e.

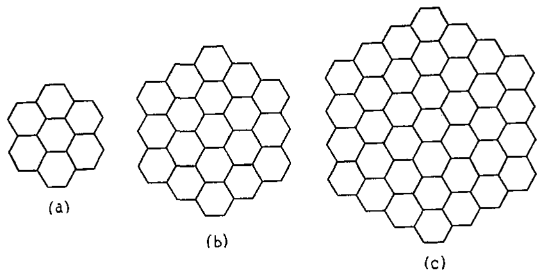

FIG. 4. The aromatic hydrocarbons (a) $C_{24}H_{12}$, (b) $C_{54}H_{18}$, and (c) $C_{96}H_{24}$.

$$i_2 = i_1 + i_3.$$

The values found on solution of these equations are $i_1 = 3/17$, $i_2 = 24/17$, and $i_3 = 21/17$. These correspond to a completed circuit i_1 about one hexagon and another completed circuit i_3 about three hexagons, the strength of the equivalent magnetic dipole being 66/17. A similar calculation for a benzene hexagon gives the value 1; the quantity $k = 66/17$ accordingly represents the relative strengths of the induced magnetic dipoles for the anthracene network of three hexagons and the benzene circuit of one hexagon, difference in the linear electron density σ being neglected.

To obtain the susceptibility difference ΔK we make the following calculation. For naphthalene and higher aromatic hydrocarbons the average C–C distance[7] is 1.41A, corresponding to $\Delta K = -38.0 \times 10^{-6}$ for a six-electron hexagon. In general we write for ΔK the expression

$$\Delta K = -38.0 \times 10^{-6} \times k\sigma f, \tag{6}$$

in which σ is the electron density per C–C bond and f a correction factor described below. Values of σ as well as of k are included in Table I; for anthracene, for example, σ has the value 14/16, there being 14 p_z electrons and 16 C–C segments in the network. The factor f is designed to correct for the assumption that the electrons move along rectilinear paths between the carbon atoms. In benzene we assumed the transit from atom to atom to be along circular arcs. For the condensed ring systems we may correspondingly replace the outermost rectilinear segments by circular arcs, as shown in Fig. 3 for anthracene. This introduces a correction[8] of 23 percent ($f = 1.23$), leading to $\Delta K = -159 \times 10^{-6}$ for anthracene. Table I includes the results of a similar treatment of several hydrocarbons.

In order to predict approximate values of the principal susceptibilities K_1 ($= K_2$) and K_3 ($= K_1 + \Delta K$) of these substances we may adopt the following empirical procedure. The molal susceptibility of H_2 is -4.00×10^{-6}; we accept -2.00×10^{-6} for H bonded to C. The atomic susceptibility of diamond is -6.00×10^{-6}; we accept this for aliphatic carbon. Now in the aliphatic carbon atom there are four L electrons contributing to the susceptibility in all directions, whereas in the aromatic carbon atom only three remain to be considered, the fourth being involved in the calculation of ΔK. For aromatic carbon, aside from the p_z electron, we accordingly assume the atomic susceptibility -4.5×10^{-6}. The principal susceptibilities of a hydrocarbon are thus given by the approximate expressions

$$K_1 = K_2$$
$$= -(2.0\, n_{\mathrm{H}} + 6.0\, n_{\mathrm{C}\ al} + 4.5\, n_{\mathrm{C}\ ar}) \times 10^{-6} \tag{7}$$

and

$$K_3 = K_1 + \Delta K, \tag{8}$$

TABLE I.

	σ	k	$-\Delta K \times 10^6$	$-K_1 \times 10^6$	$-K_3 \times 10^6$
Benzene, C_6H_6	1	1	49	39	88
Naphthalene, $C_{10}H_8$	10/11	12/5	104	61	165
Anthracene, phenanthrene, $C_{14}H_{10}$	7/8	66/17	159	83	242
Pyrene, $C_{16}H_{10}$	16/19	84/13	237	92	329
Naphthacene, chrysene, etc., $C_{18}H_{12}$	6/7	156/29	214	105	319
Triphenylene, $C_{18}H_{12}$	6/7	60/11	217	105	322
Perylene, $C_{20}H_{12}$	5/6	111/13	314	114	428
Picene, dinaphthanthracene, etc., $C_{22}H_{14}$	11/13	227/33	268	127	395
$C_{24}H_{12}$	4/5	52/3	572	132	704
$C_{54}H_{18}$	3/4	2667/29	2770	279	3050
$C_{96}H_{24}$	8/11	67333/227	8200	480	8680

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[7] L. Pauling, L. O. Brockway and J. Y. Beach, J. Am. Chem. Soc. **57**, 2705 (1935).

[8] The error introduced by using the values of relative currents for rectilinear segments is small.

TABLE II.

	Observed			Calculated	
	$-K_1\cdot 10^6$	$-K_2\cdot 10^6$	$-K_3\cdot 10^6$	$-K_1(K_2)\times 10^6$	$-K_3\cdot 10^6$
Benzene, C_6H_6	37	37	91	39	88
Durene, $C_{10}H_{14}$	77	86	141	79	128
Hexamethylbenzene, $C_{12}H_{18}$	101	103	164	99	148
Hexaethylbenzene, $C_{18}H_{30}$	165	165	231	159	208
Biphenyl, $C_{12}H_{10}$	67	67	175	74	172
Terphenyl, $C_{18}H_{14}$	98	98	260	109	256
Quaterphenyl, $C_{24}H_{18}$	129	129	345	144	340
1,3,5-Triphenylbenzene, $C_{24}H_{18}$	131	131	347	144	340
Fluorene, $C_{13}H_{10}$	73	73	194	80	178
Naphthalene, $C_{10}H_8$	39	43	187	61	165
Anthracene, $C_{14}H_{10}$	46	53	273	83	242
Phenanthrene, $C_{14}H_{10}$	74	74	240	83	242
Pyrene, $C_{16}H_{10}$	81	81	303	92	329
Chrysene, $C_{18}H_{12}$	88	88	306	105	319
1,2; 5,6-Dibenzanthracene, $C_{22}H_{14}$	110	110	358	127	395

in which n_{H}, $n_{\mathrm{C}\ al}$, and $n_{\mathrm{C}\ ar}$ represent the numbers of atoms of these kinds in the molecule.[9] Values calculated in this way are included in Tables I and II.

The hydrocarbons $C_{24}H_{12}$, $C_{54}H_{18}$, and $C_{96}H_{24}$ included in the table have the hexagonal symmetry D_{6h}, as shown in Fig. 4. It is interesting to note that the shape of the molecule has a large effect on the susceptibility; ΔK for the nearly circular molecule $C_{24}H_{12}$ is over twice that for the long molecules picene, etc. ($C_{22}H_{14}$), although the molecules differ only a little in composition. Pyrene (compared with naphthacene) shows the same effect. Aside from this, the configuration of the molecule is of little significance, the susceptibilities for isomers such as anthracene and phenanthrene being the same. Branching of the chain of benzene residues has a small effect (compare naphthacene and triphenylene).

Comparison with experiment

In Table II there are given the available experimental values of the principal susceptibilities of aromatic hydrocarbon molecules, from the papers of Krishnan and his collaborators.[1b, 1c, 10] It should be mentioned that in some cases the values have been obtained from crystal susceptibilities in a straightforward manner, with the use of the results of x-ray investigations of molecular orientations, but that in other cases the values given depend on various assumptions (such as that K_3-K_1 for phenyl and phenylene groups has the value found for benzene). It is seen that with certain exceptions mentioned below the observed and calculated values agree to within about 10 percent, the disagreement probably being due in part to experimental error and in part to theoretical inaccuracy.

The largest differences between calculated and observed values are shown by naphthalene and anthracene. I feel confident that the differences are due to errors in the reported experimental values, especially since good agreement between experiment and theory is found for phenanthrene.

The principal susceptibilities of graphite, per mole of carbon atoms, are reported[11] as $K_1=-5\times 10^{-6}$ and $K_3=-275\times 10^{-6}$. It is to be noted that the value of K_1 is less than for diamond (-6×10^{-6}), and agrees with our assumed value -4.5×10^{-6} to within the accuracy of its determination. The very large magnetic anisotropy of graphite shows that the p_z electrons are free to move over large areas of the hexagonal network of carbon atoms in the crystal. Extrapolating from the values of Table I, we find that molecules about 40A in diameter would have an anisotropy equal to that observed for graphite. It is interesting that the anisotropy and the average susceptibility of graphite are decreased by decreasing the size of the crystal grains.[12]

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[9] The expressions could probably be made more accurate by the introduction of various constitutive correction terms (such as corresponding to Pascal's system). At present it does not seem worth while to attempt to refine the simple and straightforward treatment given above.

[10] The values for hexaethylbenzene are those given by N. Ganguli, Zeits. f. Krist. **93**, 42 (1936), and for 1,2; 5,6-dibenzanthracene those given by K. S. Krishnan and S. Banerjee, Zeits. f. Krist. **91**, 173 (1935).

[11] K. S. Krishnan, Nature **133**, 174 (1934).

[12] S. Paramasivan, Ind. J. Phys. **4**, 139 (1929); K. S. Krishnan and N. Ganguli, Current Science **3**, 472 (1935).

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A THEORY OF THE COLOR OF DYES[1]

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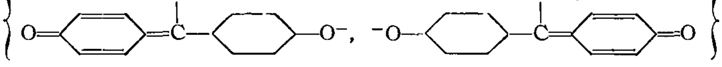
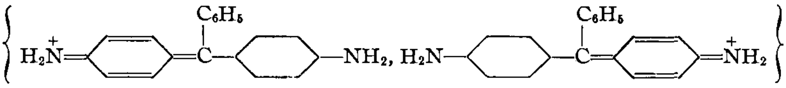
Communicated September 18, 1939

It has become recognized during recent years that the color of dyes is associated with the resonance of electric charge from atom to atom of the dye molecule.[2, 3, 4, 5, 6] Because of the complexity of the problem, however, it has not been easy to expand this idea into a theory of color permitting the rough quantitative calculation of the frequencies and intensities of the absorption bands of dyes. I have now developed a theory of this nature; the theory and some of the results of its application are described briefly in the following paragraphs.

The long-wave-length absorption band of a dye such as benzaurin or Döbner's violet has been associated with resonance of the type



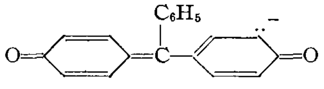
, benzaurin,



Döbner's violet;

the normal state involving the symmetric combination of the structures and the upper state their antisymmetric combination. It is obvious that many other structures are also involved, since the electrons have vanishingly small probability of jumping from one end to the other of a large molecule, but make the transit instead by moving from atom to adjacent atom.

There are two types of intermediate structures which need consideration for benzaurin, involving respectively a negatively charged carbon atom (for example, the structure



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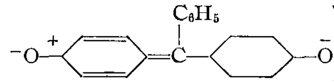
and a positively charged carbon atom (for example, the structure



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All of these structures would be considered in a complete treatment; in developing a theory with minimum complexity, however, we may ignore the more unstable structures. It is seen that the structures with negatively charged carbon are less stable than those with positively charged carbon for two reasons: the latter are stabilized by Kekulé resonance of one ring (the former by none), and the degree of electronegativity of carbon favors its assumption of a positive rather than a negative charge. We accordingly neglect structures of the first type, and consider only those of the second type, corresponding to *resonance of a positive charge about the molecule* (the motion of the positive charge from atom to atom resulting, of course, from an electron jump in the opposite direction).

To set up the secular equation the following assumptions are made:

(1) All structures with a given charge distribution may be combined to a resultant structure, with energy H_{ii} given by known values of resonance energies and bond energies.

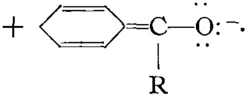
(2) The wave functions for these resultant structures are mutually orthogonal.

(3) The exchange integral H_{ij} between two resultant structures has the constant value ϵ if the structures differ through the motion of a charge from one carbon atom to an adjacent carbon atom (or slightly different values for C—O, C—N, etc.); for two structures differing by larger motion of the charge H_{ij} is negligibly small.

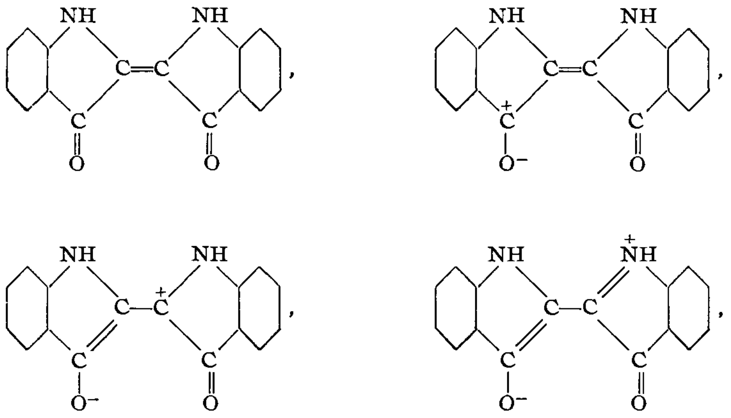
A secular equation set up in this way is similar in form to that obtained in the molecular-orbital treatment; it differs from the latter in respect to the interpretation of the exchange integrals and the variation in H_{ii} values. Each root of our equation represents an energy level of the molecule, whereas in the molecular-orbital treatment sums of roots are taken to obtain the molecular energy levels.

The value of the integral ϵ has been determined empirically by use of the frequency of the strong absorption band of the triphenylcarbonium cation. Using this, other energy quantities can be evaluated from the absorption frequencies for other molecules.

It is found that the Coulomb energy of a resonating charge with other charges in the molecule plays an important part in determining the energy levels and absorption frequencies. It has been recognized[7] that the absorption spectra of various substances with symmetrical molecules, such as the sulfonephthaleins R—T—R (with R = O, OH, NH_2, etc., and T = $—C_6H_5—C(C_6H_4SO_3H)—C_6H_5—$), are closely similar, whereas the related substances with unsymmetrical molecules R—T—R′ have spectra of a different type. It is found on calculation with the Coulomb energy terms ignored that the symmetrical and unsymmetrical molecules should give rise to similar spectra. The existence of two types of spectra results from the action of the Coulomb energy. In the symmetrical cation $[HO—T^+—OH]^+$ the positive charge moves freely, and in the corresponding anion $[^-O—T—O^-]^-$ the Coulomb energy remains nearly constant as the positive charge moves about in the molecule, because withdrawal from one O^- accompanies approach toward the other; hence there is close similarity in the spectra of these ions. In the unsymmetrical molecule $^-O—T^+—OH$, however, the Coulomb energy causes a pronounced change in the positions of the energy levels and the nature of the spectrum.

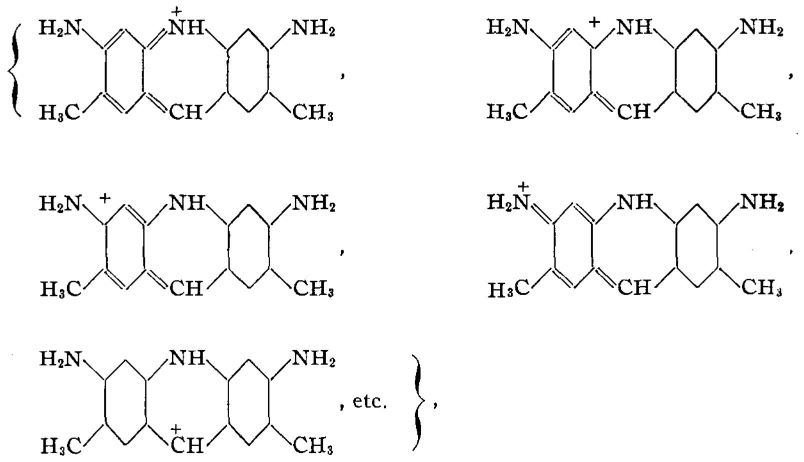
The carbon-oxygen double bond in all ketones involves resonance of the structures $R_2C::\ddot{O}:$ and $R_2\overset{+}{C}:\underset{..}{\ddot{O}}:^-$. For substances such as acetophenone, benzophenone, phorone, etc., in which the carbonyl bond is conjugated with an unsaturated or aromatic group, resonance with other structures occurs, such as  This deepens the color of the substance, the carbonyl absorption being shifted from the ultraviolet to the visible region of the spectrum. The bathochromic effect of the conjugation is limited by the Coulomb energy of separating the charges in the molecule; in a proton-donating solvent such as concentrated sulfuric acid the energy of separation of the charges is decreased by the field of the environment, and the color becomes deeper.

In a great many dyes, including benzaurin, discussed above, it is the carbonyl group which is the source of the resonating charge; indigo may be mentioned as an additional example, with many structures contributing, such as



and many others, including those in which both carbonyl groups are ionized. The —N=O, $-\overset{+}{N}\begin{matrix}\nearrow O\\ \searrow O^-\end{matrix}$ and —N=N— groups play a similar rôle for the nitroso, nitro, and azo dyes, respectively.

The resonating positive charge in Döbner's violet is formed not by internal ionization but rather by external ionization. Other colored cations of this general type are numerous; the cation of acridine yellow, for example, can be ascribed the structure

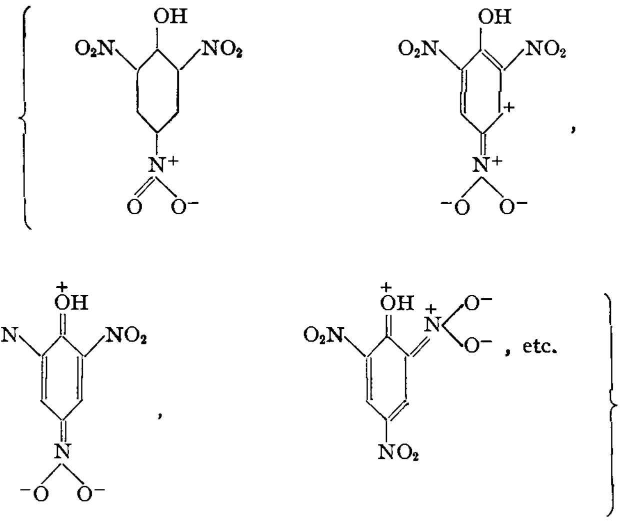


and similar structures can be written for the pyridine, quinoline, azine, oxazine, thiazine, and carbocyanine dyes, and many others

The theory permits quantitative predictions to be made regarding the intensities of absorption bands. The band of longest wave-length, representing the transition from the normal state with nodeless wave function (describing the position of the resonating charge) to the excited state with a wave function (or two wave functions, in case of degeneracy) with a single nodal plane, is predicted to be the most intense band for many dyes. (A similar result has been found for conjugated double-bond systems by Mulliken[6] by application of the molecular-orbital treatment.) The agreement between predicted and observed values of the integrated absorption coefficient is good.

The arguments given above to show that even in anions such as the benzaurin anion it is a positive charge rather than a negative charge which carries on the principal resonance about the molecule are not universally applicable. Thus in the triphenylmethyl anion, $[(C_6H_5)_3C]^-$, the negative charge is expected to move from atom to atom in very nearly the same way as the positive charge in the triphenylcarbonium cation, $[(C_6H_5)_3C]^+$. It is observed that the spectra of the anion and the cation are similar, but not identical.

In an aromatic nitro compound such as picric acid resonance of the type



is expected, giving rise to the color of the substance. The aromatic hydrocarbons have large polarizabilities in the planes of their molecules, because of the mobility of the p_z electrons. Hence an aromatic hydrocarbon molecule lying parallel to a molecule of picric acid or a similar substance at the minimum distance of approach (about 3.5 Å) would stabilize the structures with separated charges in the picric acid molecule by effectively increasing the dielectric constant in the expression for the Coulomb energy. (The orientation of permanent dipole molecules would not in general contribute to this effective dielectric constant, because of the high frequency of the charge-resonance; the effective orientation of the surrounding dipoles would be produced only by the average rather than the instantaneous dipole moment of the central molecule. Hence large electronic polarizability of surrounding molecules is needed to produce the effect under discussion.) This would deepen the color of the picric acid. In addition it gives rise to an interaction potential between the picric acid molecule and the hydrocarbon molecule corresponding to attraction and formation of a bond with energy of the order of magnitude of 2 kcal./mole, as observed for molecular compounds of this type. We conclude that of the many possible explanations which have been suggested for molecular compounds of this sort[8] the polarization theory in the form described above is the probably correct one.[9]

Detailed accounts of the application of the theory of color to specific problems, including the methods of formulation and solution of the equations giving the energy levels and wave functions, will be published elsewhere.

I am indebted to Dr. S. Weinbaum, Dr. B. Hicks, Dr. D. P. Stevenson, and Mr. P. A. Shaffer, Jr., for assistance with the calculations, and to Dr. G. Schwarzenbach and Dr. L. G. S. Brooker for encouragement in this attack on the problem of the color of dyes.

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A THEORY OF FERROMAGNETISM

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The properties of ferromagnetic substances are in reasonably good accord with the theory of Weiss.[1] In this theory it is postulated that the atomic magnets tend to be brought into parallel orientation not only by an applied magnetic field but also by an inner field which is proportional to the magnetization of the substance. The inner field is not due to magnetic interaction of the magnetic moments of the molecules, but to electrostatic interactions, which are related to the orientation of the magnetic moments of electrons through the Pauli principle. During the past twenty-five years many efforts have been made to develop a precise theory of the interactions that produce the inner field, and to account in this way for the observed magnetic properties of ferromagnetic substances, but these attempts have not been successful—no one has published a theory of the electronic structure of ferromagnetic substances that permits reasonably good predictions to be made of the values of the saturation magnetic moment and the Curie temperature.

I have now formulated a theory of ferromagnetism that seems to provide a simple explanation of the phenomenon. In the following paragraphs it is shown that the straightforward application of the theory to iron leads, with use only of spectroscopic data for the iron atom, to the predicted values 2.20 Bohr magnetons for the saturation magnetic moment per iron atom and 1350° K for the Curie temperature; these values are in reasonable agreement with the experimental values, 2.22 magnetons and 1043° K, respectively.

The theory can also be applied to cobalt and nickel, and to alloys. In this application, however, a complicating factor must be considered—

the contribution of two different values for the atomic magnetic moment. Satisfactory agreement between theory and experiment is obtained when the ratio of contributions of the two atomic moments has the value assigned to it in a discussion of the electronic structure of these metals that was published fifteen years ago.[2]

The Nature of the Theory.—In discussion of the transition metals the electrons may be divided into two classes, the conduction electrons and the atomic electrons. The conduction electrons are the electrons for which the exchange integrals between adjacent atoms are large, and the atomic electrons are the electrons for which the exchange integrals are small. Some investigators have thought that the electrons occupying $4s$ and $4p$ orbitals comprise the conduction electrons, and those occupying the $3d$ orbitals (plus those in inner shells) comprise the atomic electrons. The first quantum mechanical theory of ferromagnetism is that of Heisenberg.[3] It was shown through the work of Hund, Heitler and London, and others that the exchange integral between electrons with antiparallel spin on the same atom usually has positive sign, whereas that between electrons with antiparallel spin on different atoms has negative sign. In consequence, atomic electrons align their spins parallel, to the extent permitted by Pauli's principle. Moreover, it would be expected that atoms that have a magnetic moment, because of the presence of one or more unpaired electrons on each atom, would tend to align their moments antiparallel. The atomic moments of atoms in a crystal would then tend to divide into two classes, such that the moments of the neighbors of each atom are oriented antiparallel to the moment of that atom. This would give rise to antiferromagnetism (when the moments of the two kinds of atoms are equal) or to ferrimagnetism (when the moments are unequal). Heisenberg assumed, in order to account for the phenomenon of ferromagnetism, that under certain circumstances the exchange integrals of electrons with antiparallel spins on adjacent atoms are positive; the atomic moments would then tend to line up parallel to one another. Heisenberg's theory is unsatisfactory in that there is no independent evidence in support of the assumption that exchange integrals between atoms are ever positive; this remains an *ad hoc* assumption. Moreover, the theory does not provide a reasonable explanation of the observed values of the saturation magnetic moment.

A somewhat different suggestion about the origin of ferromagnetism was made by Bloch.[4] The conduction electrons usually occupy the low levels of a conduction band of orbitals in pairs, with opposed spins. Pauli[5] pointed out that at temperature equilibrium a few of the pairs, occupying the uppermost levels, would be uncoupled by thermal agitation, one of the electrons being raised to a slightly higher level. These uncoupled electrons could then orient themselves independently in a magnetic field; Pauli in this way explained the temperature-independent paramagnetism observed for the alkali metals and some other metals. Bloch observed that under some circumstances (proper ratio of exchange integrals to the density of states in energy) the exchange energy of the conduction electrons could accomplish some uncoupling, producing a set of conduction electrons occupying separate orbitals, and with parallel spins. The theory has been discussed further by Slater,[6] who has suggested that a rather weak interaction between 3*d* orbitals on adjacent atoms would give rise to a narrow band of levels, with high density of states in energy, and that the conditions for ferromagnetism might be satisfied in this way. In order to account for the observed moment 2.22 magnetons per atom for iron, the assumption is made that 0.22 electron per atom is transferred from the 3*d* orbitals to the 4*s* orbital, constituting the main conduction band; the atomic moment is then ascribed to the hole of 2.22 unoccupied orbitals of the 3*d* subshell, which contains 5.78 electrons.

Recently it was pointed out by Zener[7] that the atomic moments, in parallel orientation, might react with the electrons in the conduction band in such a way as to uncouple some of the pairs, producing a set of conduction electrons occupying individual orbitals, and with spins parallel to the spins of the atomic electrons. Zener assumed that the conduction band for the transition metals is formed by the 4*s* orbitals of the atoms, and that there is somewhat less than one conduction electron per atom in iron, cobalt, and nickel. Like Slater, he attributed the atomic magnetic moments to the partially filled 3*d* subshell.

The new theory is based upon the assumption that there are about six conduction electrons per atom in the transition metals. In the first discussion of the new metallic valences[2] the value 5.78 was assigned as the normal metallic valence of the atoms chromium, manganese, iron, cobalt, and nickel. This value was obtained by subtracting from the total number of outer electrons of iron (eight electrons, outside of the argon shell) the number 2.22 of unpaired electrons, as indicated by the value 2.22 for the saturation magnetic moment of iron. It now seems probable that the valence is equal exactly or nearly exactly to six. In the resonating-valence-bond theory of metals[8] it is assumed that the 3*d*, 4*s*, and 4*p* orbitals of an atom hybridize to form bond orbitals, which are combined with bond orbitals of other atoms in the crystal, with use of Bloch functions, to produce orbitals that are occupied by electron pairs. These orbitals are closely similar to those used for occupancy by single electrons or by two electrons with opposed spins in the usual electron theory of metals. It might be expected that as many atomic orbitals could be combined in this way into orbitals for conduction electrons (bonding electrons) as satisfy the criterion of large overlapping, characteristic of good bond orbitals.[9] The best bond orbital that can be formed from

$3d$, $4s$, and $4p$ orbitals is a $3d^5 4s 4p^3$ orbital, for which the bond strength has value 3.000. Two equivalent orbitals orthogonal to the first one can be constructed. It has been found that a fourth, a fifth, and a sixth of nearly equal strength can also be made, but that a seventh orbital, orthogonal to the other six, is a much poorer bond orbital. Hence it seems not unreasonable to assume that only six bonds will be formed by an atom in a metal, and that the remaining orbitals may be occupied by electrons which interact only weakly with electrons on other atoms.

In iron, cobalt, and nickel there are some unpaired atomic electrons, giving rise to an atomic magnetic moment. There are also six electrons per atom which occupy a conduction band—these are the valence electrons. It is assumed that the direct interaction of the atomic electrons on neighboring atoms is small, and that the exchange integral is, as is customary, negative. If this interaction is larger than the interaction with the conduction electrons, which will be discussed immediately, the moments on adjacent atoms will tend to align themselves in the antiparallel orientation, and the substance will be antiferromagnetic. If the direct interaction energy of the moments is smaller than the possible interaction energy with the conduction electrons, however, the substance will be ferromagnetic.

The conduction electrons occupy metallic orbitals which are formed by linear combination of atomic bond orbitals, which are *dsp* hybrids. A metallic electron, which may be considered to move from atom to atom through the crystal, interacts with the electrons producing the atomic moment of each atom to the extent that a bond orbital of the atom contributes to the metallic orbital. The exchange integral for the interaction is positive in sign, according to Hund's principle, and the interaction results in stabilization if the spin of the metallic electron is parallel to the atomic moment, and in destabilization if the spin is antiparallel. There is, then, the possibility of stabilization of the metal crystal if the atomic moments are aligned parallel to one another, and a significant number of metallic electrons, occupying separate metallic orbitals, align themselves with spins parallel to the atomic moments. If the energy of interaction of a metallic electron with an atomic moment is $-\epsilon$ for parallel spin and $+\epsilon$ for antiparallel spin, the width of the conduction band, at the top of the doubly occupied conduction levels, that can be occupied by single electrons, with parallel spin, will be equal to 2ϵ. The energy of uncoupling the first pair of electrons (occupying the topmost level) is zero, so that a gain in stabilization through the change in energy -2ϵ will be achieved by uncoupling this pair of electrons. The gain in energy for the last pair is, however, zero, and the average change in energy is $-\epsilon$ per electron pair, or $-\epsilon/2$ per electron. If n conduction electrons are thus uncoupled, the ferromagnetic crystal will be stabilized through this interaction by the energy change $-n\epsilon/2$. The energy required to reverse the direction of an atomic moment is equal to $2n\epsilon$; accordingly the energy of interaction of the atomic moments and the uncoupled conduction electrons acts in the way corresponding to a Weiss field.

Quantitative calculations can be made on the basis of the assumption that the density of levels in energy for the conduction band is given by the simple expression for the free electron in a box, and the interaction energy ϵ of a *dsp* hybrid conduction electron and the atomic moment can be calculated from the spectroscopic values of the energy of interaction of electrons in the isolated atom. The results of this calculation for iron are discussed in the following section.

Application of the Theory to Iron.—We assume, in essential accordance with earlier conclusions,[2, 8] that six of the eight outer electrons of the iron atom are valence electrons, occupying d^3sp^2 orbitals, and the remaining two are atomic electrons.

The electron configuration of the atom in the metal is accordingly assumed to be $3d^54s4p^2$. This assumption differs considerably from the usual assumption that the electron configuration is close to $3d^8$—for example, Slater's assumption that the configuration is $3d^{7.78}4s^{0.22}$. It is interesting to note, however, that the normal state[10] of the isolated iron atom is not based on the configuration $3d^8$ but on the configuration $3d^64s^2$; its Russell-Saunders symbol is ^5D. The first excited state is $3d^74s\ ^5F$, and the third configuration to appear, with increasing energy, is $3d^64s4p$. There are, in fact, twenty-eight Russell-Saunders states that appear in the FeI spectrum below the first state, $3d^8\ ^3F$, that is assigned to the configuration $3d^8$. The spectroscopic data indicate that the $4s$ atomic orbital is more stable than the $3d$ orbital by about 1.2 ev, and that the energy of a $4p$ electron is only about 1.4 ev greater than that of a $3d$ electron. The configuration $3d^54s4p^2$ accordingly lies about 4 ev above the normal configuration, $3d^64s^2$, and only 1.6 ev above the configuration $3d^8$. The bond energy of six valence electrons can, of course, easily effect the promotion to the assumed configuration $3d^54s4p^2$.

The exchange energy $-\epsilon(4s, 3d)$ of a $4s$ electron and a $3d$ electron with parallel spin can be calculated from the separation of the states $3d^74s\ ^5F$ and $3d^74s\ ^3F$. The separation of these states (averaged over the levels with different values of total moment J) is 4947 cm^{-1}. In the ^5F state the $4s$ electron has spin parallel to the spins of three $3d$ electrons, and in the ^3F state it has spin antiparallel to the spins of these three $3d$ electrons. The value of the exchange energy per electron is accordingly $-4947/6 = -825$ cm^{-1}. For $-\epsilon(3d, 3d)$ one sixth of the difference in energy of $3d^64s^2\ ^5D$ and $3d^64s^2\ ^3D$ was used; its value is -4826 cm^{-1}. The evaluation of $-\epsilon(4p, 3d)$ as -470 cm^{-1} is similar, although somewhat less straightforward, because it involves averaging over a number of Russell-

Saunders states. Assuming that the valence electrons at the top of the band have the average hybrid character $3d^3 4s4p^2$, the interaction energy of one of these valence electrons and an atomic electron, assumed to be approximately a $3d$ electron, is found to be -2707 cm^{-1}, or -0.334 ev, with probable error about 10%.

The interaction energy of the valence electron with the two atomic $3d$ electrons, with parallel spins, is accordingly -0.67 ev, and the width of the energy band that would be occupied by uncoupled valence electrons is 1.34 ev. The number of orbitals in this band can be calculated from the equation for the distribution of energy levels for an electron in a box. The number of levels per atom is

$$n_0 = 4\pi V (2m)^{3/2} E^{3/2}/3h^3,$$

where V is the atomic volume, m is the mass of the electron, E is the kinetic energy of the electron, and h is Planck's constant. For iron, with $V = 11.72 \times 10^{-24}$ cm^3, and six electrons per atom, which can occupy three orbitals, in pairs, the value of E, the energy of the top level occupied by conduction electrons if they are all paired, is calculated to be 23.3 ev. Differentiation of this equation leads to the equation

$$dn = 2\pi V (2n)^{3/2} E^{1/2} dE/h^3$$

as the number of levels dn with the width in energy dE. Substitution of the value 1.34 ev for dE leads to the value 0.26 for dn. Accordingly we predict that 0.26 of the conduction electrons will be uncoupled by interaction with the atomic moments, and will align themselves parallel to these moments.

The experimental values of the gyromagnetic ratio and the observed magnetic moments for paramagnetic compounds of transition metals show that the orbital moment is nearly completely quenched. On multiplying 2.26 by the ratio 1.946/2.000 of the gyromagnetic ratio to the spin value, the predicted value of the saturation magnetic moment per atom for iron is obtained as 2.20 magnetons, in excellent agreement with the experimental value, 2.22 magnetons.

The calculated energy of interaction of an atomic moment and the Weiss field (0.26 uncoupled conduction electrons per atom) for magnetic saturation is 0.135 ev, or 3070 cal. mole^{-1}. According to the Weiss theory the Curie temperature is equal to this energy of interaction divided by $3k$, where k is Boltzmann's constant. The effect of spatial quantization of the atomic moment, with spin quantum number S, is to introduce the factor $(S + 1)/S$; that is, the Curie temperature is equal to $n\epsilon(S + 1)/3Sk$. For iron, with $S = 1$, the predicted value for the Curie constant is 1350°K, in rough agreement with the experimental value, 1043°K.

Cobalt and Nickel.—The discussion of the magnetic properties of cobalt and nickel is somewhat more complicated than that for iron, because of the necessity of giving consideration to the metallic orbital. It has been pointed out[8] that on the basis of the resonating-valence-bond theory of metals a metallic structure, showing large electronic conductivity, can occur only if many of the atoms in the metal have available one orbital not ordinarily occupied by an electron; this orbital can act as receptor for an additional electron, permitting the unsynchronized resonance of the shared electron pairs in the metal. When the metallic orbital is occupied by an electron the atom has a negative charge, and another atom in the metal has a positive charge; it is the motion of these negative charges and positive charges through the metal that gives rise to electronic conduction. (A discussion of the relation between metallic conductivity and negatively charged and positively charged atoms in the metal on the basis of the conventional electronic theory of metals has been given by Slater.)[11] An atom of cobalt, with six valence electrons and three atomic electrons, essentially $3d$ electrons, can have the spins of the atomic electrons parallel by utilizing all of its orbitals; a metallic orbital is made available only if two of the atomic electrons have opposed spins. The metal can be described as having some atoms with resultant spin quantum number 3/2 and some atoms with spin 1/2. In the same way the atom of nickel can be described as having some atoms, without a metallic orbital, with spin 1 and some atoms, with a metallic orbital, with spin 0. The number of atoms without a metallic orbital has been estimated[8] to be 28%. In the following calculations we use the value 28.5%, which is obtained from the value 28.57 for the electron number that marks the upper boundary of the ferromagnetic region, as given by the intercept of the curve of values of saturation magnetic moment corrected by extrapolation for isoelectronic sequences to the value 0°K for the Curie temperature (Taglang).[12]

With this assumption and use of the value 1.94 for the g-factor the average magnetic moment per atom of cobalt is calculated to be 1.52 magnetons. The spectroscopic data for cobalt do not provide very reliable values for the interaction energies of $3d$, $4s$, and $4p$ electrons. The data for chromium and manganese, when compared with those for iron, indicate that the interaction energies increase by 5% with unit increase in the atomic number. We accordingly use the value 0.70 ev for ϵ, which leads to 0.20 uncoupled valence electrons per atom. The predicted saturation magnetic moment for cobalt is thus 1.72 magnetons, in good agreement with the experimental value 1.71 magnetons. The value of the Curie temperature is calculated with use of the average value of the magnetic moment per atom and the average value of $(J + 1)/J$ to be 1190°K, which is somewhat smaller than the experimental value 1393° K.

In nickel 28.5% of the atoms, without a metallic orbital, have two atomic electrons with parallel spins, and magnetic moment 1.94 (corresponding to $J = 1$, with $g = 1.94$). The value of the interaction energy ϵ is 0.74 ev, and the calculated number of uncoupled valence electrons per atom is 0.064. The saturation magnetic moment per atom is thus calculated to be 0.617, in good agreement with the observed value 0.606 magnetons. The calculated value of the Curie temperature, 367° K, is considerably smaller than the observed value, 631° K.

For alloys of iron, cobalt, nickel, and copper the calculated values of saturation magnetic moments agree closely with the observed values; in particular, the maximum value of about 2.48 magnetons at electron number about 26.3 is reproduced by the theory. There is, however, only rough agreement between the observed and calculated values of the Curie temperature.

An obvious refinement of the simple theory for cobalt and nickel and their alloys can be made which leads to a significant increase in the calculated value of the Curie temperature. The foregoing calculation for nickel, for example, is based upon the assumption that the uncoupled valence electrons spend equal amounts of time on the nickel atoms with $J = 1$ and the nickel atoms with $J = 0$. However, the stabilizing interaction of the spins of the valence electrons and the parallel atomic moments would cause an increase in the wave function for the valence electrons in the neighborhood of the atoms with $J = 1$ and the parallel orientation. This effect also produces a change in the shape of the curve of saturation magnetization as a function of temperature. The details of this refined theory will be published later.

The simple theory accounts for the deviation of the slope of the curve of saturation magnetic moment against average electron number from the values $+1$ and -1 by about 10% as resulting from an induced moment contributed by the conduction electrons. This explanation was suggested and given empirical support by Forrer[13] and Taglang.[12]

Gadolinium.—For gadolinium the saturation magnetic moment is 7.12 magnetons and the Curie temperature is 290° K.[14] There is little doubt that three of the ten outer electrons of gadolinium are valence electrons and the other seven are atomic electrons occupying $4f$ orbitals, with spectroscopic state ^8S. These seven atomic electrons would give rise to the magnetic moment 7.00 magnetons, and the small increment may be attributed to uncoupled valence electrons.

Spectroscopic data are not available to permit an independent estimate of the magnitude of the interaction energy of a valence electron and the seven atomic electrons. If we assume the value 0.31 ev for this quantity, ϵ, the calculated value of the Curie temperature, 290° K, is equal to the observed value, and the calculated value of the saturation magnetic moment, 7.19 magnetons, is slightly greater than the observed value, 7.12. The small disagreement might be explained as resulting from a small contribution of orbital moment, reducing the g-factor from 2 to 1.98; the value 1.95 ± 0.03 for the g-factor has been reported from microwave resonance absorption measurements of gadolinium metal in the paramagnetic region.[15]

Other Interactions.—In the foregoing calculations the direct exchange interactions of the atomic electrons on neighboring atoms have been neglected. These exchange interactions are expected in general to tend to cause the atomic moments on adjacent atoms to align themselves in the antiparallel orientation. If these interactions and other interactions (such as those involving an unsymmetrical distribution of the electrons in an electron-pair bond between adjacent atoms) are less important than the interactions that stabilize the parallel orientation of the atomic moments the substance will be ferromagnetic at low temperatures, and the value of the saturation magnetic moment will be that calculated by the above methods. However, the neglected interactions, although they are not expected to change significantly the saturation magnetic moment, could have a large effect on the calculation of the Curie temperature.

It has been pointed out by Bozorth[16] that not all of the alloys of the iron-group transition metals have ferromagnetic saturation moments that correspond to the simple theory of six valence electrons and 0.715 metallic orbital per atom. It is likely that the exceptional alloys show ferrimagnetism or antiferromagnetism—that in these alloys the interactions that stabilize antiparallel orientation of the moments of adjacent atoms are stronger than those favoring parallel orientation. Until these interactions have been subjected to quantitative treatment the theory of ferromagnetism, ferrimagnetism, and antiferromagnetism will remain incomplete.

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THE NATURE OF BOND ORBITALS AND THE ORIGIN OF POTENTIAL BARRIERS TO INTERNAL ROTATION IN MOLECULES

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Twenty years ago Kemp and Pitzer[1] discovered that the relative rotation of the two methyl groups about the carbon-carbon bond in ethane is not completely free but is restricted by a potential barrier about 3.0 kcal/mole high, with three maxima and three minima in a complete rotation, corresponding to the trigonal symmetry of the methyl groups. It was soon found that rotation about single bonds is restricted in many molecules, and many experimental values for the height of the potential barrier have been obtained by the analysis of thermodynamic quantities (entropy, heat capacity) and especially by the methods of microwave spectroscopy.

Progress has been slow in the development of a satisfactory theory for the potential barriers, despite the efforts of several investigators. The theoretical attack was begun by Eyring,[2] who made approximate quantum-mechanical calculations of the interactions of the hydrogen atoms of the two methyl groups. The various suggestions and calculations about the importance of van der Waals repulsion between attached groups, electrostatic interactions of the charge distributions in the bonds between the two carbon atoms and the attached groups, and intrinsic lack of cylindrical symmetry in the axial chemical bond itself have been summarized recently by Wilson,[3] who tested these hypotheses by comparison with the values of the potential barriers that have been determined experimentally and reached the conclusion that the potential barriers to internal rotation "must in some way be an inherent property of the axial bond itself and not due in any substantial measure to direct forces between the attached atoms or those parts of the electron distribution which are out on the attached bond any considerable distance." References to the earlier theoretical papers and to the sources of most of the values of potential barriers mentioned later in this paper are given by Wilson.

I have developed a simple theory of these potential barriers, described in the following paragraphs. According to this theory, the potential barriers are not a property of the axial bond itself, but result from the exchange interactions of electrons involved in the other bonds (adjacent bonds) formed by each of the two atoms, as determined by the overlap between the parts of the adjacent bond orbitals that extend from each of the two atoms toward the other.

Concentration of Bond Orbitals.—The four bonds formed by a carbon atom can be discussed with use of tetrahedral orbitals formed by hybridization of the *s* orbital and the three *p* orbitals of the neon shell.[4, 5] The description of these orbitals as sp^3 tetrahedral orbitals is, however, only a first approximation. Even for the hydrogen atom, for which the 1*s* orbital is far more stable than any other orbital, hybridization occurs on bond formation. This effect has been described[5] as *concentration* of the bond orbitals. For example, in the approximate variation treatment of the hydrogen molecule by Wang[6] and the corresponding treatment of the hydrogen molecule-ion by Finkelstein and Horowitz,[7] use is made of an orbital that has the form of a 1*s* orbital but with changed effective nuclear charge, found by minimization of the energy to be 1.17 and 1.23, respectively. The change in the value of the effective nuclear charge is equivalent to hybridizing the 1*s* orbital of the hydrogen atom with the 2*s*, 3*s*, and higher orbitals, including *s* orbitals in the continuum. These higher *s* orbitals make a total contribution of 2 per cent to the hybrid bond orbitals. Also, a significant improvement in the approximate wave function can be obtained by adding to the *s* orbital a term containing a cosine function, which we may describe as a *p* orbital. This *p* term is a hybrid of 2*p*, 3*p*, and higher *p* orbitals. The effective nuclear charge that minimizes the energy is about twice that for the *s* orbital, leading to approximately the same spatial extent. It was shown by Rosen[8] for the hydrogen molecule and by Dickinson[9] for the hydrogen molecule-ion that the energy is minimized when the *p* terms occur in the wave function with coefficients 0.10 and 0.15, respectively, corresponding to 1 and 2 per cent of *p* character in the hybrid orbitals. These amounts of *p* hybridization are found, despite the fact that the promotion energy for the *p* terms is about 330 kcal/mole, slightly larger than the ionization energy of the hydrogen atom, 313 kcal/mole. The promotion energy for the higher *s* terms is also about 330 kcal/mole. (I am indebted to Dr. Brian Gray for carrying out the expansions of the wave functions in the set of hydrogen-atom functions with effective nuclear charge unity, and evaluating the promotion energies.)

We may accordingly expect that the bond orbitals of the carbon atom will be found on careful examination to be hybrids with some *d*, *f*, etc., character, in addition to the main sp^3 tetrahedral character. A rough estimate of the contributions of *d* and *f* terms to the hybrid bond orbital can be made by assuming the bond energy to be proportional to the strength of the bond orbital, as determined by the angular distribution,[5] and taking the promotion energy for both *d* and *f* as equal to the ionization energy of the carbon atoms. This calculation leads to coefficients approximately 0.15 for both the *d* term and the *f* term, corresponding to about 2 per cent *d* character and 2 per cent *f* character in the tetrahedral orbitals.

The calculation is made in the following way. The bond orbital is taken to be

$$\Psi = \alpha s + \beta p_z + \gamma d_z + \delta f_z, \qquad (1)$$

in which s, p_z, d_z, and f_z are the orbitals with maximum values along the z-axis (the bond direction); normalized to 4π, their angular parts are

$$\begin{aligned} s &= 1, \\ p_z &= \sqrt{3}\cos\theta, \\ d_z &= \sqrt{5/4}\,(3\cos^2\theta - 1), \\ f_z &= \sqrt{7/4}\,(5\cos^3\theta - 3\cos\theta) \end{aligned}$$

The value of this function in the bond direction, called the "strength of the bond orbital," is

$$S = \alpha + \sqrt{3}\beta + \sqrt{5}\gamma + \sqrt{7}\delta \qquad (2)$$

The effective bond energy is assumed to be the product of S and a bond-energy parameter b, corrected by subtracting the terms $\gamma^2 P_d$ and $\delta^2 P_f$, in which P_d and P_f are the promotion energies for the d and f terms:

$$\text{Bond energy} = bS - \gamma^2 P_d - \delta^2 P_f \qquad (3)$$

The value of b is taken to be 36 kcal/mole, which leads to bond energy 82 kcal/mole, corresponding to an average bond formed by a carbon atom (C—C, 82.3; C—H, 99.6; C—O, 81.0; etc.). The promotion energies are taken to be $P_d = 300$ kcal/mole and $P_f = 350$ kcal/mole, somewhat larger than the ionization energy of carbon, 260 kcal/mole, as indicated by consideration of the energies of the lowest s, p, d, f Epstein functions for the hydrogen atom.[10] In accordance with the minimum-energy theorem of quantum mechanics, we vary the parameters γ and δ to make the bond energy a maximum. (A satisfactory approximation is to take $\alpha = {}^1/_4$; then $\beta^2 = {}^3/_4 - \gamma^2 - \delta^2$.) It is found that both γ and δ then have the value 0.15, with $\beta = 0.84$, and the bond orbital has the simple angular dependence

$$\psi = 0.33 + 0.85\cos\theta + 0.50\cos^2\theta + \cos^3\theta \qquad (4)$$

This function has a maximum value (bond strength) of 2.68, which is 34 per cent greater than for an sp^3 orbital—a large effect of 2.25 per cent d character and 2.25 per cent f character. The nodal cone lies at 113.8° from the bond direction, only slightly shifted from the sp^3 value 109.5°. The negative lobe contains 7 per cent of the distribution function ψ^2, considerably less than the 11 per cent for sp^3 orbitals. The value of the function is larger than that of the sp^3 tetrahedral orbital from the bond axis out to 44°, and then becomes smaller, being about two-thirds as great (less than half the electron density) from 65° to 140°. The concentration of the orbital in the bond direction is well described by the average value of $\cos\theta$ (weighted with the distribution function ψ^2), which is 0.771 for function 4, and only 0.312 for an sp^3 orbital.

The hybrid orbital has cylindrical symmetry, and accordingly the introduction of d character and f character in the axial bond itself does not lead to an interaction dependent on the relative azimuthal orientation of the two groups.

The Interaction of the Concentrated Hybrid Orbitals.—The interaction of the two electrons occupying one adjacent bond orbital of each of two atoms forming an axial bond can be discussed by expanding the adjacent bond orbitals in terms of orbitals described with reference to the axial bond direction, which may be taken as the z-axis. The interaction energy of these two electrons (which with two other electrons, on adjacent atoms, form bonding electron pairs) includes the resonance integral[11] with the coefficient $-1/2$ (rather than the $+1$ that occurs in the energy for a bond), and accordingly the negative sign of the resonance integral itself leads to repulsion between the two electrons and maximum stability when the overlapping is a minimum. In the expansion in functions about the bond direction there will occur σ terms (independent of the azimuthal angle φ), π terms (with factor $\cos \varphi$ or $\sin \varphi$), δ terms ($\cos 2\varphi$), and ϕ terms ($\cos 3\varphi$). The interaction of two functions with σ and ϕ character gives rise to an interaction energy proportional to $\cos 3\varphi$, where φ represents the relative azimuthal orientation of the two groups. This is the term of lowest order that occurs if one of the groups has trigonal symmetry (such as the methyl group).

A very rough estimate of the height of the potential barrier may be made. The f term in an adjacent bond orbital as given in equations (1) and (4), which has its axis in a direction 70.5° from the z-axis determined by the axial bond, can be expanded in terms of f orbitals referred to this z-axis, and it is found that the coefficient of the normalized f orbital $\sqrt{35/8} \sin^3 \theta \cos 3\varphi$ is 0.664δ, or 0.100 for $\delta = 0.150$. The strength of this orbital is 2.09, and hence it contributes 0.209 to the strength of the hybrid bond orbital. We may expect the corresponding term in the resonance integral to be approximately $(0.209/1.732)^2$ times as great as for two π orbitals, as in the carbon-carbon double bond, which is about 61 kcal/mole.[12] Taking into account also the factor $-1/2$ for non-bonding rather than bonding interaction, we obtain 0.44 kcal/mole. Each of the three C—H bonds of one methyl group interacts with each of the three of the other group; hence we predict that the potential barrier for ethane and substituted ethanes (forming single bonds only) should be about $9 \times 0.44 = 4.0$ kcal/mole high. This value is completely unreliable, and no significance should be attached to its rough agreement with the experimental values 2.7–3.0 kcal/mole for ethane, 3.30 for CH_3CH_2F, 3.18 for CH_3CHF_2, and 3.3 for propane.

The smaller value 2.56 kcal/mole found for CH_3CHOCH_2 shows the decrease that we would expect to result from the change in bond angles caused by the three-membered ring. If the change is distributed equally over the five other bond angles, increasing them from 109.5° to 120°, the expansion of the f orbital introduces the coefficient 0.514δ in place of 0.664δ and hence leads to a predicted barrier 77 per cent as great as for unstrained substituted ethanes, in good agreement with experiment ($2.56 = 0.77 \times 3.32$).

There are other predictions that can be made on the basis of this theory, and there is further good agreement with experiment. First, it is predicted that the staggered configuration of substituted ethanes and similar molecules is the stable one. The staggered configuration has been verified for CH_3CH_2Cl, CH_3CF_3, CH_3SiH_3, CH_3SiH_2F, CH_3SiF_3, and several other molecules.

Also, the height of the barrier changes from molecule to molecule in the predicted way. The barrier interaction involves the same integral over the radial parts of the wave functions as the axial bond itself, and it would accordingly be expected that for molecules in which the bond orbitals have similar hybrid character the barrier height would be a constant fraction of the bond energy. In particular, for different substituted ethanes essentially the same barrier would be found, provided that the substituent groups are not large enough to cause steric effects, which would increase the barrier height. Approximate constancy is observed for ethane and substituted ethanes, as mentioned above.

The energy of a carbon-silicon bond and that of a carbon-germanium bond are about three-quarters as great as that of a carbon-carbon bond, and it would accordingly be predicted that the height of the barrier in molecules containing these bonds would be about three-quarters as great, that is, about 2.3 kcal/mole; observed values are 1.70 for CH_3SiH_3, 1.56 for CH_3SiH_2F, 1.32 for CH_3SiHF_2, and 2.5 for CH_3GeH_3 (perhaps uncertain). (Professor E. B. Wilson, Jr., has just written me that the value for methyl germane is probably 1.2.)

Only bond orbitals, and not orbitals for unshared pairs, hybridize with f character, and accordingly we predict that an OH group would interact with a methyl group one-third as strongly as a methyl group itself would, and an NH_2 group would interact two-thirds as strongly; for CH_3OH and CH_3NH_2 we predict barrier heights about 1.0 and 2.0 kcal/mole, respectively; the observed values are 1.07 and 1.90.

We may describe the double bond as involving two tetrahedral orbitals of each of the two bonded atoms; that is, as two bent single bonds.[5] It would then be expected that the interaction energy of a methyl group with a carbon atom forming a single bond and a double bond would be somewhat smaller than that between two methyl groups, that is, somewhat smaller than 3 kcal/mole. The observed barrier height for methyl ethylene ($CH_3—CH=CH_2$) is 1.98 kcal/mole, in agreement with expectation. Similar values are found in the related substances $CH_3—CH=C=CH_2$ (1.59) and $CH_3—CH=CHF$ (2.15). Configurations have not been determined for these substances; we may predict that a hydrogen atom of the methyl group will be staggered with respect to the single bond on the other carbon atom.

In aldehydes and related substances the height of the potential hump is somewhat less than in methyl ethylene: 1.15 kcal/mole for CH_3CHO, 1.08 for CH_3CFO, 1.35 for CH_3CClO, and 1.27 for CH_3COCN. Configurations in agreement with our prediction have been reported for the first three, a methyl hydrogen atom being staggered with respect to the single bond formed by the other carbon atom.

For acetic acid, CH_3COOH, in which the bond from carbon to the OH group has about 35 per cent double-bond character and that to the oxygen atom about 65 per cent double-bond character, as determined from the interatomic distances, we would predict for the potential hump a value about one-third that in acetaldehyde. This prediction is borne out by experiment, the height of the barrier being 0.48 kcal/mole.

For nitromethane, CH_3NO_2, and methyl difluoroborane, CH_3BF_2, symmetry requires that the potential barrier correspond to a sixfold axis. The experimental values for the barrier height are very small, 0.006 and 0.014 kcal/mole, respectively. These very small values show that the contributions of the corresponding orbitals to the hybrid bond orbitals are also very small. The orbitals that could give rise to a potential barrier proportional to cos 6φ are the i orbitals, with azimuthal quantum number $l = 6$. Because of the many nodal cones and the large promotion energy of the *i* orbitals, it is to be expected that they would not make any important contribution to the hybrid bond orbitals.

The general qualitative agreement with experiment provides support for the theory that the potential barriers to internal rotation result from the interaction of adjacent hybrid bond orbitals with a small amount of *f* character. The magnitude of the potential barriers, about 4 per cent of the energy of the axial bond in case that there are three interacting bonds on each of the two atoms and proportionately less for a smaller number of bonds, is also reasonable. A detailed quantum-mechanical treatment of restricted rotation carried out along the lines sketched here should yield results that would permit a detailed test of the theory to be made; in the meantime I believe that the above simple treatment and the extensive empirical support of the theory provide justification for it.

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* Communication No. 2285.

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Chapter 9

ENTROPY AND MOLECULAR ROTATION IN CRYSTALS AND LIQUIDS

Contents

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THE ENTROPY OF SUPERCOOLED LIQUIDS AT THE ABSOLUTE ZERO

By Linus Pauling and Richard C. Tolman

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Introduction

In formulating the third law of thermodynamics Nernst[1] and Planck[2] assumed that a given substance at the absolute zero would have the same entropy in the form of a supercooled liquid as in the crystalline form. It was correctly pointed out by Lewis and Gibson,[3] however, that a supercooled liquid or glass at the absolute zero might be expected in many cases to have a greater entropy than the corresponding crystal, since there might be a greater randomness in the arrangement of the molecules of a liquid,

[1] Nernst, *Nachr. Kgl. Ges. Wiss. Göttingen, Math.-physik. Klasse,* **1906,** p. 1.

[2] Planck, "Thermodynamik," Walter de Gruyter and Co., Berlin, **1921,** 6th ed., p. 273.

[3] Lewis and Gibson, This Journal, **42,** 1529 (1920).

and it has been shown experimentally by Gibson and Giauque[4] that glycerol in the form of a glass does, as a matter of fact, appear to have a greater entropy at the absolute zero than the same amount of glycerol in the crystalline form.

The purpose of the present article is to investigate the entropy of supercooled liquids at the absolute zero by the methods of statistical mechanics. We shall in this way obtain a more precise idea of the factors which can make the entropy of a supercooled liquid or glass greater than that of the corresponding crystal. Indeed, we shall be able to show that the excess entropy of a glass is related in a simple and definite manner to the properties of the glass when regarded as a quantum system with its degrees of freedom in the *next to the lowest quantum state.* Incidentally, we shall also show that different crystalline forms of a substance have the same entropy at the absolute zero, irrespective of the number of atoms in the unit of structure of the crystal, in contradiction to the suggestion recently made by Eastman[5] that the entropy is greater, the larger the number of atoms in the unit cell.

Our method of determining the difference in entropy between the crystal and glass will be to calculate the entropy increase which results from a reversible evaporation of crystal, followed by reversible reduction of pressure and condensation into the glass. To perform the computation we shall need vapor-pressure formulas for the crystal and glass. We shall derive these vapor-pressure formulas with the help of statistical mechanics, and in carrying out the derivations shall employ the language and methods of Ehrenfest and Trkal.[6] Our formula for the vapor pressure of the crystal will be in agreement with that given by these authors. The formula for the vapor pressure of a glass, however, will contain a new factor which has not previously been elucidated in a quantitative manner.

The γ-Weight $\{\gamma\}$ Corresponding to a Given State

In order to derive the desired vapor-pressure formulas we shall regard the state of a system of s degrees of freedom as represented by the position of a point in a $2s$ dimensional phase space (γ-space) corresponding to the s-coördinates $q_1 \ldots . q_s$ and s momenta $p_1 \ldots . p_s$ which determine the behavior of the system. We shall find it convenient to distinguish three types of degrees of freedom: (1) "fully excited" degrees of freedom such that the corresponding coördinates and momenta can be regarded as governed by the classical laws of motion, thus allowing the representative point to assume a continuous range of positions in the γ-space; (2) "partially excited" degrees of freedom such that the corresponding coördinates and

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[4] Gibson and Giauque, THIS JOURNAL, **45**, 93 (1923).

[5] Eastman, *ibid.*, **46**, 39 (1924).

[6] Ehrenfest and Trkal, *Proc. Amsterdam Akad.*, **23**, 162 (1920); *Ann. Physik*, **65**, 609 (1921).

momenta can assume only values belonging to some particular quantized state, thus restricting the representative point to particular hyper-surfaces in the space; (3) "frozen-in" degrees of freedom such that the corresponding coördinates and momenta are in the lowest possible quantum state and the representative point is correspondingly located in the γ-space.

In order to determine the probability of a given state of our system, we shall employ the concept of γ-weight, which will be denoted by the symbol $\{\gamma\}$. The γ-weight of a given state will be determined by moving the representative point in the γ-space through all positions which correspond to the state in question. In general, the point will move throughout continuous hyper-volumes corresponding to fully excited degrees of freedom and will assume locations on definite quantum hyper-surfaces corresponding to partially excited or frozen-in degrees of freedom. In the case of the fully excited degrees of freedom we shall assign a weight equal to the continuous hyper-volume generated in the γ-space by the representative point. In the case of the other degrees of freedom, which are affected by quantum restrictions, we shall assign to each quantum hyper-surface the volume in the γ-space which lies between it and the next higher quantum hyper-surface, thus introducing the weight h for each degree of freedom involved. The total γ-weight $\{\gamma\}$ is obtained by combining the separate weights thus obtained.

The γ-Weight of Vapor and Crystal at Very Low Temperatures

Let us now consider a system of volume V containing $X, Y, Z \ldots$ atoms of different sorts, *all* combined in molecules of composition $\xi, \eta, \zeta \ldots$ and mass M. Let N molecules be in the form of a vapor with potential energy $N\chi$ and N' condensed in the form of a *perfect* crystal with potential energy $N'\chi'$. Furthermore, let the temperature be low enough so that all rotations and oscillations of the vapor molecules, as well as all degrees of freedom in the crystal, can be regarded as frozen in. Consider, however, that the $3N$ degrees of freedom corresponding to the translations of the vapor molecules are fully excited. Finally, let the total energy of the system E lie in the range between E_0 and $E_0 + \mathrm{d}E_0$. We can then write for the γ-weight of the above state of the system

$$\{\gamma\} = \frac{X!\,Y!\,Z!}{N!\,\sigma^N}\, h^{3(X+Y+Z)-3N}\; V^N\, \frac{(2\pi MK)^{3/2N}}{\Gamma\left(\frac{3}{2}N\right)}\,\frac{3}{2}NK^{-1}\,\mathrm{d}E_0 \tag{1}$$

where σ is the symmetry factor for the molecule and K, the translational kinetic energy of the vapor molecules, is connected with the total energy E and the potential energies of crystal and vapor molecules by the equation

$$E = K + N_\chi + N'\chi' \tag{2}$$

The method of obtaining the above expression for the γ-weight of the state of the system needs but little elucidation. Starting from an initial phase of the system which belongs to the state which we are considering, we make the N vapor molecules pass through the total volume V and assume all linear velocities which are consistent with the kinetic energy K which is available. As a result of this operation, the representative point in our space generates a 6 N dimensional hyper-volume which is given by the last terms in Equation 1, the term V^N arising from the translation of the molecules throughout the volume available, and the term $\frac{(2\pi MK)^{3/2N}}{\Gamma\left(\frac{3}{2}N\right)} \frac{3}{2} NK^{-1} \mathrm{d}E_0$ being the volume of the hyper-spherical shell of 3 N dimensions which is determined by the restriction that the kinetic energy must lie in a range $\mathrm{d}E_0$ in width. We then multiply by the factor $h^{3(X+Y+Z)-3N}$ in order to introduce the weight corresponding to the frozen-in degrees of freedom, and finally multiply by the factorial term ($X!\ Y!\ Z!$) which gives the number of ways of permuting the atoms so as to obtain further equivalent phases starting from the original phase of the system. This factorial term, however, has to be divided by $N!$ since our translation of the molecules through the volume V has already included this number of permutations, and by σ^N since the interchange of symmetrically placed atoms in a given molecule would leave the molecule in the same rotational quantum state.

The Vapor Pressure of a Crystal at Very Low Temperatures

To determine the vapor pressure of the crystal we must now find what distribution of the molecules between crystal and vapor will lead to the maximum value of the γ-weight as given by Equation 1. Using for greater convenience the logarithm of the γ-weight, and varying with respect to the number of molecules in the vapor state, we obtain as the condition for a maximum

$$\begin{aligned}\delta \log \{\gamma\} = {} & -\delta N \log \sigma - 3\,\delta N \log h + \delta N \log V + \\ & \frac{3}{2}\delta N \log 2\,\pi\, MK + \frac{3}{2} N\,\delta N \frac{\mathrm{d} \log K}{\mathrm{d}N} - \frac{3}{2}\delta N \log \frac{3}{2} N = 0 \qquad (3)\end{aligned}$$

where certain approximations have been introduced which become negligible when N is very large. Introducing the obvious condition (see Equation 2)

$$\delta K = (\chi' - \chi)\ \delta N \qquad (4)$$

giving the kinetic energy of the molecules the value which it must have at the high dilutions involved

$$K = \frac{3}{2} N kT \qquad (5)$$

where k is the Boltzmann constant, and putting for the pressure of the vapor

$$p = \frac{N}{V} kT \qquad (6)$$

it can be shown that Equation 3 reduces to

$$\log p = \frac{\chi' - \chi}{kT} + \frac{5}{2} \log kT + \frac{3}{2} \log \frac{2\,\pi\, M}{h^2} - \log \sigma \qquad (7)$$

which is the desired expression for the vapor pressure of a perfect crystal at very low temperatures.

Number of Arrangements of Molecules in a Supercooled Liquid

Similar methods to the above can be used to determine the γ-weight of a system composed of N molecules of vapor and N' molecules of supercooled liquid. In this case, however, an exceedingly important difference arises when we consider the number of ways of arranging the molecules which make up the liquid phase.

In a perfect crystal having a given size, shape and orientation each molecule occupies a definite equilibrium position about which it will oscillate when the temperature is raised, and the total number of different exemplars of the crystal which can be obtained will be found by permutations of the atoms which do not involve any change in the equilibrium positions of the molecules. In the case of a supercooled liquid, however, especially one composed of complicated molecules, there may be a number of ways of fitting the molecules together and still obtaining a glass occupying the same space. Hence, in addition to the exemplars which can be formed from a given sample of the glass by permutations of the atoms, we must also consider rearrangements which involve a shifting of the actual positions occupied by molecules.

In determining the number of arrangements which involve a shift in the position of the molecules we must proceed, however, with some care. We are going to apply our considerations to a system which has all its degrees of freedom frozen-in, and shall in any case assign a weight equal to the area $h = \int\int dq dp$ to each degree of freedom. Hence, a shift in the position of a molecule which does not move it out of the limits already allowed to it as belonging to the lowest quantum state must not be counted. That such a possibility might arise may be seen from the trivial example furnished by the quantization of the motion of a ball rolling back and forth in a bowl with a flat bottom, which in the lowest quantum state could be anywhere on the flat surface, or of a dipole rotator which in a force-free field might have any orientation in the state of zero rotation. To avoid difficulties of this kind, let us consider the properties of the glass when its degrees of freedom corresponding to the coördinates which locate the positions of its molecules have been excited to the first quantum state. If rearrangements are then possible which involve shifts in the mean positions of the molecules, the number of such different arrangements must be contained in the expression for the γ-weight of the glass.

In the case of glasses made from complicated molecules, it would seem probable that such shifts would be possible. On the other hand, in the case of a liquid made from a simple monatomic substance, it might be impossible to obtain any condensed phase at the absolute zero having greater possibilities of rearrangement than belong to a crystal. This latter would seem to be borne out by the fact that the entropy of liquid helium, at the lowest temperatures where measurements have been made, has already dropped to less than one entropy unit.

As to the number of arrangements involving shifts in the equilibrium positions of the molecules of the liquid, this will obviously be some function of the number of molecules N' in the liquid, and in the next section we shall show that in the cases to be considered the function must have the form $ca^{N'}$, where c and a are constants.

Vapor Pressure of a Supercooled Liquid

In accordance with the foregoing, we can obtain an expression for the γ-weight of a system containing N molecules of vapor and N' of supercooled liquid by multiplying the corresponding expression for the case of a crystal by the number of ways of arranging the liquid molecules as discussed in the preceding section. Referring to Equation 1 we thus obtain

$$\{\gamma\} = \frac{X!\,Y!\,Z!}{N!\,\sigma^N}\; h^{3(X+Y+Z)-3N}\phi(N')\; V^N \frac{(2\,\pi\, MK)^{3/2N}}{\Gamma\left(\frac{3}{2}N\right)}\frac{3}{2}\,NK^{-1}\,\mathrm{d}E_0 \qquad (8)$$

where we have represented the number of such arrangements by $\phi(N')$.

Determining, just as in the case of the crystal, the conditions for a maximum value of the γ-weight, we can then obtain in analogy to Equation 7 the following expression for the vapor pressure of the glass

$$\log p = \frac{\chi' - \chi}{kT} + \frac{5}{2}\log kT + \frac{3}{2}\log\frac{2\,\pi\, M}{h^2} - \log\sigma - \frac{\mathrm{d}\log\phi(N')}{\mathrm{d}N'} \qquad (9)$$

where the last term arises from the possibility for rearrangements of the molecules of the glass.

We can now, however, easily determine the nature of the unknown function occurring in this last term. Since we shall consider that we have taken a large enough sample of glass so that the vapor pressure is independent of the size of the sample, it is evident that the last term must be a constant independent of the number of molecules in the glass N'. Let us then write

$$\frac{\mathrm{d}\log\phi\;(N')}{\mathrm{d}N'} = \log a \qquad (10)$$

where a is a constant. Integrating, we can obtain $\log\phi(N') = N'\log a +$ const., or

$$\phi(N') = c\,a^{N'} \qquad (11)$$

where c is a constant. Substituting in (9) we obtain for the vapor pressure of a supercooled liquid

$$\log p = \frac{\chi' - \chi}{kT} + \frac{5}{2}\log kT + \frac{3}{2}\log\frac{2\,\pi\, M}{h^2} - \log\sigma - \log a \qquad (12)$$

Our method of development also provides some measure of information as to the magnitudes that the quantity a can be expected to assume, and hence some idea as to the probable differences in the entropies of crystals and glasses which we may expect to encounter. Equation 11 gives us an expression for the number of ways in which we can arrange the N' molecules of a glass and still obtain an exemplar of the glass. If we should increase the number of molecules by one, the number of such arrangements would become

$$\phi(N'+1) = c\,a^{N'+1} = a\,\phi(N') \qquad (13)$$

Hence, the quantity a may be regarded as the average number of ways in which a single molecule can be rearranged in the liquid. In accordance with our previous considerations, however, it is evident that these rearrangements must be drastic enough so that the new position of the molecule would also correspond to a rearrangement when the positional degrees of freedom of the molecules are excited to the next to the lowest quantum state, with the further condition that the new positions of the molecules could not be obtained by a mere permutation of atoms. On the basis of this interpretation, it is evident that a will be a small number which increases as the complexity of the molecules increases.

Difference in Entropy of Crystal and Glass

We may now use Equations 7 and 12 for the vapor pressure of crystal and glass to calculate the change in entropy when we pass from crystal to glass at temperatures near the absolute zero.

For convenience and in accordance with a familiar formulation of the third law of thermodynamics, let us take our starting point for entropy measurements such that the entropy of the crystal is zero at the extremely low temperature involved. Starting with the crystal let us then form by reversible evaporation one mole of vapor at the vapor pressure. The entropy of the gas thus formed will evidently be

$$S = A\left[\frac{\chi - \chi' + \frac{5}{2}kT}{T}\right] \qquad (14)$$

where A is Avogadro's number. Changing now from the vapor pressure p as given by Equation 7 to unit pressure, we obtain

$$\Delta S = Ak\log p = A\left[\frac{\chi' - \chi}{T} + \frac{5}{2}k\log T + \frac{3}{2}k\log\frac{2\pi M}{h^2} - \log\sigma\right]$$

which combined with (14) gives us

$$S = A\left[\frac{5}{2}k\log T + k\log\frac{(2\pi M)^{3/2}k^{5/2}}{h^3} + \frac{5}{2}k - \log\sigma\right] \qquad (15)$$

which is, of course, the familiar Sackur[7] expression for the entropy of a monatomic gas at temperature T and unit pressure with the constant terms as first correctly obtained by Tetrode.[8]

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[7] Sackur, *Ann. Physik*, **36**, 958 (1911); **40**, 67 (1913); *Nernst-Festschrift*, **1912**, p. 405.

[8] Tetrode, *Ann. Physik*, **38**, 434 (1912); **39**, 255 (1912).

Continuing the process we may now change the pressure on the gas to the vapor pressure of the glass as given by (12) and then carry out a reversible condensation. These steps will be seen to involve the entropy change

$$\Delta S = -A\left[\frac{5}{2}k\log T + k\log\frac{(2\pi \mathrm{M})^{3/2}k^{5/2}}{h^3} + \frac{5}{2}k - \log\sigma - k\log a\right] \qquad (16)$$

which combined with (15) gives us

$$S = A\ k\ \log a = R\ \log a \qquad (17)$$

as the desired expression for the entropy of one mole of a supercooled liquid or glass at the absolute zero. Remembering the interpretation of *a* given above, we see that the entropy of supercooled liquids at the absolute zero may be expected to vary from zero for simple molecules to a few calories per degree per mole for complicated molecules.

Some Points of Interest

Before leaving these matters it is of interest to note that our considerations afford no basis for ascribing greater entropy to crystals with a complicated unit of structure than to those having a simple unit. Provided there is only a single set of equilibrium positions for the atoms that make up the crystal, the entropy will be the same for different crystalline forms of the same substance.

In the case, however, of solid solutions where variability of composition is possible we may expect increased entropy owing to the possibilities of increased randomness of arrangement just as with liquid and gaseous solutions. Also, other special cases might arise where a greater degree of randomness would be possible than in pure, perfect crystals, but such cases could be given a special treatment and would cause no confusion.

It is also of interest to examine the entropy of a system containing a number of individual crystals placed and oriented at random. If the individual crystals are large enough so that we make no appreciable error in assuming all the degrees of freedom belonging to atoms in the crystals as frozen-in, and if reversible evaporation and recondensation to form again the original crystals are possible, then it is evident that we may also ascribe zero entropy to such a set of crystals.

In conclusion, there is a point in connection with the γ-weight of crystals and glasses as given by Equations 1 and 8 which will bear further elucidation. In setting up these expressions it might appear as if we had incorrectly neglected the possibility of rearranging the molecules of the crystal or glass so as to give different positions, shapes or orientations to the whole condensed phase. It should be noted, however, that we are going to apply our considerations to a calculation of the vapor pressure of a given crystal or glass, and hence are interested in the rearrangements that can be brought about by the evaporation and recondensation of a small portion of the original crystal or liquid. Under these circumstances the position, shape and orientation of the condensed phase is maintained constant by the condition that most of it will not evaporate at all and, hence, determines the location of the phase as a whole. The matter might be made clearer if we regarded N' not as the total number of molecules in the condensed phase, but as the number of molecules in a layer on the surface of the phase taken of sufficient depth so that no change in the results would arise from an increase of depth.

Summary

In the foregoing article we have applied the methods of statistical mechanics to a determination of the entropy of crystals and supercooled glasses, and have reached the following conclusions.

1. The difference per mole in the entropy of a given substance at the absolute zero in the form of a glass and crystal can be given by an equation of the form $S_{\text{glass}} - S_{\text{crystal}} = R \log a$, where a is a small number increasing with the complexity of the molecule.

2. The exact nature of the quantity a is given by the equation, $\phi(N') = c\,a^{N'}$, which gives the number of ways in which we can arrange the mean positions of the N' molecules of a glass, when the degrees of freedom corresponding to the positional coördinates are excited to the first quantum state, excluding arrangements which could be obtained by a permutation of atoms.

3. The entropy of a perfect crystal at the absolute zero is not dependent on the complexity of the unit of crystal structure.

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THE ROTATIONAL MOTION OF MOLECULES IN CRYSTALS

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Abstract

It is shown by the discussion of the wave equation for a diatomic molecule in a crystal that the motion of the molecule in its dependence on the polar angles θ and ϕ may approach either one of two limiting cases, oscillation and rotation. If the intermolecular forces are large and the moment of inertia of the molecule is large (as in I_2, for example), the eigenfunctions and energy levels approach those corresponding to oscillation about certain equilibrium orientations; if they are small (as in H_2), the eigenfunctions and energy levels may approximate those for the free molecule, even in the lowest quantum state.

It is found in this way that crystalline hydrogen at temperatures somewhat below the melting point is a nearly perfect solid solution of symmetric and antisymmetric molecules, the latter retaining the quantum weight 3 for the state with $j=1$ as well as the spin quantum weight 3. This leads to the expression

$$S = -n_A R \log n_A - (1-n_A)R\log(1-n_A) + n_A R \log 9 + S_{tr},$$

in which S_{tr} is the translational entropy, for the entropy of the solid at these temperatures. At lower temperatures (around 5°K) the solid solution becomes unstable relative to phases of definite composition, and the entropy falls to

$$S = n_A R \log 3 + S_{tr},$$

the entropy of mixing and of the quantum weight 3 for $j=1$ being lost at the same time. Only at temperatures of about 0.001°K will the spin quantum weight entropy be lost.

Gradual transitions covering a range of temperatures and often unaccompanied by a change in crystal structure, reported for CH_4, HCl, the ammonium halides, and other substances, are interpreted as changes from the state in which most of the molecules are oscillating to that in which most of them are rotating. The significance of molecular rotation in the interpretation of other phenomena is also discussed.

I. Introduction

THE calculation of the difference in entropy of gaseous molecular hydrogen and crystalline hydrogen has recently been made by Giauque and Johnston.[1] At temperatures between the melting point (14°K) and about 10°K the heat capacity of the solid is well represented by a Debye function with $\beta\nu = 91°$. Assuming the validity of extrapolation to 0°K by means of this function, it is found that the difference in entropy of the solid at 0°K and the gas at standard conditions is 29.7 ± 0.1 E. U. The molal entropy of the gas at standard conditions is given by the Sackur-Tetrode equation as 34.00 E. U., using the band spectrum value of the moment of inertia, and taking into account the symmetry number term $(-R \log 2)$, the entropy of mixing of sym-

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[1] W. F. Giauque and H. L. Johnston, J. A. C. S. **50**, 3221 (1928).

metric and antisymmetric molecules, present in the ratio of 1:3(−1/4 *R* log 1/4−3/4 *R* log 3/4), and the nuclear spin quantum weight of the antisymmetric molecules (3/4 *R* log 3). Thus the molal entropy of ordinary crystalline hydrogen (the metastable mixture of symmetric and antisymmetric molecules in the ratio of 1:3) at temperatures somewhat below the melting point is found to be 4.3 ± 0.1 E. U. in addition to the translational entropy. In the attempt to account for this deviation from the value zero to be expected from the third law of thermodynamics, it was found necessary to carry through the quantum mechanical discussion of the motion of molecules in crystals.

Before proceeding with this task, it may be illuminating to mention the concept of the motion of a molecule in a crystal which we would form on the basis of classical mechanics. All but six of the degrees of freedom for the molecule can be assigned to represent relative motions of the atoms within the molecule, corresponding to internal oscillations. The six remaining degrees of freedom can be represented by the three coordinates x, y, z of the center of mass of the molecule referred to an arbitrarily chosen set of axes, and the Eulerian angles φ, θ, χ determining the orientation of the molecule with respect to the same axes. In case the forces between atoms in a molecule are much stronger than those between atoms in different molecules, a crystal of the substance may be considered as a first approximation to be a collection of rigid molecules held in a regular arrangement by the rather weak intermolecular forces. Each molecule will remain in the neighborhood of its equilibrium position, the coordinates x, y, z varying through only a small region of values about x_0, y_0, z_0. Similarly, there will be one or more sets of values of φ, θ, χ for which the potential energy is a minimum, corresponding to equilibrium orientations of the molecule. There are two types of motion then possible for the molecule. If the potential energy for values of φ, θ, χ in the neighborhood of φ_0, θ_0, χ_0 is very small compared with that for other values, the difference being much larger than kT, the average molecule at the temperature T will carry out only small vibrations about its equilibrium orientation. This may be spoken of as oscillation about the equilibrium orientation. But if the potential energy undergoes a total variation smaller than kT, the kinetic energy of the average molecule will suffice to carry it into any orientation, so that the molecule will undergo non-uniform rotation, speeding up as it passes through the equilibrium orientations and slowing down as it goes over the potential maxima. A molecule with a given amount of energy and acted upon by a given potential would according to the classical theory assume a succession of orientations corresponding either to one or to the other of these possibilities, oscillation or rotation.

The introduction of the quantum mechanics does not require this picture to be changed essentially. The allowed states of the system can approximate either of two extremes, oscillation and rotation, or can lie between these extremes, approximating neither more closely than the other. For with the quantum mechanics, in contradistinction to the classical theory, the transition from one extreme to the other is unbroken.

II. THE DIATOMIC MOLECULE IN A CRYSTAL

In Fig. 1 there is shown the structure of the orthorhombic crystal iodine as determined with the use of x-rays.[2] The atoms are joined in pairs to form molecules by strong shared-electron-pair bonds, and the molecules are grouped together in such a way that the figure axis for each assumes a definite orientation. This is the equilibrium orientation, with the polar angle $\theta = 0$, say. The symmetry of the molecule requires that there also be another equilibrium orientation at $\theta = \pi$.

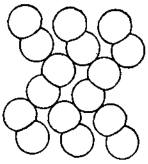

Fig. 1. The arrangement of atoms in one layer in a crystal of iodine. It is seen that the atoms are in groups of two(the molecules I_2) which are oriented by the intermolecular forces.

Let us consider a diatomic molecule in such a crystal. As a first approximation we may neglect the translational oscillations of the molecule under consideration and both the translational and rotational motion of the other molecules in the crystal. The wave equation then may be written

$$\nabla^2\psi + \frac{8\pi^2 I}{h^2}(W - V)\psi = 0, \tag{1}$$

in which I is the moment of inertia of the molecule and $V = V(\theta, \varphi)$ is a potential function representing the averaged interaction of the molecule with surrounding molecules. The simplest form that can be given this function and have it represent a diatomic molecule with two equilibrium orientations is

$$V = V_0(1 - \cos 2\theta), \tag{2}$$

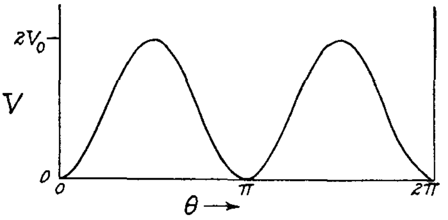

Fig. 2. The potential function $V = V_0\ (1 - \cos 2\theta)$.

in which V_0 is a constant. This potential function is shown in Fig. 2. The wave equation then becomes

$$\frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial\psi}{\partial\theta} + \frac{8\pi^2 I}{h^2}(W - V_0 + V_0\cos 2\theta)\psi = 0. \tag{3}$$

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[2] P. M. Harris, E. Mack and F. C. Blake, J. A. C. S. **30**, 1583 (1928).

The characteristic value equation in θ obtained from this has not been solved except for limiting cases. The corresponding problem in a plane has, however, been fully treated. If the molecule were restricted to motion in a plane the wave equation would be

$$\frac{d^2\psi}{d\theta^2} + \frac{8\pi^2 I}{h^2}(W - V_0 + V_0 \cos 2\theta)\psi = 0 \tag{4}$$

or, writing

$$\alpha = \frac{2\pi^2 I}{h^2}(W - V_0)$$

$$q = \frac{\pi^2 I V_0}{2h^2},$$

$$\frac{d^2\psi}{d\theta^2} + (4\alpha + 16q \cos 2\theta)\psi = 0. \tag{5}$$

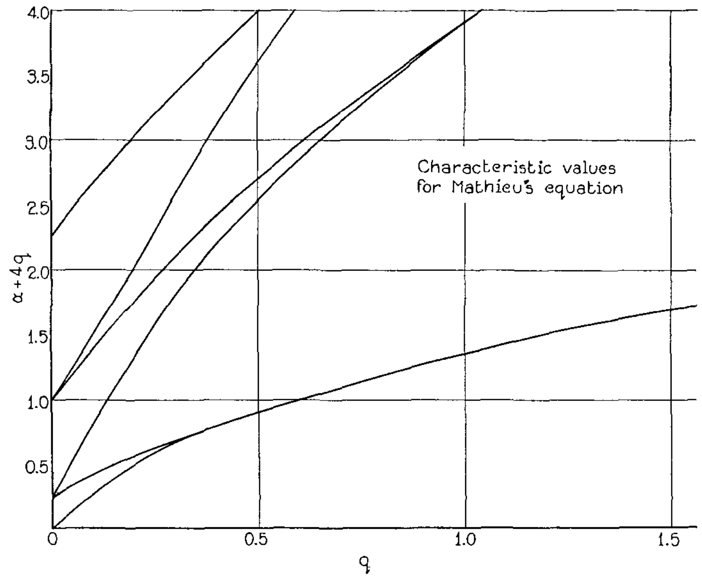

Fig. 3. The characteristic values for the six lowest Mathieu functions.

This equation is Mathieu's equation in the usual form.

The requirement that ψ be periodic in θ with the period 2π leads to the functions known as Mathieu functions.[3] These are usually designated by the symbols ce_0, se_1, ce_1, se_2, ce_2, etc. The functions and the corresponding characteristic values of α as functions of q have been evaluated by Goldstein.[4] The energy values for the five lowest states are shown in Fig. 3. It is seen

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[3] E. Mathieu, Liouville's Jour. **13**, 137 (1868); Whittaker and Watson, "Modern Analysis," pp. 404–428. E. U. Condon, Phys. Rev. **31**, 891 (1928), pointed out that the Mathieu functions of even order are the eigenfunctions for the plane pendulum.

[4] S. Goldstein, Trans. Cambridge Phil. Soc. **23**, 303 (1927).

that for $q=0$ Eq. (5) reduces to the equation for the plane rotator, with energy levels $W_m=(m^2h^2/8\pi^2I)$. For q large the eigenfunction ψ is appreciably different from zero only for values of θ close to 0 and π, and approximates a combination of Hermite orthogonal functions, the eigenfunctions for the harmonic oscillator. The energy levels for this case are $(n+1/2)\ h\nu_0$, in which $\nu_0=h(2q)^{1/2}/\pi I$. Each energy level shows two-fold degeneracy, the corresponding eigenfunctions being approximately

$$\frac{1}{2^{1/2}}\{\psi_n\theta/\theta_0+\psi_n(\theta-\pi)/\theta_0\}\ \text{ and }\ \frac{1}{2^{1/2}}\{\psi_n\theta/\theta_0-\psi_n(\theta-\pi)/\theta^0\},$$

in which $\psi_n(\theta/\theta_0)$ and $\psi_n((\theta-\pi)/\theta_0)$ represent Hermite orthogonal functions of the indicated arguments, and θ_0 is given by the equation $h\nu_0/2=V_0\theta_0{}^2$.

This can be used as the basis of a perturbation treatment of the problem, using the method of variation of constants,[5] as in the treatment of aperiodic phenomena.[6] It is found that in case it were possible to carry out an experiment to determine whether the molecule were undergoing vibrations about $\theta=0$ or about $\theta=\pi$, with the use of a method of investigation involving an interaction unsymmetrical in the two atoms composing the molecule, the probability of observing the molecule in one orientation rather than the other would vary in a way corresponding to the molecule's changing end for end with a frequency given by the separation of adjacent energy levels (ce_0 and se_1, ce_1 and se_2, etc) divided by h. Reference to Fig. 3 shows that this frequency is very small for q large, justifying the interpretation of the corresponding states as oscillational states, the molecule oscillating about an equilibrium orientation and changing end for end only rarely. But for q small this frequency becomes large, approaching the principal frequency of motion of the molecule; then we say that the molecule is rotating, its rotation being made somewhat non-uniform through interactions with other molecules. The energy levels in this case approximate those for the free plane rotator, and their behavior for small values of q can be conveniently followed by perturbation methods using the rotator eigenfunctions as zeroth order eigenfunctions.

These considerations, involving a hypothetical investigation of the orientation of the molecule, are, while illuminating, not essential to the discussion of the type of motion of the molecule. We can define the motion of the molecule in a given state as oscillational in case the eigenfunction for that state can be closely approximated by a combination of Hermite functions and the energy of the state is given approximately by $(n+1/2)\ h\nu_0$. For rotational motion the eigenfunction and energy level should approximate those for a free rotator. This definition is equivalent to that given above: the study of Goldstein's Fourier series representation of the Mathieu functions shows that the transition of the eigenfunctions from approximation to Hermite

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[5] P. A. M. Dirac, Proc. Roy. Soc. **A112**, 661 (1926); J. C. Slater, Proc. Nat. Acad. **13**, 7 104 (1927); M. Born, Zeits f. Physik **40**, 172 (1926).

[6] See the clear exposition given the process of radioactive decomposition by M. Born, Zeits. f. Physik **58**, 306 (1929).

functions to approximation to sines and cosines takes place rather sharply at the value of q where the separation of adjacent energy levels becomes appreciable. A similar treatment can be applied to the spatial rotator with two potential minima. The discussion of the qualitative course of the energy levels and the nature of the eigenfunctions is similar to that given above, and a detailed treatment is not needed for our purposes.

III. Rough Criteria for Oscillation and Rotational Motion

Let us tentatively assume that the motion is oscillationa. Then we can approximate the lower part of $V(\theta)=V_0(1-\cos 2\theta)$ by a parabola by expanding in powers of θ and $\theta-\pi$ obtaining $-2V_0\theta^2$ and $-2V_0(\theta-\pi)^2$ as the expansions in the neighborhood of $\theta=0$ and $\theta=\pi$. These correspond to energy levels

$$W_n = (n+1)h\nu_0, \quad n = 0, 1, 2, 3, \cdots \tag{6}$$

for the two-dimensional harmonic oscillator, with

$$\nu_0 = \frac{1}{\pi}\left(\frac{V_0}{I}\right)^{1/2}. \tag{7}$$

In case that $W_n=(n+1)\ h\nu_0$ is less than $2V_0$, the top of the potential hill separating the two-valleys, the molecule will change orientation only rarely. (The exceptional case with V_0 and n small for which there is a large probablity of the molecule turning end for end even when its energy is not sufficient to carry it over the hill, is discussed later). But for W_n larger than $2V_0$ the motion will be rotational. Thus we obtain the following criteria:

$$\begin{aligned} n+1 &< \frac{2\pi(IV_0)^{1/2}}{h}, \quad \text{oscillational motion,} \\ n+1 &> \frac{2\pi(IV_0)^{1/2}}{h}, \quad \text{rotational motion.} \end{aligned} \tag{8}$$

The uncertain quantity of these expressions is V_0. A rough value for it can be obtained from the observed heat capacity of the solid. If the molecules oscillate about equilibrium orientations the molal heat capacity would be given as a first approximation by the sum of a Debye function of parameter $\beta\nu$, corresponding to the translational oscillations, and twice an Einstein function of parameter $\beta\nu_0=h\nu_0/k$, with ν_0 the characteristic frequency of Eq. (7). It is found that such a curve does not give a very close fit with observed heat capacities since the model is too greatly simplified; but the heat capac, ity curve does show that $\beta\nu$ and $\beta\nu_0$ are nearly the same for many substances- and a rough value for them can be obtained by taking three times the temperature at which the heat capacity reaches 5 cal/mole degree; that is, half the high-temperature value for five degrees of freedom.[7] Values of

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[7] This procedure is based on the fact that an Einstein function reaches half its maximum value at the temperature $0.33\beta\nu_0$.

TABLE I.

Molecule	$\beta\nu_0$	Θ	n_0+1	V_0	Heat of fusion and transition
				cal/mole	cal/mole
I_2	75°	0.053°	350	25000	4000
N_2	65°	2.33°	7.0	450	222
O_2	70°	2.06°	8.5	600	306
CO	75°	2.65°	7.1	500	354
CH_4	55°	8.5°	1.6	90	242
HCl	160°	14.9°	10.7	1700	760
HBr	125°	11.9°	10.5	1300	803
HI	105°	9.2°	11.4	1200	897
H_2	<135°	82°$_0$	<0.4	<56	28

$\beta\nu_0$ for several substances[8] are given in Table I, together with the characteristic temperature for rotational degeneracy, Θ, which is related to the moment of inertia I (obtained from band spectral data) by the equation

$$\Theta = \frac{h^2}{8\pi^2 Ik} \cdot \tag{9}$$

The heat capacity of solid hydrogen provides no information regarding $\beta\nu_0$ for H_2. An upper limit for $\beta\nu_0$ can, however, be found in the following way. It is seen that for many substances the total heat change accompanying transitions and fusion is about equal to $V_0/2$ (compare columns 6 and 7 of Table I). Assuming this to hold for H_2, we find $V_0 = 56$ cal/mole, which, from the trend of the ratio $V_0/\Delta H$ with molecular weight, can be accepted as a maximum value. This corresponds to $\beta\nu_0 < 135°$. The approximate constancy of $\beta\nu_0$ in the series I_2, O_2, N_2 suggests a value of this order of magnitude for H_2 also; it and derived quantities are included in Table I.

In terms of $\beta\nu_0$ and Θ the criteria 8 become

$$\begin{aligned} n + 1 &< \beta\nu_0/4\Theta, \quad \text{oscillational motion,} \\ n + 1 &> \beta\nu_0/4\Theta, \quad \text{rotational motion.} \end{aligned} \tag{10}$$

The transition from oscillational to rotational motion should occur for $n = n_0$, with

$$n_0 + 1 = \frac{\beta\nu_0}{4\Theta} \cdot \tag{11}$$

Values of n_0+1 are given in Table I. There are also included data for unsymmetric molecules such as HCl. For these a reasonable potential function

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[8] Since these calculations were made some direct verification of them has been provided by the work of L. Vegard (Nature **125**, 14 (1930)) who has obtained spectra from solid nitrogen at very low temperatures involving an electronic transition, a change in oscillation within the molecule, and an additional energy change corresponding to frequencies of 40 cm^{-1} and 69 cm^{-1} which he interprets as oscillational jumps for the molecule in the lattice. One of these frequencies probably is the frequency of rotational vibration of the molecule. 40 cm^{-1} and 69 cm^{-1} correspond to $\beta\nu_0 = 57°$ and 99° respectively, the first of which is in good agreement with the rough value 65° of Table I.

is $V = V_0(1-\cos\theta)$, corresponding to an electric dipole in a uniform field. This leads to a transitional value n_0 given by

$$n_0 + 1 = \frac{\beta\nu_0}{\Theta}. \tag{12}$$

For CO it is doubtful as to whether 11 or 12 is more nearly applicable; the former has been used.

The value $n_0+1<0.4$ found for H_2 shows that *even in the lowest state* the molecules are rotating freely, the intermolecular forces producing only small perturbations from uniform rotation. Indeed, the estimated $\beta\nu_0<135°$ corresponds to $V_0<28\,k$, which is small compared with the energy difference $164\,k$ of the rotational states $j=0$ and $j=1$, giving the frequency with which the molecule in either state reverses its orientation. The perturbation treatment shows that with this value of V_0 the eigenfunctions and energy levels in all states closely approximate those for the free spatial rotator.[9]

The other extreme is provided by I_2, for which the transition from oscillation to rotation takes place at about $n=300$. At the melting point the molecules are in states with $n=10$ or 15, so that there are no rotating molecules in this crystal. This agrees with the fact that equilibrium positions for the atoms have been found by x-ray methods.

The remaining substances form intermediate cases, the molecules in lower states oscillating and in higher states rotating. Whether the transition to rotational states takes place in the main before the crystal melts will be considered in Section V.

IV. CRYSTALLINE HYDROGEN AND ITS ENTROPY

In ordinary crystalline hydrogen there are three molecules with $j=1$ for every one with $j=0$. The eigenfunctions for these molecules approximate those for free molecules, namely

$$j = 0,\ \psi_0 = 1/(4\pi)^{1/2},$$
$$j = 1,\ \psi_1 = (3/4\pi)^{1/2}\cos\theta,\ (3/4\pi)^{1/2}\sin\theta\cos\phi,\ (3/4\pi)^{1/2}\sin\theta\sin\phi, \tag{13}$$

in terms of angles θ and ϕ relative to an arbitrary coordinate system. These rotating molecules interact with each other as though they were nearly spherically symmetrical.[10] Hence we expect the crystal to have a close-packed structure—cubic close-packed, say, with molecules at 000, $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$. This agrees with the known cubic symmetry of crystalline hydrogen.[11] The

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[9] It is worthy of especial mention that in the state with $j=0$ the molecules are to be considered as rotating when V_0 is sufficiently small (less than the separation of the levels $j=0$ and $j=1$) even though the energy of the state ($\sim V_0$) is not sufficient to carry the molecule over the potential maximum ($2V_0$). This is shown by the close approximation of the corresponding eigenfunction to the lowest tesseral harmonic and by the high frequency of end-for-end interchange given by the perturbation treatment, starting with oscillational eigenfunctions.

[10] The forces holding the rotating molecules result from interpenetration of the molecules, as for the noble gases.

[11] The observed density 0.0808 at 11°K corresponds to a unit with $a=5.46$A, the distance between adjacent molecules being 3.86A.

x-ray investigation of the crystals should not lead to the determination of atomic positions, but only of molecular positions.

In cubic close-packing each molecule is surrounded by twelve others, whose interaction with the central molecule can be represented by a potential function of cubic point-group symmetry in case that the twelve molecules are spherically symmetrical or oriented at random. The energy change produced by this potential function, f say, is

$$W^1 = \iint \psi f \bar{\psi} \sin \theta d\theta d\phi,$$

which is easily shown by the consideration of the symmetry of f to be the same for all four eigenfunctions. Thus a molecule of symmetrical hydrogen, with $j=0$, has in a crystal the same energy as a molecule of antisymmetrical hydrogen, with $j=1$. As a result the two forms of hydrogen should form a complete series of nearly perfect solid solutions, and, moreover, the energy content of the crystal, aside from rotational energy, should be independent of the composition. This has been verified by the measurements of Clusius and Hiller,[12] who found symmetrical hydrogen to have the same heat capacity and heat of fusion as the 1:3 mixture.

Additional experimental verification that molecules of hydrogen in condensed phases are in states approximating those for free molecules is provided by the Raman effect measurements of McLennan and McLeod.[13] A comparison of the Raman frequencies found by them and the frequencies corresponding to the rotational transitions $j=0 \rightarrow j=2$ and $j=1 \rightarrow j=3$ (Table II) shows that the intermolecular interaction in liquid hydrogen produces only a very small change in these rotational energy levels.

TABLE II.

Transition	Raman effect	Band spectra
$j=0 \rightarrow j=2$	354 cm^{-1}	347 cm^{-1}
$j=1 \rightarrow j=3$	588	578
$0 \rightarrow 1$ in intramolecular oscillation	4149	4159

These considerations permit a calculation of the entropy of crystalline hydrogen at temperatures somewhat below the melting point. Ordinary crystalline hydrogen, consisting of the symmetrical and antisymmetrical forms in the ratio of 1:3, has an entropy of mixing of $-(1/4)R$ log $(1/4)$ $-(3/4)R$ log $(3/4)$, for the solid solution can be considered ideal. The symmetrical molecules have a quantum weight 1 in the normal state, with $j=0$, and the antisymmetrical molecules a quantum weight 9, corresponding to the three rotational eigenfunctions for $j=1$, each of which is associated with any one of the three spin eigenfunctions. This gives a predicted total entropy of the solid at temperatures just below the melting point of

$$S_{H_2} = -(\tfrac{1}{4})R\log(\tfrac{1}{4}) - (\tfrac{3}{4})R\log(\tfrac{3}{4}) + (\tfrac{3}{4})R\log 9 + S_{tr} = 4.39\text{E. U.} + S_{tr}, \quad \text{(14a)}$$

[12] K. Clusius and K. Hiller, Zeit. f. phys. Chem. **B4,** 158 (1929).

[13] J. C. McLennan and J. H. McLeod, Nature **123,** 160 (1929).

in which S_{tr} is the translational entropy. This value is in excellent agreement with the experimental value $4.3 \pm 0.1 + S_{tr}$ of Giauque and Johnston.[14] In general a mixture containing n_A mole-fraction of antisymmetric molecules would have

$$S = -n_A R \log n_A - (1 - n_A) R \log (1 - n_A) + n_A R \log 9 + S_{tr}. \quad (14b)$$

At very low temperatures a separation of the three rotational levels with $j=1$ will take place. This is a second-order effect, depending on the mutual orientation of two or more molecules. As an illustration, let us assume that we could obtain a crystal of pure antisymmetric hydrogen. At temperatures not too near 0°K the molecules would be in cubic close-packing, and an arbitrary molecule could be represented by any one of the three eigenfunctions with $j=1$. But there are possible states of the crystal somewhat more stable than those in which the three rotational eigenfunctions with $j=1$ are represented by random molecules. Thus if each molecule were in the state with $j=1$, $m=0$, corresponding to the eigenfunction $(3/4\pi)^{1/2} \cos \theta$, with θ referred to trigonal axes which for the various molecules are oriented as are the figure axes of CO_2 in crystals of this substance, then the energy of the crystal would be less than that of a crystal in which the three eigenfunctions with $j=1$ were represented at random. In crystalline CO_2 each molecule is surrounded by twelve others, of which the six in the equatorial plane point towards the central molecule, bringing six oxygen atoms to within 3.25A, while the other six molecules place oxygen atoms 4.12A away. As a result the stable orientation for the central molecule is along the trigonal axis. The distribution function $\psi^2 = 3/4\pi \cos^2\theta$ for a hydrogen molecule with $j=1$ and $m=0$ shows a tendency for the molecule to line up parallel to the axis $\theta=0$, leading to the decreased energy of the CO_2-similar structure described above. Since this is a second-order effect the energy decrease will be considerably smaller than V_0, of the order of magnitude of $V_0/5$. With V_0 equal to about 28 k at the most, the temperature at which this structure would become stable relative to the random one would be of the order of magnitude of 5°K.

With other simple ratios of symmetric to antisymmetric molecules other structures might become stable at very low temperatures. Since the energy change depends on the interaction of two antisymmetric molecules, which would drop off very rapidly as the molecules were separated, crystals containing only a small fraction of antisymmetric molecules would be unstable, breaking down into two phases, pure crystalline symmetric hydrogen and crystals with n_A (the mole-fraction of antisymmetric molecules) equal to 1, 1/2, or some other simple fraction. This process, involving diffusion of the molecules, might take some time, so that care would be necessary to insure equilibrium in the study of mixtures with n_A small.

The entropy change accompanying this transition is predicted to be

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[14] The possibility of the expression of the entropy of hydrogen as the sum of these terms was first noted by Giauque, who observed that it indicated the formation of nearly ideal solid solutions between symmetrical and antisymmetrical hydrogen and the retention of the quantum weight 9 for the latter.

$$S = -n_A R \log n_A - (1 - n_A) R \log (1 - n_A) + n_A R \log 3 \qquad (15)$$

corresponding to the restriction of each antisymmetric molecule to one of the three rotational states with $j = 1$, and to the removal of the entropy of mixing of the solid solution existing above the transition temperature.[15] The entropy of the crystals then becomes

$$S = n_A R \log 3 + S_{tr}. \qquad (16)$$

The discovery of a transition which we identify with this has been reported by Simon, Mendelssohn, and Ruhemann,[16] who measured the heat capacity of hydrogen with $n_A = 1/2$ down to 3°K. They found that the heat capacity, after following the Debye curve down to about 11°K, rose at lower temperatures, having the value 0.4 cal/deg., 25 times that of the Debye function, at 3°K. The observed entropy of transition down to 3°K, at which the transition is not completed, was found to be about 0.5 E.U. That predicted by Eq. (15) for the transition is 2.47 E.U.

In crystals for which n_0 is large, such as iodine, the lowest symmetric and the lowest antisymmetric state have practically the same energy and properties, and each corresponds to one eigenfunction only. As a result a mixture of symmetric and antisymmetric molecules at low temperatures will behave as a perfect solid solution, each molecule having just its spin quantum weight, and the entropy of the solid will be the translational entropy plus the same entropy of mixing and spin entropy as that of the gas. This has been verified for I_2 by Giauque.[17] Only at extremely low temperatures will these entropy quantities be lost.

V. THE TRANSITION FROM OSCILLATIONAL TO ROTATIONAL MOTION

A consideration of the values of n_0 for CH_4, N_2, O_2, and the hydrogen halides indicates that these molecules oscillate at low temperatures but go over mainly to rotational states before the melting point is reached. This process should be accompanied by thermal phenomena, as is shown by the following argument. With $n < n_0$ the eigenfunctions in θ and ϕ change only slightly as n is increased; the probability function $\psi\bar{\psi}$, with maxima in the neighborhood of the equilibrium values of θ and ϕ, falls off rapidly from these maxima, and increase in n causes only some spread, corresponding to larger amplitudes of oscillation. But a radical change takes place as n goes through the transition value. The eigenfunctions change completely in nature, becoming much more nearly constant, as may be verified by a study of the Fourier series coefficients given by Goldstein for the Mathieu functions. This change increases the repulsive forces between molecules, and tends to spread the crystal lattice

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[15] The entropy $n_A R$ log 3 arising from the three spin eigenfunctions for antisymmetrical molecules will be lost only at temperatures of the order of magnitude of 0.001°K, at which the very small nuclear interaction energy would become appreciable. It may be pointed out that the magnitude of the interaction energy with other molecules for the three states with $j = 1$. as compared with the spin-rotation interaction energy is such as not to permit coupling of j and the spin moment to form a resultant.

[16] F. Simon, K. Mendelssohn, and M. Ruhemann, Naturwiss. **18**, 34 (1930).

[17] Personal communication.

as soon as an appreciable number of molecules have begun to rotate. But spreading the lattice decreases the forces between molecules and decreases $\beta\nu_0$ and V_0, so that more molecules can rotate. The effect builds up to give a transition, which often is not accompanied by an essential change in the structure of the crystal. The transition is usually not sharp, but covers a range of temperature of several degrees, and is foreshadowed on the low temperature side by an abnormal increase in heat capacity.

Such a transition is shown by methane.[18] The heat capacity rises rapidly from 18°K to a very sharp maximum (over 48 cal/mole deg.) at 20.4°, and then drops sharply to 4.6 cal/mole deg. at 22.8°. The temperature of transition agrees with the low value (about 1) predicted for n_C. A methane crystal between 20° and 90.6°K (the melting point) would be described as consisting of rotating molecules in cubic close-packing;[19] below 20° the tetrahedral molecules oscillate about equilibrium orientations. It would be very interesting to have Raman effect or infrared spectral data for solid methane; above 20° the lines should very closely approximate the rotation lines for the gaseous molecules, and below that temperature should show pronounced changes, the frequencies of the lines increasing and tending to become constant as the motion approaches harmonic oscillation.

The course of the heat capacity curves also indicates that the transitions shown by N_2 and O_2 at 35.4° and 43.76° respectively are accompanied by the setting in of rotation of the molecules. This is supported by the known crystallographic symmetry of the high temperature forms; nitrogen cubic (indicating cubic close-packing of N_2 molecules) and oxygen hexagonal (indicating hexagonal close-packing).

The gradual transitions shown[20] by HCl (at 98°K), HBr (at 89°, 113°, and 117°K), and HI (at 70° and 126°K) are to be given a similar interpretation.[21] Each of the successive transitions in HBr and HI may be connected with incipient rotation about one crystal axis and the expansion of the crystal along that axis alone. In every case freely rotating molecules would assume a close-packed arrangement (cubic close-packing of molecules has been found with x-rays by Simon and Simson[22] for the high temperature form of HCl); on cooling below the temperature at which oscillation sets in the molecules may merely orient themselves, giving a structure similar to that of CO_2, for example, or the orientation may be accompanied by a change of position of molecular centers. That this takes place for HCl is indicated by the low symmetry of the low-temperature form shown by Simon and Simson's powder photographs.

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[18] K. Clusius, Zeits. f. phys. Chem. **B3**, 41 (1929).

[19] J. C. McLennan and W. G. Plummer, Phil. Mag. **7**, 761 (1929), have found that powder photographic data indicate cubic close-packing of the molecules.

[20] W. F. Giauque and R. Wiebe, J. Am. Chem. Soc. **50**, 101 (1928); **50**, 2193 (1928); **51**, 1441 (1929).

[21] Giauque and Wiebe suggested essentially this explanation, writing "The results suggest the following possibility: the transition starts as a changing thermal equilibrium between energy states of the hydrogen iodide molecule, both in the same crystal lattice, but when a sufficient concentration of the higher energy state has been reached, the system becomes unstable and changes to a new crystalline form."

[22] F. Simon and C. v. Simson, Zeits. f. Physik **21**, 168 (1924).

It is predicted that the dielectric constants of solid HCl, HBr, and HI at temperatures just below the melting points will be very high and dependent on the temperature, the values being given by Debye's theory of the orientation of electric dipole molecules; while the low-temperature forms will have low dielectric constants nearly independent of the temperature.

In general it is to be expected that rotational motion of molecules and complex ions of sufficiently low moment of inertia will set in below the melting point of the crystals. This condition of low moment of inertia is satisfied by complexes containing hydrogen atoms and one heavy atom. Thus the forces orienting the tetrahedral ammonium ion in an ammonium salt are much stronger than those acting on a methane molecule, so that the ion will oscillate until a much higher temperature than 20°K is reached; but this temperature of transition to rotational motion is still considerably below the melting point.

The transitions have been observed. Simon[23] and co-workers found from heat capacity measurements that ammonium chloride, bromide, and iodide show a gradual transition covering about a 10° range in the neighborhoood 240°K, the nature of the phenomenon not depending essentially on the anion.[24] X-ray studies showed the crystal structure to be the same before and after the transition, which is accompanied by a small volume change, less than 1%. These investigators attribute the transition to the ammonium ion, but make no other suggestions as to its nature. The observed phenomena are just those expected to accompany the transition from oscillation to rotation of the ammonium ion, however. The increase in the transition temperature in the series NH_4I (−42.5°C), NH_4Br (−38.0°C), NH_4Cl (−30.4°C) further shows the expected effect of increasing interionic forces accompanying decreasing anion radius.[25]

The rotation of the ammonium ion in salts at ordinary temperatures provides justification for the customary treatment of the ion as spherically symmetrical in the theoretical discussion of the structure of ionic crystals. Further, the rotation of molecules such as NH_3 and H_2O about symmetry axes accounts for the fact that these molecules occupy positions in crystals with symmetry elements not compatible with those of the non-rotating molecule. Thus in $Ni(NH_3)_6Cl_2$ the NH_3 molecules lie on four-fold axes, and in alum the H_2O molecules on three-fold axes. The rotation of the molecules,

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[23] F. Simon, Ann. d. Physik **68**, 263 (1922); F. Simon and C. v. Simson, Naturwiss. **38**, 880 (1926); F. Simon, C. v. Simson, and M. Ruhemann, Zeit. f. phys. Chem. **129**, 339 (1927).

[24] A very small hump in the heat capacity curve at −30° was also found for ammonium fluoride; the interpretation of this is uncertain (the structure of this crystal is not the same as that of the other ammonium halides).

[25] Small maxima in the heat capacity curves of organic compounds are probably often due to the transition from oscillational to rotational motion of a part of the molecule. Thus the maxima shown by *o*-xylene, *m*-xylene, and hexamethylbenzene (reported by H. M. Huffman, G. S. Parks and A. C. Daniels, J.A.C.S., **52**, 1547 (1930) would be attributed to the rotation of the methyl groups, which have a low moment of inertia and can rotate about the single bond holding the group to the rest of the molecule. *p*-xylene shows no maximum, indicating that the orienting forces on the methyl group are larger, raising the transition temperature above the melting point.

however, gives them an effective infinite symmetry axis, which is compatible with these positions.

The possibility of rotation introduces considerable uncertainty in the conclusions reached by Hendricks[26] in regard to the nature of the aliphatic carbon chain. From the x-ray study of crystals of the mono-alkyl substituted ammonium halides he found that in a number of these crystals the alkyl ammonium ion lies on a four-fold axis of symmetry, a result which apparently excludes the usual staggered chain of carbon atoms, and which caused him to suggest that the chain really is straight. But the moment of inertia of a staggered chain about an axis along the chain would be very small, and we would expect rotation about this axis at ordinary temperatures, giving the chain an effective infinite symmetry axis, which is compatible with the x-ray data. Accordingly, Hendricks' investigation does not require that the staggered aliphatic chain be given up.[27]

It has been found by Lyons and Rideal that solid unimolecular films on water of long chain hydrocarbons with polar ends exist in two possible forms, one with an area of 20.6A^2 per molecule, and the other, stable at higher temperatures, with an area of 26.2A^2 per molecule.[28] These authors suggest[29] that in the more compact form the staggered chains are interlocked, and fit together more closely than at higher temperatures when interlocking is not effective. This explanation is made somewhat more precise by the application of the considerations discussed in this paper. At low temperatures interlocking does take place, the molecules oscillating about certain equilibrium orientations. With increasing temperature rotation sets in, and the film expands; in this state the molecules would be well represented as circular cylinders with a radius equal to the maximum radius of the staggered chain. The phenomenon is exactly analogous to that giving rise to gradual transitions in crystals.

In molecules C_2X_6, such as ethane, C_2H_6, there exists the possibility of the two ends of the molecule rotating or oscillating relative to each other. In case that X is a large atom, as in C_2I_6, the interaction of the two ends of the molecule will be large, and they will carry out small oscillations about the relative orientation in which the atom groups fit closely together, the six atoms X defining the corners of an octahedron. But in C_2H_6 the interaction of the two ends of the molecule will be small, and they will rotate freely about the single bond connecting the carbon atoms, with a frequency which is simply related to the rotational frequency of the entire molecule about its figure axis. The determination of the energy levels characteristic of this motion for molecules of this type, by means of Raman effect or infrared measurements, would permit the evaluation of the potential energy of the molecule as a function of the relative orientation of its ends.

I acknowledge with gratitude the inspiration and assistance received through conversations with Professor W. F. Giauque of the Chemistry Department of the University of California.

[26] S. B. Hendricks, Zeits. f. Krist. **67**, 465 (1928); **68**, 189 (1928); additional paper in press.

[27] Dr. Hendricks has informed me that he agrees with this conclusion.

[28] I am indebted to Professor J. W. Mc Bain for directing my attention to this work.

[29] C. G. Lyons and E. K. Rideal, Nature **125**, 455 (1930).

[Reprint from the Journal of the American Chemical Society, **57**, 2680 (1935).]

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 506]

The Structure and Entropy of Ice and of Other Crystals with Some Randomness of Atomic Arrangement

BY LINUS PAULING

Investigations of the entropy of substances at low temperatures have produced very important information regarding the structure of crystals, the work of Giauque and his collaborators being particularly noteworthy. For example, the observed entropy of crystalline hydrogen shows that even at very low temperatures the molecules of orthohydrogen in the crystal are rotating about as freely as in the gas;[1] subsequent to this discovery the phenomenon of rotation of molecules in crystals was found to be not uncommon. Also the entropy values of carbon monoxide[2] and nitrous oxide[3] show that in crystals of these substances the molecules are not uniquely oriented, but have instead a choice between two orientations, presumably the opposed orientations CO and OC or NNO and ONN along fixed axes. It is pointed out in this note that the observed entropy of ice at low temperatures provides strong support for a particular structure of ice, and thus gives an answer to a question which has been extensively discussed during the past few years.

It has been generally recognized since the discovery of the hydrogen bond[4] that the unusual properties of water and ice (high melting and boiling points, low density, association, high dielectric constants, etc.) owe their existence to hydrogen bonds between water molecules. The arrangement of oxygen atoms (but not of hydrogen atoms) in crystals of ice is known from x-ray studies;[5] it is not a close-packed arrangement (as of sulfur atoms in the high-temperature form of hydrogen sulfide), but a very open one, like that of the silicon atoms in high-tridymite. Each oxygen atom in ice is tetrahedrally surrounded by four other oxygen atoms at the distance 2.76 Å., and it has been assumed that it is bonded to these atoms by hydrogen bonds, the number of hydrogen atoms being just that required to place one hydrogen atom between each pair of oxygen atoms. (Similarly in high-tridymite there is an oxygen atom between each pair of silicon atoms; we might say that each silicon atom is attached to four others by oxygen bonds.)

The question now arises as to whether a given hydrogen atom is midway between the two oxygen

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[1] W. F. Giauque and H. L. Johnston, THIS JOURNAL, **50**, 3221 (1928); L. Pauling, *Phys. Rev.*, **36**, 430 (1930).

[2] J. O. Clayton and W. F. Giauque, THIS JOURNAL, **54**, 2610 (1932).

[3] R. W. Blue and W. F. Giauque, *ibid.*, **57**, 991 (1935); K. Clusius, *Z. Elektrochem.*, **40**, 99 (1934).

[4] W. M. Latimer and W. H. Rodebush, THIS JOURNAL, **42**, 1419 (1920).

[5] D. M. Dennison, *Phys. Rev.*, **17**, 20 (1921); W. H. Bragg, *Proc. Phys. Soc.* (London), **34**, 98 (1922); W. H. Barnes, *Proc. Roy. Soc.* (London), **A125**, 670 (1929).

atoms it connects or closer to one than to the other. The answer to this is that it is closer to one than to the other. In the gas molecule the O–H distance is 0.95 Å., and the magnitudes of the changes in properties from steam to ice are not sufficiently great to permit us to assume that this distance is increased to 1.38 Å. In ice each hydrogen atom is about 0.95 Å. from one oxygen atom and 1.81 Å. from another.

We now ask whether each hydrogen atom (or rather hydrogen nucleus) has a choice of two positions along its oxygen–oxygen axis, independent of the positions of the other hydrogen nuclei. The answer is in the negative; for we know that the concentration of $(OH)^-$ and $(H_3O)^+$ ions in water is very small, and we expect the situation to be essentially unchanged in ice. Hence the hydrogen nuclei will assume positions such that each oxygen atom (with at most very few exceptions) will have two hydrogen atoms attached to it.

Let us now make the following assumptions (to be supported later by a discussion of the entropy) regarding the structure of ice.

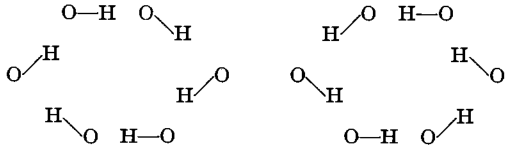
(1) In ice each oxygen atom has two hydrogen atoms attached to it at distances of about 0.95 Å., forming a water molecule, the HOH angle being about 105° as in the gas molecule.

(2) Each water molecule is oriented so that its two hydrogen atoms are directed approximately toward two of the four oxygen atoms which surround it tetrahedrally, forming hydrogen bonds.

(3) The orientations of adjacent water molecules are such that only one hydrogen atom lies approximately along each oxygen–oxygen axis.

(4) Under ordinary conditions the interaction of non-adjacent molecules is not such as to appreciably stabilize any one of the many configurations satisfying the preceding conditions with reference to the others.

Thus we assume that an ice crystal can exist in any one of a large number of configurations,[6] each corresponding to certain orientations of the water molecules. The crystal can change from one configuration to another by rotation of some of the molecules or by the motion of some of the hydrogen nuclei, each moving a distance of about 0.86 Å. from a potential minimum 0.95 Å. from one oxygen atom to another one 0.95 Å. from an adjacent oxygen atom. It is probable that both processes occur. As an example of a change from one to another configuration, we may consider one of the puckered rings of six oxygen atoms occurring in ice



Change from one of the two cyclic arrangements of hydrogen nuclei to the other is permitted by our postulates. The fact that at temperatures above about 200Å. the dielectric constant of ice is of the order of magnitude of that of water shows that the molecules can orient themselves with considerable freedom, the crystal changing under the influence of the electric field from unpolarized to polarized configurations satisfying the above conditions. On cooling the crystal to low temperatures it freezes into some one of the possible configurations; but it does not go over (in a reasonable period of time) to a perfect crystal with no randomness of molecular orientation. It will have at very low temperatures the entropy $k \ln W$, in which W is the number of configurations accessible to the crystal.

Let us now calculate W, using two different methods.

There are N molecules in a mole of ice. A given molecule can orient itself in six ways satisfying condition 2. However, the chance that the adjacent molecules will permit a given orientation is $^1/_4$; inasmuch as each adjacent molecule has two hydrogen-occupied and two unoccupied tetrahedral directions, making the chance that a given direction is available for each hydrogen of the original molecule $^1/_2$, and the chance that both can be located in accordance with the given orientation $^1/_4$. The total number of configurations for N molecules is thus $W = (^6/_4)^N = (^3/_2)^N$.

The same result is given by the following equivalent argument. Ignoring condition 1, there are 2^{2N} configurations with hydrogen bonds between adjacent oxygen atoms, each hydrogen nucleus having the choice of two positions, one near one oxygen atom and the other near the other. Some of these are ruled out by condition 1. Let us now consider a given oxygen atom and the four surrounding hydrogen atoms. There are sixteen arrangements of the four hydrogen nuclei. Of

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(6) One of the large number of configurations is represented by the structure of ice suggested by J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933); these authors also suggested that at temperatures just below the melting point (but not at lower temperatures) the molecular arrangement might be partially or largely irregular.

these ten are ruled out by condition 1—one gives $(H_4O)^{++}$, four give $(H_3O)^+$, four $(OH)^-$ and one O^{--}. This condition for each oxygen atom thus permits only $^6/_{16} = {}^3/_8$ of the configurations, the total number of permitted configurations being accordingly $W = 2^{2N}(^3/_8)^N = (^3/_2)^N$.

The contribution of this lack of regularity to the entropy of ice is thus $R \ln {}^3/_2 = 0.805$ E. U. The observed entropy discrepancy of ice at low temperatures is 0.87 E. U., obtained by subtracting the entropy difference of ice at very low temperatures and water vapor at standard conditions, for which the value 44.23 E. U. has been calculated from thermal data by Giauque and Ashley,[7] from the spectroscopic value 45.101 E. U. for the entropy of water vapor given by Gordon.[8] The agreement in the experimental and theoretical entropy values provides strong support of the postulated structure of ice.[9]

The structure of ice is seen to be of a type intermediate between that of carbon monoxide and nitrous oxide, in which each molecule can assume either one of two orientations essentially independently of the orientations of the other molecules in the crystal, and that of a perfect molecular crystal, in which the position and orientation of each molecule are uniquely determined by the other molecules. In ice the orientation of a given molecule is dependent on the orientations of its four immediate neighbors, but not directly on the orientations of the more distant molecules.

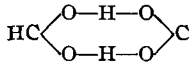
It should be pointed out that a finite residual entropy calculated for a substance from experimental data obtained at temperatures extending down to a certain temperature, with extrapolation below that point, may arise either from failure of the experimenter to obtain thermodynamic equilibrium in his calorimetric measurements or from error in the extrapolation. Measurements made under ideal conditions and extended to sufficiently low temperatures would presumably lead to zero entropy for any system.

Other Crystals with Residual Entropy

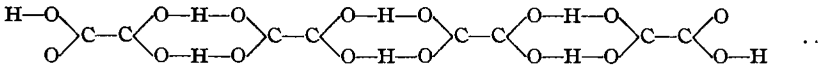
Our knowledge of the structure of crystals permits the prediction to be made that many other crystals will be found to have residual entropy at very low temperatures as a result of some randomness of atomic arrangement. It is probable, however, that experimental verification of the residual entropy would be difficult for most of the cases mentioned below.

Diaspore, $AlHO_2$, contains groups OHO with hydrogen bonds.[10] As in water, we expect the hydrogen nucleus to be closer to one oxygen atom than to the other. Inasmuch as there is no restriction on the choice of the two positions, each oxygen atom forming only one hydrogen bond, this would lead to a residual entropy of $R \ln 2$ per mole of $AlHO_2$. The same residual entropy is expected per HO_2 group for other crystals containing this group (staurolite).

Hydrogen bonds may not always lead to residual entropy. For example, the crystal lepidocrocite,[11] FeOOH, contains infinite strings of oxygen atoms joined by hydrogen bonds, ${}^{\mathrm{O}}\mathrm{H}_{\mathrm{O}}\mathrm{H}^{\mathrm{O}}\mathrm{H}_{\mathrm{O}}\mathrm{H}^{\mathrm{O}}\mathrm{H}$. If we assume that the choice of two positions by a hydrogen nucleus is restricted by the requirement that each oxygen have one and only one attached hydrogen, then there are two accessible configurations per string. This lack of definiteness does not lead to an appreciable residual entropy for a large crystal.

In the double molecules of formic acid, with the structure[12]  and in other monocarboxylic acids forming double molecules, we expect that the interaction within a carboxyl group is strong enough to permit only the two configurations in which one hydrogen nucleus is attached to each carboxyl group to be stable at low temperatures. This would lead to a residual entropy of $^1/_2\, R \ln 2$ per RCOOH.

By a similar argument we calculate for β-oxalic acid (anhydrous), which contain finite strings[13] of molecules



the residual entropy $R \ln 2$ per mole of $(COOH)_2$, whereas α-oxalic acid, containing layers with the dealized structure[13] in which there are infinite sequences of carboxyl groups attached by hydrogen bonds, would have no appreciable residual

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(7) W. F. Giauque and M. F. Ashley, *Phys. Rev.*, **43**, 81 (1933).

(8) A. R. Gordon, *J. Chem. Phys.*, **2**, 65 (1934).

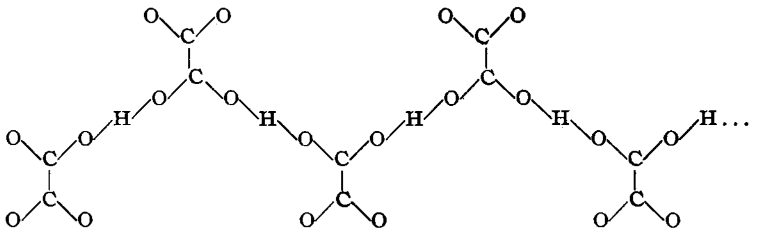
(9) The existence of this residual entropy of ice at very low temperatures was discovered by Giauque and Ashley (ref. 7), who preliminarily ascribed it to the persistance of rotation of ortho-water molecules (comprising $^3/_4$ of the total) about their electric-moment axes, giving an entropy of $^3/_4\, R \ln 2 = 1.03$ E. U.

(10) F. J. Ewing, *J. Chem. Phys.*, **3**, 203 (1935).

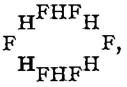
(11) F. J. Ewing, *ibid.*, **3**, 420 (1935).

(12) L. Pauling and L. O. Brockway, *Proc. Nat. Acad. Sci.*, **20**, 336 (1934).

(13) S. B. Hendricks, *Z. Krist.*, **91**, 48 (1935).



entropy. The experimental verification of this prediction by heat capacity measurements and the study of the equilibrium between the two forms might be practicable.

At present it is not possible to predict with confidence whether the hydrogen nucleus between two fluorine atoms connected by a hydrogen bond has the choice of two positions (as for oxygen atoms) or not. The FHF distance of 2.35 Å. is somewhat greater than twice the H–F distance in HF, 0.91 Å., although the difference (29%) is not so great as for OHO and H–O (45%). The question would be answered by a determination of the residual entropy of potassium hydrogen fluoride, KHF_2, or of some other crystal containing the HF_2 group; the residual entropy would be R ln 2 if the potential function for the hydrogen nucleus has two minima rather than one. The same residual entropy would also be shown by KH_2F_3, KH_3F_4, etc. If crystalline hydrofluoric acid contains cyclic molecules $(HF)_6$, with the structure  $\begin{matrix} {}^{H}FHF_{H} \\ F\qquad F \\ {}_{H}FHF^{H} \end{matrix}$, the two-minimum function and the restriction that one hydrogen is attached to each fluorine would lead to a residual entropy of $^1/_6$ R ln 2 per mole of HF.

Hydrogen bonds between unlike atoms, as in NH_4F, would not lead to residual entropy.

Residual entropy may also result from the multiplicity of stable positions for atoms other than hydrogen. In γ-Al_2O_3 and γ-Fe_2O_3 the oxygen ions are arranged in a close-packed framework, which provides nine positions for every eight cations. The x-ray data[14] indicate that the cations are distributed essentially at random among these positions, leading to a residual entropy of $^3/_2\ R \ln {}^{27}/_{16} = 1.558$ E. U. per mole of R_2O_3. In pyrrhotite,[15] $Fe_{1-\delta}S$, the sulfur atoms have a hexagonal arrangement, the iron atoms being distributed apparently at random among the positions provided, of which they occupy the fraction $1 - \delta$. In the cubic tungsten bronzes,[16] Na_xWO_3, the sodium ions occupy the fraction x of the available positions. These crystals would presumably show residual entropy of mixing of the ions W^{5+} and W^{6+} as well as the entropy of random distribution of the sodium ions. A somewhat similar case is provided by the hexagonal form of silver iodide,[17] in which at room temperature each silver atom has the choice of four or five positions a few tenths of an Ångström apart. At liquid air temperatures, however, most of the atoms settle into one position, so that no residual entropy would be shown.

Many crystals show an uncertainty in structure similar to that of CO and NNO or of solid solutions. For potassium cyanate the x-ray data[18] indicate that each cyanate ion has the choice of two orientations, NCO and OCN, which would lead to the residual entropy R ln 2. In spinel, $MgAl_2O_4$, and other crystals with the spinel structure, the bivalent and trivalent cations are distributed with considerable randomness among the available positions,[19] leading to a residual entropy corresponding to a crystalline solution. In muscovite,[20] $KAl_2(AlSi_3)O_{10}(OH)_2$, one aluminum and three silicon atoms per formula are distributed, presumably with considerable randomness, among the available tetrahedral positions. The same phenomenon, leading to residual entropy, without doubt occurs in many aluminosilicates.

Crystals of cadmium bromide[21] and nickel bromide[22] prepared in certain ways show a type of randomness which does not lead to any appreciable residual entropy, provided that the crystals are not extremely small. This randomness of structure ("Wechselstruktur," alternating layer structure) consists in a choice between two positions for each layer of a layer structure, leading to an entropy of k ln 2 for each layer, which remains

(14) G. Hägg and G. Söderhohn, *Z. physik. Chem.*, **B29**, 88 (1935); G. Hägg, *ibid.*, **B29**, 95 (1935); E. J. W. Verwey, *Z. Krist.*, **91**, 65 (1935); E. Kordes, *ibid.*, **91**, 193 (1935).

(15) G. Hägg and I. Sucksdorff, *Z. physik. Chem.*, **B22**, 444 (1933).

(16) G. Hägg, *ibid.*, **B29**, 192 (1935).

(17) L. Helmholz, *J. Chem. Phys.*, **3**, 740 (1935).

(18) S. B. Hendricks and L. Pauling, THIS JOURNAL, **47**, 2904 (1925).

(19) T. F. W. Barth and E. Posnjak, *J. Washington Acad. Sci.*, **21**, 255 (1931); F. Machatschki, *Z. Krist.*, **80**, 416 (1931).

(20) L. Pauling, *Proc. Nat. Acad. Sci.*, **16**, 123 (1930); W. W. Jackson and J. West, *Z. Krist.*, **76**, 211 (1930).

(21) J. M. Bijvoet and W. Nieuwenkamp, *ibid.*, **86**, 466 (1933).

(22) J. A. A. Ketelaar, *ibid.*, **88**, 26 (1934).

inappreciable, inasmuch as the number of layers in a crystal (other than an extremely small crystal) is very small compared with the number of atoms.

In this connection it might be mentioned that there exists the possibility that ice may crystallize with such an alternating layer structure. The oxygen-atom arrangement assigned to ice corresponds to superimposing double oxygen layers in the sequence ABAB—(A at 00, B at $^1/_3$ $^2/_3$, C at $^2/_3$ $^1/_3$ of a hexagonal net). The sequence ABCABCABC— would also lead to an arrangement (diamond) such that each oxygen atom is surrounded by four others arranged tetrahedrally, which is indeed, so far as I can see, just as satisfactory as the reported arrangement. There is no good evidence that such a cubic modification of ice has been observed. However, the arbitrariness of orientation which we have found to exist for the water molecules in ice suggests that there may also be an arbitrariness in the sequence of double oxygen layers, with configurations such as ABABABCBCB— occurring. Such an alternating layer structure would have hexagonal symmetry, might develop faces at angles corresponding to the axial ratio $c/a = 1.63$, and would not be distinguishable so far as residual entropy is concerned from a crystal with fixed oxygen atom arrangement. The x-ray data show that the sequence of layers is not completely random, the structure being essentially ABABAB—; it is possible, however, that a change in the sequence, corresponding to twinning on the basal plane, occurs occasionally.

I am indebted to Professor W. F. Giauque for discussing the question of the structure and entropy of ice, as well as related questions, with me.

Summary

It is suggested that ice consists of water molecules arranged so that each is surrounded by four others, each molecule being oriented in such a way as to direct its two hydrogen atoms toward two of the four neighbors, forming hydrogen bonds. The orientations are further restricted by the requirement that only one hydrogen atom lie near each O–O axis. There are $(^3/_2)^N$ such configurations for N molecules, leading to a residual entropy of $R \ln {}^3/_2 = 0.805$ E. U., in good agreement with the experimental value 0.87 E. U.

The structure and entropy of other crystals showing randomness of atom arrangement are discussed.

PASADENA, CALIF. RECEIVED SEPTEMBER 24, 1935

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Quantum Mechanics and the Third Law of Thermodynamics

Rodebush[1] has recently discussed certain points concerning the third law of thermodynamics in terms of quantum mechanics. His recognition of the significance of quantum mechanics in considering the behavior of solutions and glasses at low temperatures we believe to be of interest, and we agree with the more important of his conclusions. However, there have arisen some questions of interpretation in which we differ from the statements of his paper. We have thought it of value to present here, as explicitly as possible and at the risk of some duplication of ideas, an outline of these points and a discussion of their bearing on the expected behavior of the systems under treatment. It is our opinion that the views presented below have been in the main accepted by investigators interested in the theory of the third law; however, so far as we are aware no equivalent discussion has been published.

Without entering into the question of the relation between statistical mechanics and thermodynamics, we accept as giving a value for the entropy of the system in which we are interested the expression $k \ln N$, in which N is the number of independent wave functions for the system compatible with our knowledge as to its condition. Following the plan adopted by Rodebush, we first discuss the case of an optically active substance.[2] An isolated molecule of such a substance in its lowest rotational and vibrational state and known to be in the dextro configuration[3] is to be represented by a single wave function corresponding to this configuration, and will have the quantum weight 1, and not 2. On the other hand, if the molecule is in one of the two lowest energy states corresponding to the accurate solution of the wave equation (as could be determined by an energy measurement extending over a period of time long compared to the time required for spontaneous dextro-levo conversion), it is to be represented by a single wave function which is either symmetric or antisymmetric relative to inversion about a center, and which is formed by linear combination of the dextro and levo wave functions. It will then not be known whether the molecule is a dextro or a levo molecule. Only in the case that neither its optical activity nor its (exact) energy is known can we assign to it the quantum weight 2.

By analogy with the simple case of the optical isomers Rodebush generalizes the many-minima problem exemplified by glasses and crystalline solutions with the following statement. "We have a number of configurations of the same energy separated by energy crests. By symmetric and antisymmetric linear combinations of wave functions,[4] we obtain a total number of wave functions equal to the degeneracy; that is to say, the total number of configurations having the same energy. Thus, instead of each configuration having a distinct energy, each configuration has now a large number of closely spaced energy levels."

Here we prefer to state the situation in a somewhat different way, as follows. The system in its low temperature condition and known to have a particular configuration[5] (one of N possible configurations) is to be represented by one of an appropriate set of N wave functions, corresponding to the N configurations. If not the configuration, but the energy of the system is to be investigated with great accuracy, by means of observations extending over a very long period of time, the set of wave functions of interest is that corresponding to accurate solution of the wave equation (these wave functions being linear combinations of those corresponding to the N configurations). The energy value found by experiment would be one of the multiplet of N levels corresponding to the low temperature condition. We cannot, however, make use of the two sets of wave functions simultaneously, but must use either the configuration wave functions or the multiplet wave functions, or some other equivalent set. In other words, both the configuration and the exact energy of the system cannot be simultaneously known. If either is known a single wave function (of the set of N) is sufficient to describe the system and the system will then have the quantum weight 1, and not N. However, if neither the configuration nor the exact energy of the system is known, we may use either set of N wave functions (or any other set formed from them by linear combinations) to describe it, and its quantum weight will then be N.

The behavior of systems on cooling to a very low temperature ($kT \ll h\nu$, where ν is the frequency of the lowest oscillational state) may be outlined in the case of an ideal solution somewhat as follows.[6] If ν^* is the frequency of transition among the various configurations (as given by the corresponding resonance integral divided by h), the energy spread of the multiplet levels will be of the order of $h\nu^*$. If the cooling be done so slowly that a time very long compared to $1/\nu^*$ is allowed at each temperature, the loss of heat will be such as to correspond to a loss of entropy of $k \ln N$, since the multiplet levels under such conditions may be regarded as discrete. On rapid cooling to the same low temperature, the energy of the system will be determinable only to within about $h/2\pi\tau$, where τ is the time of observation at the temperature in question. If this uncertainty in energy is large compared to $h\nu^*$ there will still remain N states (N independent wave functions) of the system falling within the observable energy limits, and the entropy will be $k \ln N$. Only after a long time of observation at this temperature can these limits be narrowed sufficiently to permit the statement that a single state is represented and the entropy is zero.

A real solution or glass differs from an ideal solution or glass, discussed above, in that one of its configurations, corresponding to a pure crystalline substance or a mixture of pure crystalline substances, possesses an energy lower than any other. If such a system be subjected to very slow cooling, or be held for a long time at a low temperature as discussed above, it will ultimately attain this configuration (mainly by transition through excited vibrational states rather than by penetration of potential barriers), and will therefore have zero entropy. On cooling sufficiently rapidly to exclude effectively transitions between configurations, or on holding at the low temperature for a time shorter than required for these transitions to occur, the multiplicity N will be retained by the system, its entropy then remaining greater than zero.

It may be pointed out that the discussion of the entropy of a real solution or glass on the basis of quantum mechanics, as just given, is identical with the discussion of the problem in the pre-quantum-mechanical era. On the other hand, the quantum mechanics has introduced a significant change in the discussion of the entropy of an ideal solution or glass. Before the development of quantum mechanics there was no conceivable mechanism leading to the loss of the final $k \ln N$ of entropy at very low temperatures for an ideal solution or glass, defined as having N configurations with exactly the same energy. The quantum-mechanical mechanism leading to the loss of this entropy is the resonance of the system among the N configurations.

Rodebush has also implied that the accuracy with which very low temperatures can be measured is restricted by the uncertainty principle and by the nature of the substance under investigation. However, the accuracy of a temperature measurement is not limited in a serious way by the uncertainty principle for energy, inasmuch as the relation between the uncertainty in temperature and the length of time involved in the measurement depends on the size of the thermometer, and the uncertainty in temperature can be made arbitrarily small by sufficiently increasing the size of the thermometer; we assume as the temperature of the substance the temperature of the surrounding thermostat with which it is in either stable or metastable equilibrium, provided that thermal equilibrium effective for the time of the investigation is reached.

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Department of Chemistry,
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March 30, 1936.

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[1] W. H. Rodebush, J. Chem. Phys. **2**, 669 (1934).

[2] For a thorough discussion of this see F. Hund, Zeits. f. Physik **43**, 805 (1927).

[3] We shall use the word configuration in this paper to represent the approximate relative spatial arrangement of the nuclei of the atoms in the system under consideration (neglecting the effect of the vibrational motion on the nuclear positions).

[4] At the request of Professor Rodebush, the wording of this sentence has been changed slightly from that in his paper.

[5] We assume each configuration to be in its lowest vibrational state.

[6] We believe that the ideas discussed in this connection parallel those of Rodebush, but have thought it worth while to give them in greater detail.

Chapter 10

NUCLEAR STRUCTURE; SUPERCONDUCTIVITY; QUASICRYSTALS

Contents

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THE CLOSE-PACKED-SPHERON MODEL OF ATOMIC NUCLEI AND ITS RELATION TO THE SHELL MODEL

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Read before the Academy by invitation of the Committee on Arrangements, October 11, 1965

I have found that the assumption that in atomic nuclei the nucleons are in large part aggregated into clusters arranged in closest packing leads to simple explanations of many properties of nuclei. Some aspects of the closest-packing theory of nuclear structure are presented in the following paragraphs.[1]

The treatment of nuclei such as O^{16} as aggregates of helions (alpha particles[2]) has been reasonably successful.[3] The binding energy of nucleons in O^{16} is only 13 per cent greater than that of four helions, and accordingly a wave function composed of helion wave functions would be expected to be a good zero-order approximation. For example, four equivalent orbitals centered about the corners of a tetrahedron can be formed by sp^3 hybridization of the orbitals of the shell model,[4–6] which are referred to the center of the O^{16} nucleus. This process of hybridization of orbitals provides the formal basis of the relation between the helion model (cluster model) and the shell model. Nuclei with more neutrons than protons may be described in terms of helions, tritons ($H^3 = n^2p$), and dineutrons (plus $He^3 = np^2$ for N odd). These clusters of neutrons and protons occupying localized $1s$ orbitals may be called *spherons:* the largest spheron is the helion.

There is evidence from electron-scattering experiments[7] that the density of protons is approximately constant throughout a spherical central region of a nucleus, and then falls off to zero with increasing radius, in a way that has been described[7] as constituting a "skin" with thickness about $2.4f$. This skin thickness may be ascribed in part to the nubbling of the surface by the outer hemispheres of the helions and tritons of the outermost layer of the nucleus. The observed charge distribution of the helion corresponds to a radius of about $2f$, and the packing volume $24f^3$ to the radius $1.62f$ ($1.47f$ for the triton).

The Distribution of Spherons in Layers.—Several theoretical and empirical arguments indicate that the nature of spheron-spheron interactions is not such as to limit the ligancy of a spheron to a fixed value, but that, instead, maximum stability is achieved when each spheron ligates about itself the maximum number of neighbors; aggregates of spherons, like aggregates of argonon (noble-gas) atoms or metal atoms, assume a closest-packed structure.

A simple argument leads us to conclude that the spherons in a nucleus are arranged approximately in a series of concentric layers. The energy of a nucleus is minimal for spherical (or ellipsoidal) shape; deviation from this shape, with surface irregularities greater than the spheron nubbling, decreases the number of spheron-spheron interactions and thus increases the surface energy. We conclude that there is a surface layer of spherons. For a large nucleus, the outer part of the cavity inside this surface layer is occupied by spherons in contact with the inner side of the surface layer. These spherons hence constitute another layer, within which there may be still another spheron or layer of spherons.

To avoid confusion with the shells of the shell model of the nucleus we shall refer to the layers of spherons by special names: the *mantle* for the surface layer, and the *outer core* and *inner core* for the two other layers of a three-layer nucleus.

For soft spheres, permitting about 10 per cent variation in contact distance, triangular packing (tetrahedral packing) is denser than ordinary "closest" packing, as represented in metals such as copper and magnesium. In triangular packing the coordination polyhedra have triangular faces and each sphere in an outer layer lies out from the center of a triangle, thus forming a tetrahedron. Pure triangular packing is limited to finite aggregates. The icosahedral packing shown in Figure 1, involving three layers of spheres surrounding a central sphere, is found[8] around each lattice point of the body-centered cubic lattice of the intermetallic compound $Mg_{32}(Al,Zn)_{49}$.

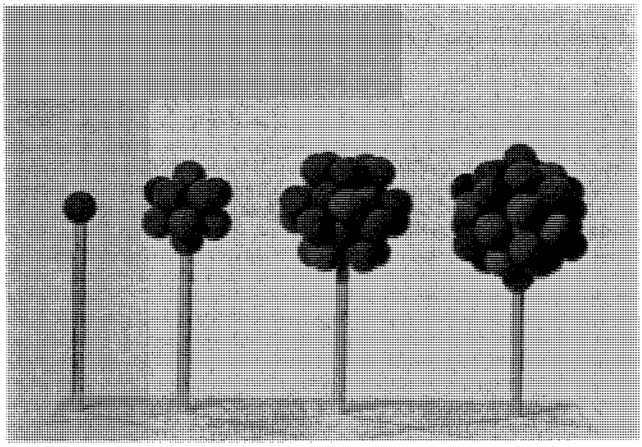

FIG. 1.—The arrangement of 45 spheres in icosahedral closest packing. At the left there is shown a single sphere, which constitutes the inner core. Next there is shown the layer of 12 spheres, at the corners of a regular icosahedron. The third model shows the core of 13 spheres with 20 added in the outer layer, each in a triangular pocket corresponding to a face of the icosahedron; these 20 spheres lie at the corners of a pentagonal dodecahedron. The third layer is completed, as shown in the model at the right, by adding 12 spheres at corners of a large icosahedron; the 32 spheres of the third layer lie at the corners of a rhombic triacontahedron. The fourth layer (not shown) contains 72 spheres.

We may use this example of triangular closest packing to derive an expression for the distribution of spheres in successive layers. The form of the expression (number of spheres proportional to the cube of a length, the radius) reflects the assumption of constancy of effective volume per sphere. The expression is

$$n_t = (n_i^{1/3} + 1.30)^3, \qquad (1)$$

which may be rewritten as

$$n_i = (n_t^{1/3} - 1.30)^3. \tag{1a}$$

Here n_t is the total number of spheres, and n_i the number not including those in the outermost layer. The number 1.30, representing the effective thickness of the outer layer, is obtained in the following way. For the structure shown in Figure 1 the numbers of spheres in successive layers, from the center out, are 1, 12, 32, 72, and the successive total numbers are 1, 13, 45, 117. The value 1.30 for the constant in equation (1) provides the best simple approximation to these numbers: it gives 0.97, 12.0, 46.0, 117. The amount of agreement suggests that equation (1) is reliable to about ±1, and the following discussion corresponds to this assumption.

The Relation between the Shell Model and Layers of Spherons.—In the customary nomenclature for nucleon orbitals the principal quantum number n is taken to be $n_r + 1$, where n_r, the radial quantum number, is the number of nodes in the radial wave function. (For electrons n is taken to be $n_r + l + 1$.) The nucleon distribution function for $n = 1$ corresponds to a single shell (for 1*s* a ball) about the origin. For $n = 2$ the wave function has a small negative value inside the nodal surface, that is, in the region where the wave function for $n = 1$ and the same value of l is large, and a large value in the region just beyond this surface.

The nature of the radial wave functions thus leads us to the following interpretation[1] of the subshells of the shell model:

1. Those subshells that occur (are occupied) with only the value 1 for the quantum number n contribute only to the outer layer of spherons (the mantle).

2. Those subshells that occur with two values of n contribute to the mantle and the next inner layer, and so on.

Thus for the neutron configuration $1s^2 2s^2 1p^6 1d^{10} 3s^2 2p^6 2d^{10} 1f^{14} 1g^{18} (1h\ 11/2)^{12}$ we assign $1s^2$ to the inner core (2 neutrons), $2s^2 1p^6 1d^{10}$ to the outer core (18 neutrons), and the remainder (62 neutrons) to the mantle.

The Assignment of Nucleons to Layers by Use of the Packing Equation.—Equation (1) has been applied in the assignment of neutrons to the mantle, outer core, inner core, and innermost core (for N very large), with the results shown in Figure 2.

The method may be illustrated by the example $N = 20$, as in Ca^{40}, to which we assign ten spherons (ten helions). For $n_t = 10$ equation (1*a*) gives $n_i = 0.62$, which we round off to the nearest integer, 1, giving one spheron (2 neutrons) in the core and 9 spherons (18 neutrons) in the mantle. The neutron configuration is thus found to be $1s^2$ for the core and $2s^2 1p^6 1d^{10}$ for the mantle. The magic number 20 is seen to correspond to completed shells for both the core (K shell) and the mantle (M shell).

The heavy bar in Figure 2 indicating completion of the K shell of neutrons in the core extends from $N = 14.4$ to $N = 26.8$. These limits correspond to 1.5 ± 1.0 neutrons in the core, 1.5 being the value for transition from 1*s* to $1s^2$, and ±1 representing the uncertainty in the equation. The bars for other completed shells have been similarly drawn, and those for completed subsubshells have been drawn with only half this width (the uncertainty, however, is as great).

In the calculations for the inner core and innermost core the decreased volume of the inner spherons (shift to tritons and dineutrons) has been taken into account. The nature of the spherons is indicated by the chart (Fig. 2) and the Z/N ratio.

To within its reliability, Figure 2 applies to protons as well as to neutrons.

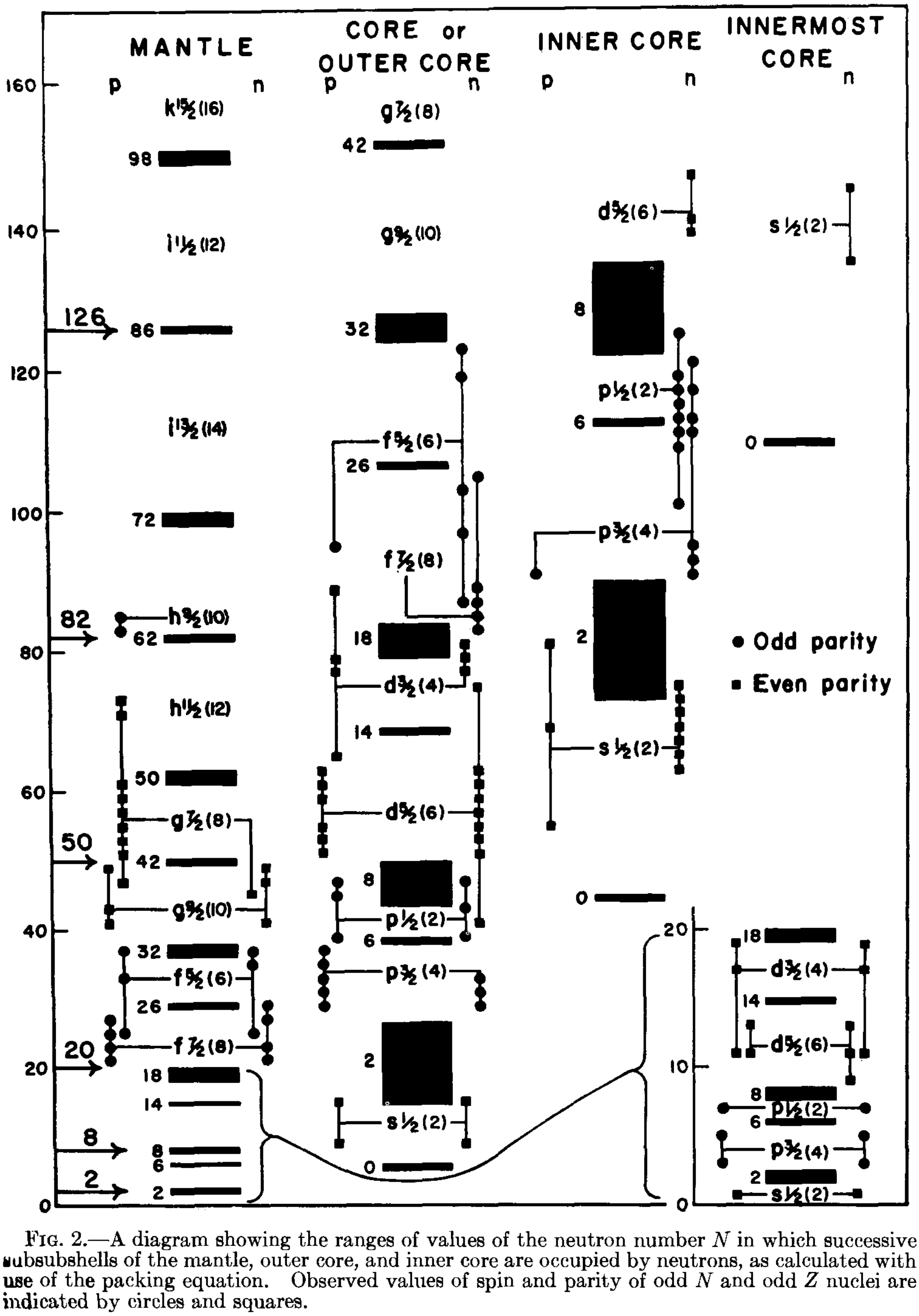

FIG. 2.—A diagram showing the ranges of values of the neutron number N in which successive subsubshells of the mantle, outer core, and inner core are occupied by neutrons, as calculated with use of the packing equation. Observed values of spin and parity of odd N and odd Z nuclei are indicated by circles and squares.

The sequence of levels shown in Figure 2 closely resembles the level diagram found by Mayer and Jensen by analysis of observed nuclear properties, with the help of the calculated level sequences for harmonic-oscillator and square-well potential functions.[9] Our packing equation provides a simple theoretical explanation of the sequence of levels. Moreover, it shows the regions of overlapping of the ranges for mantle and core subsubshells. When the spins are much different, these are the regions of existence of isomers.

Nuclear Spins and Parities.—The level sequence of Mayer and Jensen was largely derived from observed values of nuclear spins and parities. The extent to which these observations agree with the ranges given by the packing equation is shown in Figure 2. Most of the points lie within the ranges of N and Z for which a single unpaired nucleon would have the observed spin and parity (as indicated by the connecting lines). It has been pointed out by Mayer and Jensen that some of the apparent exceptions may indicate that three or five unpaired nucleons are coupled to a resultant spin; for example, a state with $J = 3/2$ and positive parity, as observed for both $Z = 11$ and $N = 11$, is an allowed state for the configuration $(d5/2)^3$.

The circles and dots in Figure 2 represent 251 odd-N or odd-Z nuclei for which spins and parities are given on the 1964 General Electric Chart of the Nuclides. The values for eleven nuclides, not accounted for by the level diagram, are not shown in the figure; they are ${}_{67}\mathrm{Ho}^{161,\,165}(7/2-)$, ${}_{93}\mathrm{Np}^{237,\,239}(5/2+)$, $\mathrm{Se}_{41}{}^{75}(5/2+)$, $\mathrm{Gd}_{89}{}^{153}(3/2+)$, $\mathrm{Dy}_{95}{}^{161}(5/2+)$, $\mathrm{Dy}_{99}{}^{165}$ and $\mathrm{Er}_{99}{}^{167}(7/2+)$, and $\mathrm{U}_{143}{}^{235}$ and $\mathrm{Pu}_{143}{}^{237}$ $(7/2-)$.

The Structural Basis of the Magic Numbers.—Elsasser[10] in 1933 pointed out that certain numbers of neutrons or protons in an atomic nucleus confer increased stability on it. These numbers, called magic numbers, played an important part in the development of the shell model;[4, 5] it was found possible to associate them with configurations involving a spin-orbit subsubshell, but not with any reasonable combination of shells and subshells alone. The shell-model level sequence in its usual form,[11] however, leads to many numbers at which subsubshells are completed, and provides no explanation of the selection of a few of them (6 of 25 in the range 0–170) as magic numbers.

The packing diagram given in Figure 2 provides a simple structural basis of the magic numbers.[1]

The magic numbers[12] are 2, 8, 20, 50, 82, and 126. Reference to Figure 2 shows that they are distinguished from all other numbers by having a single layer that is a completed shell or a core consisting of a completed shell or shells. Thus 2 is the completed K shell, $1s^2$, and 8 the completed L shell, $1s^21p^6$; 20 consists of an M shell, $2s^21p^61d^{10}$, as mantle, and a K shell as core; 50 has L as core, 82 has M as outer core and K as inner core, and 126 has N as outer core and L as inner core. For 50, 82, and 126 the mantle, with the number of nucleons required by the packing equation to surround the core, consists of a completed shell plus a subsubshell. The magic-number configurations are given in Table 1.

TABLE 1

NUCLEON CONFIGURATIONS FOR THE MAGIC NUMBERS

Magic number	Mantle	Core or outer core	Inner core
2	$1s^2$		
8	$1s^21p^6$		
20	$2s^21p^61d^{10}$	$1s^2$	
50	$2s^22p^61d^{10}1f^{14}(1g\ 9/2)^{10}$	$1s^21p^6$	
82	$3s^22p^62d^{10}1f^{14}1g^{18}(1h\ 11/2)^{12}$	$2s^21p^61d^{10}$	$1s^2$
126	$3s^23p^62d^{10}2f^{14}1g^{18}1h^{22}(1i\ 13/2)^{14}$	$2s^22p^61d^{10}1f^{14}$	$1s^21p$

Summary.—The assumption that atomic nuclei consist of closely packed spherons (aggregates of neutrons and protons in localized 1*s* orbitals—mainly helions and tritions) in concentric layers leads to a simple derivation of a subsubshell occupancy diagram for nucleons and a simple explanation of magic numbers. Application of the close-packed-spheron model of the nucleus to other problems, including that of asymmetric fission, will be published later.[13]

* Fellow of the John Simon Guggenheim Memorial Foundation.

[1] The structural interpretation of the principal quantum number of nucleonic orbital wave functions and the structural basis provided by the close-packed-spheron theory for the neutron and proton magic numbers are discussed in notes submitted to *Phys. Rev. Letters* and *Nature* (L. Pauling, 1965).

[2] The name "helion" is used for the alpha particle: Pauling, L., *Nature,* **201,** 61 (1964).

[3] A review of this field is given by Goldhammer, P., *Rev. Mod. Phys.,* **35,** 40 (1963).

[4] Mayer, M. Goeppert, *Phys. Rev.,* **75,** 1969 (1949).

[5] Haxel, O., J. H. D. Jensen, and H. E. Suess, *Phys. Rev.,* **75,** 1766 (1949); *Z. Physik,* **128,** 295 (1950).

[6] Mayer, M. Goeppert, and J. H. D. Jensen, *Elementary Theory of Nuclear Shell Structure* (New York and London: John Wiley and Sons, Inc., 1955).

[7] Hofstadter, R., *Ann. Rev. Nucl. Sci.,* **7,** 231 (1957).

[8] Bergman, G., J. L. T. Waugh, and L. Pauling, *Nature,* **169,** 1057 (1952); *Acta Cryst.,* **10,** 254 (1957).

[9] Ref. 6, p. 83.

[10] Elsasser, W. M., *J. Phys. Radium,* **4,** 549 (1933); **5,** 389, 635 (1934).

[11] Ref. 6, p. 58.

[12] The set of magic numbers is often considered to include 28. The amount of extra stability at Z or $N = 28$ is, however, much less than at 2, 8, 20, 50, 82, and 126, and I have chosen to exclude it.

[13] Pauling, L., *Science,* in press.

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STRUCTURAL BASIS OF THE ONSET OF NUCLEAR DEFORMATION AT NEUTRON NUMBER 90

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Nuclei in the mass-number range $150 < A < 190$ show a permanent oblate deformation.[1] It was recognized by Mottelson and Nilsson[2] that the onset of the change from spherical to ellipsoidal shape occurs between 88 and 90 neutrons. Evidence about the significance of the value 90 for N was reported by Brix and others.[3] Barber *et al.*[4] have made a careful study of the change in mass accompanying the addition of pairs of neutrons to nuclei in this region, and have found that the abnormal mass effect is about equally divided between the $88 \rightarrow 90$ and $90 \rightarrow 92$ changes in N. The isotopes $_{62}$Sm and $_{64}$Gd with $N = 90$ are about 0.55 MeV more stable than would be expected from linear extrapolation of the mass values for $N \leqslant 88$, and those with $N \geqslant 92$ are about 1.1 MeV more stable. The interpretation given these differences is that for $N = 90$ the deformed nucleus is 0.55 MeV more stable than a spherical nucleus, and for $N \geqslant 92$ it is 1.1 MeV more stable.[5]

No simple explanation of the onset of deformation at $N = 90$ has been advanced. I have found that a simple explanation is provided by the close-packed-spheron theory of nuclear structure.

The close-packed-spheron theory[6] incorporates some of the features of the shell model, the alpha-particle model, and the liquid-drop model. Nuclei are considered to be close-packed aggregates of spherons (heli~~c~~ons, tritons, and dineutrons), arranged in spherical or ellipsoidal layers, which are called the mantle, the outer core, and the inner core. The assignment of spherons, and hence nucleons, to the layers is made in a straightforward way on the basis of the assumption of constant volume per nucleon. The relation to the shell model is that subshells (given value of l) occurring once are assigned to the mantle, those occurring twice to the mantle and outer core, and so on.

The spheron packing equation is

$$n_t^{1/3} = n_i^{1/3} + 1.30, \qquad (1)$$

in which n_t is the total number of spherons and n_i the number not including those of the outer layer. For $N = 82$ this equation gives one spheron in the inner core (completed K shell, $1s^2$), nine in the outer core (completed M shell, $2s^2 1p^6 1d^{10}$), and 31 in the mantle [completed spin-orbit subsubshell, $3s^2 2p^6 2d^{10} 1f^{14} 1g^{18}$-$(1h_{11/2})^{1/2}$]. The equation places 11 spherons in the core at about $N = 87$ and 12 at about $N = 92$. In icosahedral packing around a single sphere there are 12 spheres in a completed second layer and 32 in the third, a total of 45. For icosahedral packing, the transition from an inner core of one spheron to one of two spherons would be expected to take place between $N = 90$ and $N = 92$. The effect of the shell structure (completed mantle at 31 rather than 32 spherons) may explain why the transition occurs over the range 88 to 92 rather than more sharply at 90 to 92.

Evidence about the nature of the transition is provided by the observed proton numbers of the stable highest-Z isotones. A useful empirical rule is that the largest proton number for a set of stable isotones is equal to the neutron number of the mantle. For example, the set of stable isotones with $N = 50$ (from $_{36}$Kr$_{50}$ to $_{42}$Mo$_{50}$) ends at $Z = 42$, which is the number of neutrons in the mantle, and the set for $N = 82$ ends at $Z = 62$ ($_{62}$Sm$_{82}$), which again is the number of neutrons in the mantle. (This rule may be interpreted as showing that a significant contribution to the structure of the normal state of a nucleus is made by those structures with all protons in the mantle; the highest-Z stable isotone then has as a contributor to its normal state the structure with a pure helion mantle and a pure neutron core.) The highest-Z stable isotones in the region near $N = 90$ are $_{60}$Nd$_{84}$, $_{62}$Sm$_{86}$, $_{64}$Gd$_{88}$, $_{66}$Dy$_{90}$, $_{66}$Dy$_{92}$, and $_{68}$Er$_{94}$. They correspond, with this rule, to a core of 12 spherons for $N = 84$ to 90 and of 13 spherons for 92 and 94.

The onset of prolate deformation is expected at 13 spherons, with two in the inner core. A stable local environment for an inner-core spheron is that in which it has ligancy 9, as in the KM core for magic number 82. We may describe this core by the symbol 3-(1)-5-1; the inner-core spheron, (1), lies in the center of the shell formed by a ring of three and a ring of five spherons, plus one spheron at the apex of the pentagonal pyramid with the ring of five as its base. [A centered icosahedron can be similarly represented as 1-5-(1)-5-1.] The corresponding structure for a two-spheron inner core and an 11-spheron outer core is 3-(1)-5-(1)-3. With this structure each of the inner-core spherons with its nine neighbors (including the other inner-core spheron) can be described as a KM complex, and the entire core can be described as two overlapping KM complexes. A diagram of a two-dimensional analog is shown in Fig. 1.

That stable nuclear structures should involve stable local structures about each of the inner-core spherons is a reasonable consequence of the mutual interdependence of structure and potential energy function and the short range of internucleonic forces.

This core, with two spherons as inner core, has a prolate deformation from spherical symmetry. On the basis of the arguments discussed above, we assign this prolate core to Nd$_{90}$, Sm$_{90}$, and Gd$_{90}$, and their heavier isotopes.[7]

A core of 13 spherons with an inner core of a single spheron (icosahedral packing) may occur for $N = 90$ (45 spherons), but not for $N \geq 92$. The energy values reported by Barber et al.[4] indicate that the change to prolate deformation is about half completed at $N = 90$. Possibly these nuclei show resonance between the prolate structure and the icosahedral spherical structure.[5]

It is unlikely that $_{66}$Dy$_{90}$ has 13 spherons in its core, because it would then have two pro-

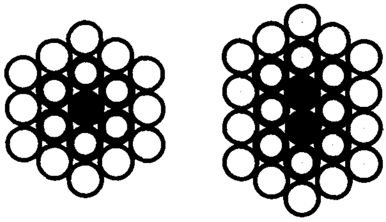

FIG. 1. Two-dimensional representation of a nearly spherical close-packed arrangement of spherons, with one in the inner core (left), and of an arrangement with prolate deformation, consequent to having two spherons in the inner core (right).

tons more than required for a pure helion mantle and pure neutron core. Hence it can be predicted that for dysprosium, prolate deformation begins at $N = 92$ rather than $N = 90$. The energy evidence of Barber et al. shows that the process has not begun at Dy_{88} and is completed by Dy_{96}.

A core with two spherons as inner core may contain from 13 to 19 spherons. The 19-spheron core has the symbol 1-5-(1)-5-(1)-5-1; each of the inner-core spherons with its neighbors forms an icosahedral complex. The 19-spheron core corresponds to N about 124 according to Eq. (1), and to $N = 118$ according to the highest-Z rule for stable isotones $({}_{80}Hg_{118}{}^{198})$. We draw the conclusion that all of the nuclei showing prolate deformation in the range $N = 90$ to 120 ($A = 150$ to 190) have a two-spheron inner core, and that[7] is the geometrical properties (the shape) of this inner core that is responsible for the deformation.

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*Fellow of the John Simon Guggenheim Memorial Foundation.

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[7] A third neutron (second spheron) first appears in the inner core at $N = 91$; ${}_{64}Gd_{91}$ has spin $\frac{3}{2}$ and negative parity, corresponding to inner-core neutron configuration $1s^2 1p$.

The Close-Packed-Spheron Theory and Nuclear Fission

Linus Pauling

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The Close-Packed-Spheron Theory and Nuclear Fission

Close packing of spherons provides a simple explanation of nuclear properties, including asymmetric fission.

Linus Pauling

Twenty-five years ago a phenomenon of tremendous importance was discovered, the phenomenon of nuclear fission. A striking feature of the fission of the uranium nucleus and other very heavy nuclei is its asymmetry: fissioning to produce a lighter and a heavier nucleus, with mass ratio about 2/3, occurs several hundred times as often as fissioning to produce two nuclei with about equal mass. Various efforts to explain asymmetric fission have had only limited success, including those based on consideration of energy release, of shell effects, of the shape of the energy function of the deformed nucleus in the saddle-point region, and of the penetration through rather than passage over the energy barrier. In this article I describe an extension of the theory of nuclear structure that provides a simple explanation of asymmetric fission and of some other properties of nuclei.

Theories of Nuclear Structure

During recent decades a great amount of knowledge about the properties of atomic nuclei has been gathered. An extensive theory of nucleonic interactions and nuclear structure [liquid-drop theory (*1*), shell theory (*2, 3*), unified theory (*4*), cluster theory (*5–7*)] has been developed that accounts reasonably well for many of these properties: the general dependence of the normal-state energy on the mass number A, nuclear diameter and charge distribution, spin and magnetic moment, energies of excited states, nature of beta decay, rate of nuclear fission and dependence on the energy and nature of bombarding particles, and several others. Some properties, however, including asymmetry of fission, mentioned above, have not hitherto been encompassed by the theory in a satisfactory way.

Recent theoretical treatments of the structure of nuclei have involved the approximate or iterative solution of the eigenvalue equation for each nucleon in a potential determined by its interaction with the other nucleons. The potentials have the Yukawa form beyond internucleonic distance about 0.5 fermi (f, 0.5×10^{-13} cm), corresponding to nucleonic core radius 0.25 fermi, and involve singlet and triplet central forces, tensor forces, and spin-orbit forces. These treatments (*8*) of finite nuclei and infinite nuclear matter (with proton-proton repulsion ignored) have provided calculated values of some properties in reasonably good agreement with experimental results. The proton and neutron densities are given by the theory as approximately constant throughout most of the volume of the nucleus; they then decrease rapidly, the thickness of the skin (90 to 10 percent of maximum) being about 2.4 f. The density of nucleons is about one nucleon per 6 f^3. These properties are essentially as found by electron scattering experiments (*9*).

For H^2, H^3, He^3, and He^4, the nucleons can be described approximately as occupying 1*s* orbitals. The core repulsion suggests that H^3 and He^3 have a triangular structure and that He^4 has a tetrahedral structure. The observed binding energies for $A = 2, 3,$ and 4 are 2.2, 8.1 (average of 7.7 and 8.5), and 28.3 Mev, respectively. These are in the ratios 1 : 3.7 : 13, deviating from the ratios 1 : 3 : 6 of the number of internucleonic interactions in the direction corresponding to stronger bonds (smaller internucleonic distance) in the helion (*10*) than in the deuteron. In He^4 the nucleonic valences are nearly saturated: a fifth nucleon (proton or neutron) has negative binding energy, and in the most stable larger nuclei the binding energy per nucleon is only 25 percent greater than in the helion.

The polyhelion model (alpha-particle model) of the nucleus (*7, 11*) has been made the basis of a useful theory. In this theory O^{16} is described as a tetrahedron of four helions (*6*) and Mg^{24} as an octahedron of six helions. (The tetrahedron, octahedron, and icosahedron are the regular triangular polyhedra—their faces are equilateral triangles and their corners are equidistant from a center, which gives them a roughly spherical shape, as shown for the icosahedron in Fig. 1.)

The shell theory has had great success in accounting for many nuclear properties (*3*). The principal quantum number n for nucleons is usually taken to be $n_r + 1$, where n_r, the radial quantum number, is the number of nodes in the radial wave function. (For electrons n is taken to be $n_r + l + 1$; l is the azimuthal quantum number.) Strong spin-orbit coupling is assumed,

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Fig. 1 (left). The arrangement of 45 spheres in icosahedral closest packing. At the left there is shown a single sphere, which constitutes the inner core. Next there is shown the layer of 12 spheres, at the corners of a regular icosahedron. The third model shows the core of 13 spheres with 20 added in the outer layer, each in a triangular pocket corresponding to a face of the icosahedron; these 20 spheres lie at the corners of a pentagonal dodecahedron. The third layer is completed, as shown in the model at the right, by adding 12 spheres at the corners of a large icosahedron; the 32 spheres of the third layer lie at the corners of a rhombic triacontahedron. The fourth layer (not shown) contains 72 spheres.

splitting each subshell into a more stable subsubshell with $j = l + \frac{1}{2}$ and a less stable subsubshell with $j = l - \frac{1}{2}$; j is the total angular momentum number for a neutron or proton. The sequence of subsubshells assigned to both neutrons and protons is given in Fig. 2, as indicated by the observed values of spin and parity of nuclei.

The Close-Packed-Spheron Model

I assume that in nuclei the nucleons may, as a first approximation, be described as occupying localized 1*s* orbitals to form small clusters. These small clusters, called spherons, are usually helions, tritons, and dineutrons; in nuclei containing an odd number of neutrons, an He^3 cluster or a deuteron may serve as a spheron. The localized 1*s* orbitals may be described as hybrids of the central-field orbitals of the shell model.

The close-packed-spheron model differs from the conventional liquid-drop model of the nucleus in having spherons rather than nucleons as the units. This is a simplification; $_{64}Gd_{90}{}^{154}$, for example, is described in terms of 45 spherons, rather than 154 nucleons.

The nature of spheron-spheron interactions is such that maximum stability is achieved when each spheron ligates about itself the maximum number of neighbors, to produce a nucleus with a closest-packed structure. A simple argument (*12*) leads to the conclusion that the spherons in a nucleus are arranged in concentric layers. The packing radius of a spheron varies from 1.28 f for the dineutron to 1.62 f for the helion. The radius (to nucleon density half that of the inner region) of the largest nucleus is 6.8 f

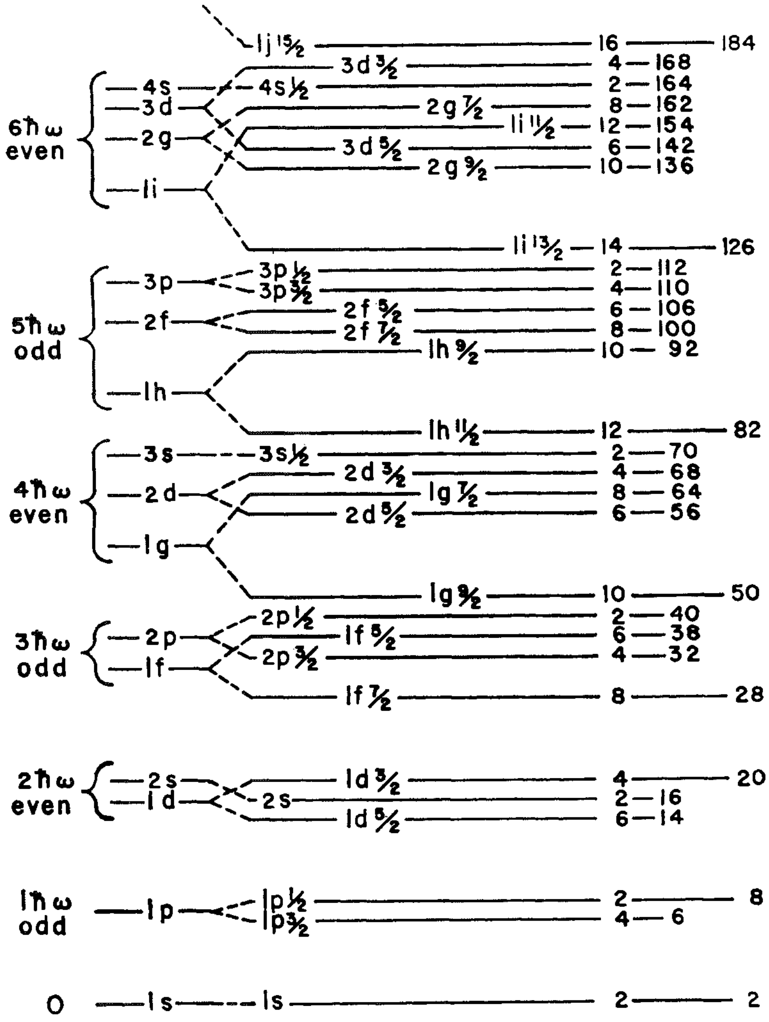

Fig. 2. The sequence of nucleonic energy levels with spin-orbit coupling, redrawn, with small changes, from *3*, p. 58.

(1.07 $A^{1/3}$ f), four times the helion radius. The thickness of the nuclear skin corresponds to the nubbled surface of the outer hemispheres of an outer layer of spherons. In a large nucleus the region within the outer layer would be lined with another layer of spherons, in contact with the outer layer, and within this layer there might be a central spheron or layer of spherons.

In a three-layer nucleus the outermost layer may be called the *mantle* and the other two the *outer core* and the *inner core*, to avoid confusion with the shells of the shell model.

The general geometrical problem of the packing of spheres has not been solved. An example of closest packing of atoms with some variation in effective radius is the icosahedral packing found (*13*) in the intermetallic compound $Mg_{32}(Al,Zn)_{49}$ (Fig. 1). The successive layers in this structure contain 1, 12, 32, and 117 spheres. These numbers are reproduced (to within ±1) by the empirical equation (*12*)

$$n_t = (n_i^{1/3} + 1.30)^3 \qquad (1)$$

in which n_t is the total number of spheres and n_i is the number not including those in the outermost layer. The number 1.30 represents the effective thickness of a layer; the form of the equation corresponds to the assignment of equal volumes to the spheres.

I have assumed that this equation applies to structures with two or more spheres in the central layer (as well as with one, as in icosahedral packing), and have applied it in the calculation of the ranges of values of the neutron number N in which successive subsubshells are occupied (*12*). (In this calculation the difference in radius of the different kinds of spherons is taken into consideration.) The assignment of quantum numbers is made with use of the following assumptions (*14*):

1) Those subshells that occur (are occupied) with only the value 1 for the principal quantum number n contribute only to the mantle.

2) Those subshells that occur with two values of n contribute to the mantle and the next inner layer, and so on.

3) For given n, the subshells are filled in order of increasing l, and for given l in order of increasing n.

Let us again take ${}_{64}Gd_{90}$ as an example. Its 45 spherons (each containing two neutrons) are expected to be distributed in layers 1, 12, 32, as shown in Fig. 1. There are three layers, and one pair of neutrons in the inner core; hence $1s^2$, $2s^2$, and $3s^2$ occur. To obtain the 12 spherons of the outer core we need $1p^6$ $1d^{10}$ $1f^6$, in addition to $2s^2$. The neutrons in the mantle then are $3s^2$ $2p^6$ $2d^{10}$ $2f^6$ $1f^8$ $1g^{18}$ $1h^{14}$.

The sequence of neutron-occupancy ranges found in this way (*12*) is

Table 1. Nucleon configurations for the magic numbers.

Magic number	Mantle	Core or outer core	Inner core
2	$1s^2$		
8	$1s^21p^6$		
20	$2s^21p^61d^{10}$	$1s^2$	
50	$2s^22p^61d^{10}1f^{14}\ (1g9/2)^{10}$	$1s^21p^6$	
82	$3s^22p^62d^{10}1f^{14}1g^{18}(1h11/2)^{12}$	$2s^21p^61d^{10}$	$1s^2$
126	$3s^23p^62d^{10}2f^{14}1g^{18}1h^{22}\ (1i13/2)^{14}$	$2s^22p^61d^{10}1f^{14}$	$1s^21p^6$

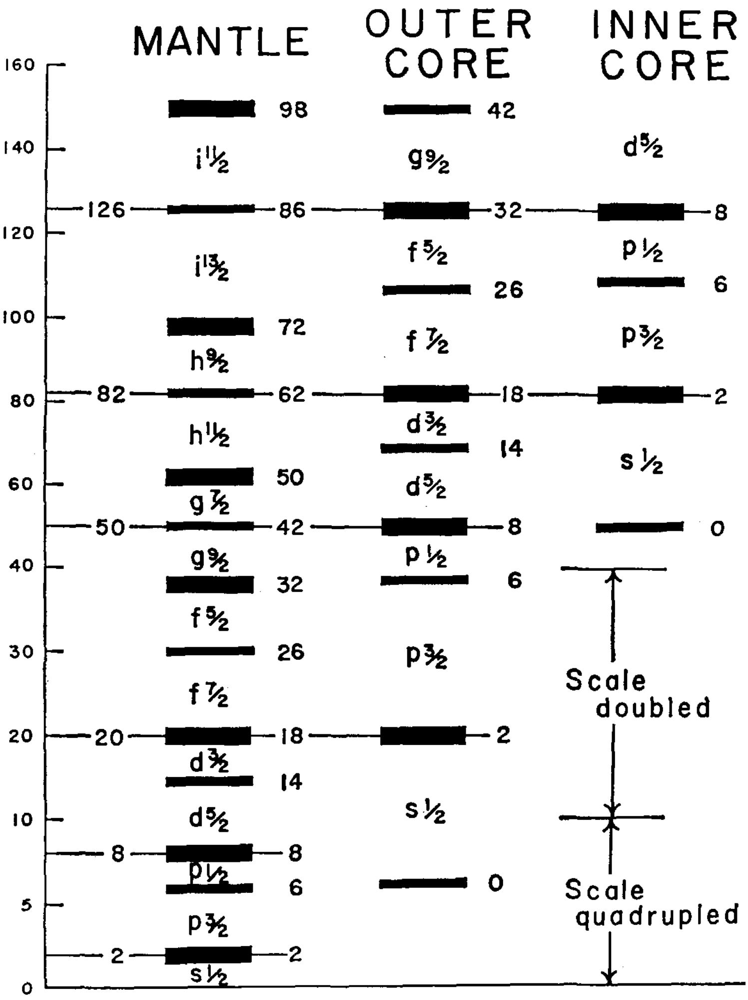

Fig. 3. Diagram showing the ranges of values of neutron number N in which spin-orbit subsubshells of the mantle, outer core, and inner core are occupied, as calculated with use of the spheron-packing equation.

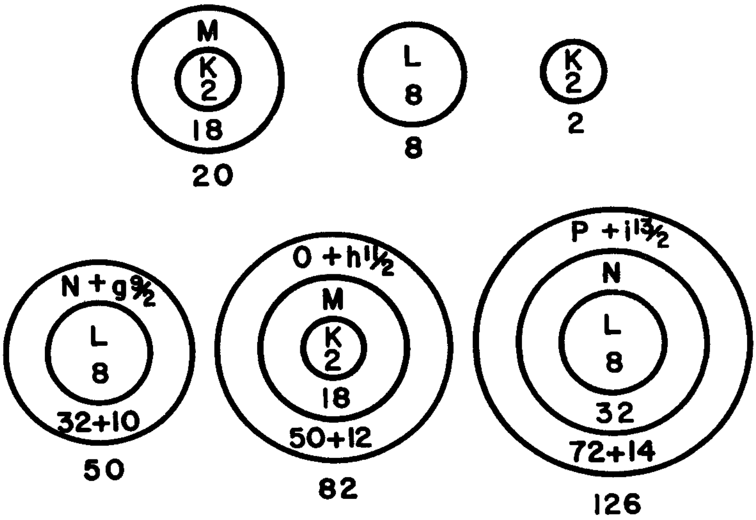

Fig. 4. The magic-number structures of nuclei.

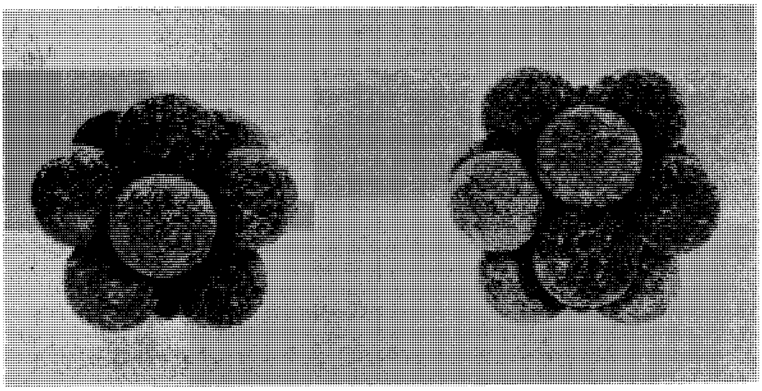

Fig. 5. Limiting stable arrangements of spherons around a central spheron. (Left) Nine outer spherons (*KM* structure); (right) 12 outer spherons (icosahedral structure).

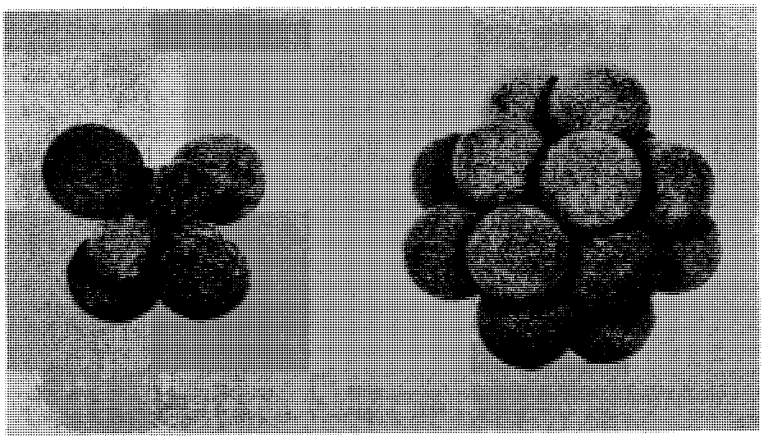

Fig. 6. Arrangement of 16 spherons around four spherons. (Left) The four inner and four of the 16 outer spherons; (right) the completed structure.

shown in Fig. 3. It closely resembles the level diagram found by Mayer and Jensen by analysis of observed nuclear properties, with the help of the calculated level sequences for harmonic-oscillator and square-well potential functions, but it differs from their diagram (Fig. 2) in that subsubshells are assigned to the separate layers and that overlapping ranges of *N* and *Z* for their occupancy are shown.

The observed values of spin and parity indicate that Fig. 3 (like the Mayer-Jensen level diagram) applies to protons as well as to neutrons.

Structural Basis of Magic Numbers

Certain numbers of neutrons and protons were recognized by Elsasser (*15*) as conferring increased stability on nuclei. These numbers are 2, 8, 20, 50, 82, and 126. (The set is sometimes considered to include 28 also.) It was in part their effort to account for these numbers that led Mayer and Haxel, Jensen, and Suess to propose their shell model with spin-orbit coupling.

The close-packed-spheron theory leads to a simple structural interpretation of the magic numbers (*16*): they are the numbers at which each layer of the nucleus achieves completion of a shell (*K*, *L*, *M*, . . ., with $2n^2$ neutrons or protons), or at which each core layer achieves completion of a shell and the mantle achieves completion of a shell and a $j = l + ½$ subsubshell.

It is to be expected that the energy gap following completion of a core shell would be greater than that following completion of a mantle shell; hence 50 is a magic number and 38 is not. The magic-number configurations are given in Table 1 and Fig. 4.

The Local Environment of Inner-Core Spherons

The magic number 20 corresponds to the *KM* structure, which is also the structure of the core for magic number 82. This structure, shown in Fig. 5 (left), involves nine spherons ligated about a smaller central spheron. Its stability may be attributed to its double completed-shell character.

As many as 12 spherons can be closely packed about a central spheron. The icosahedral arrangement of 12 about one is shown in Fig. 5 (right).

Two limiting structures with four spherons as core or inner core are shown in Figs. 6 and 7. The structure shown in Fig. 6 has the central tetrahedron of four spherons surrounded by a larger tetrahedron of four and a truncated tetrahedron of 12, a total of 16 spherons in the outer layer. The packing is triangular. This is the structure of the core for magic number 126. It has double completed-shell character, *LN*.

An interesting and possibly significant aspect of this structure is that each of the four spherons of the inner core has ligancy 9 (its neighbors are the three other inner-core spherons, three of the outer tetrahedron, and another three of the outer layer). Each of these four inner-core spherons with its nine neighbors can be described as forming a *KM* complex, and the *LN* core can be described as four interpenetrating *KM* complexes.

The conclusion that each inner-core spheron in a stable core should ligate its neighbors about itself in a way corresponding to local stability is a reasonable consequence of the self-generating character of the potential energy function for nucleons in nuclei (mutual interdependence of structure and potential energy function) and the short range of internucleonic forces.

The arrangement of 22 spherons around an inner tetrahedron of four spherons shown in Fig. 7 involves icosahedral packing: each of the four inner spherons is surrounded by an icosahedron of 12, three of which are the three other inner spherons. This structure (26 spherons, 52 neutrons) with one spheron missing may be assigned to magic number 50. The complete structure, with 26 spherons, corresponds to the stable nucleus $_{44}\mathrm{Ru}_{52}$, as discussed in the following section.

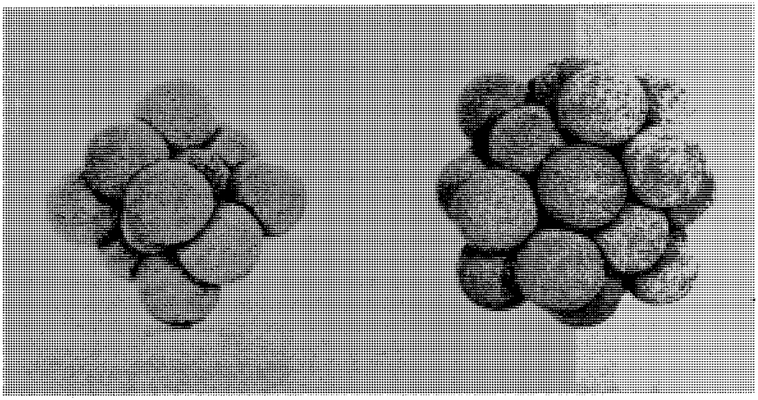

Fig. 7. Arrangement of 22 spherons around four. (Left) The four inner and ten of the 22 outer spherons; (right) the completed structure.

The Proton-Neutron Ratio

The proton-neutron ratio in nuclei has been discussed for over 50 years. Long before the neutron had been shown to exist Harkins (*17*) attempted to draw some conclusions about nuclear structure from the observed excess of neutrons over protons (he used the name neutron for a hypothetical unit of a proton combined with an electron). The course of the proton-neutron ratio is now well understood in relation to the energy change accompanying emission of an electron or positron from the nucleus (that is, conversion of an intranuclear neutron to an intranuclear proton, or the reverse), but no reasonable correlation with the structure of the nucleus has been published.

Let us consider the nucleus $_{44}\mathrm{Ru}_{52}$. As discussed above, it is assigned 26 spherons, of which 22 are in the mantle and four in the core. From Fig. 3 we might assign 37 protons to the mantle and seven to the core. This assignment gives a mantle of 11 helions and 11 tritons and a core of three helions and one triton.

However, the Coulomb repulsion of protons may be expected to cause the proton orbitals to have a greater radial extent than the corresponding neutron orbitals, and to overlap spherons of more than one layer. We may consider that for the $_{44}\mathrm{Ru}_{52}$ nucleus there is resonance between the helion-triton structure described above and a helion-dineutron structure, with the helions all in the surface layer. This structure has 22 helions in the mantle and four dineutrons in the core.

Structures of this sort, with a mantle of helions and a core of neutrons, have minimum Coulomb energy. We may expect these structures to have the minimum neutron excess compatible with stability; any more protons would be forced from the mantle into the core. In fact, $_{44}\mathrm{Ru}_{52}$ has the largest atomic number for which $N - Z$ equals 8 for a stable isotope.

The proton number equal to the

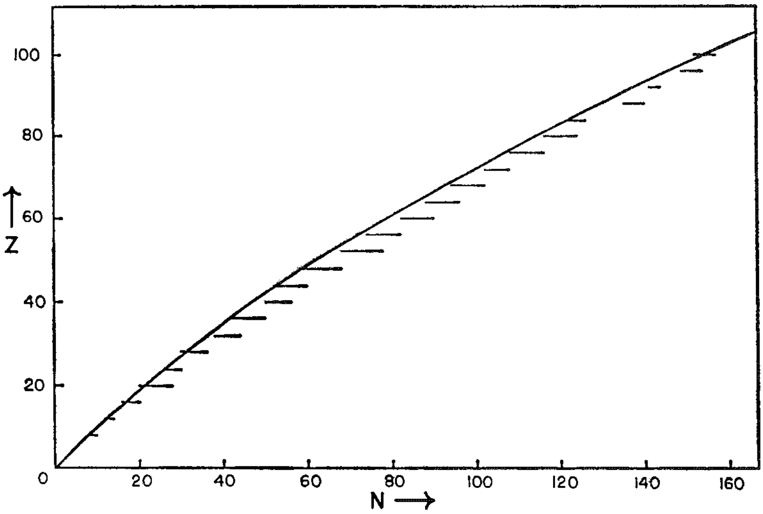

Fig. 8. A curve of proton number Z as a function of neutron number N, calculated as described in the text. The horizontal lines show the ranges of stable isotopes for alternate Z-even elements (for large Z the four most stable isotopes).

number of neutrons in the mantle may accordingly be expected to represent the high-Z boundary of the region of stability of nuclei. The curve shown in Fig. 8 has been drawn through points corresponding in this way to the neutron configurations of Table 1. The horizontal lines are the observed ranges of stability for alternate even-Z sets of isotopes (for large Z the four isotopes with the smallest half-lives).

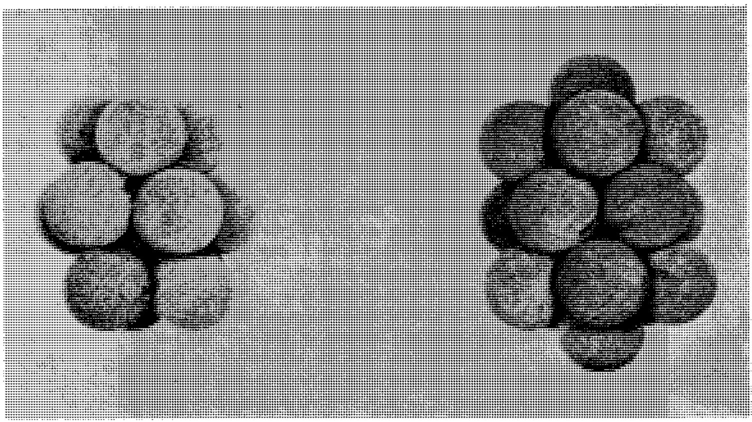

Fig. 9. Arrangement of 11 (left) and 17 (right) spherons about an inner core of two spherons. Each inner-core spheron shows *KM* ligation at left and icosahedral ligation at right.

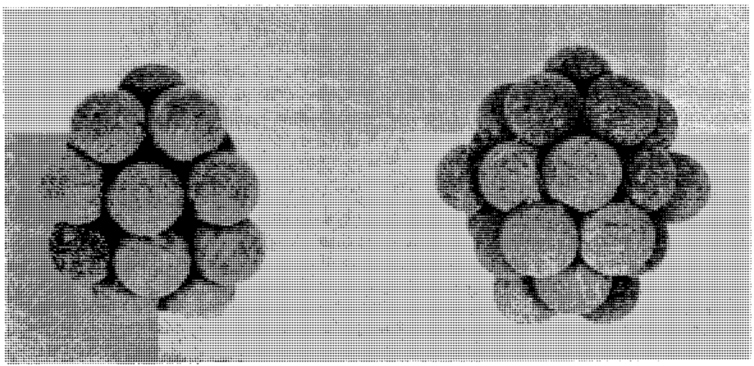

Fig. 10. Arrangement of 18 (left) and 24 (right) spherons about an inner core of five spherons with the configuration of a trigonal bipyramid.

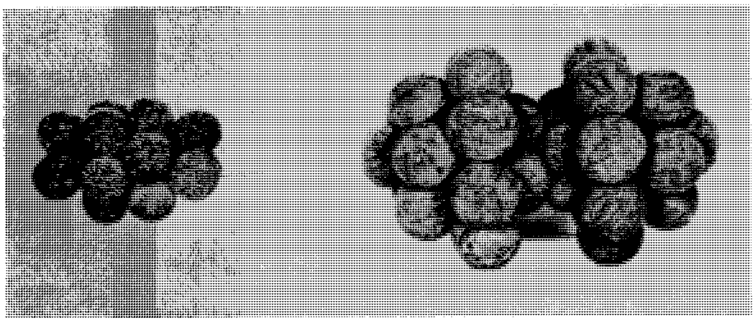

Fig. 11. (Left) An outer core of 16 spherons surrounding an inner core of three, in a linear arrangement. (Right) The same core with a portion of the mantle of the elongated nucleus. (The difference in relative sizes of core and mantle spherons is exaggerated in this and some of the other figures.)

It is seen that, in accordance with the foregoing argument, the low-N ends of these horizontal lines lie close to the curve (mean deviation, 1). The conclusion may be drawn that the structures of stable nuclei involve a significant contribution of structures with a pure neutron core and a pure helion or nearly pure helion mantle.

Permanent Deformation of Nuclei

Observed properties of many nuclei have been interpreted as showing that the nuclei are not spherical but are permanently deformed (*4*). The principal ranges of deformation are neutron numbers 90 to 116 and 140 to 156. Most of the deformed nuclei are described as prolate ellipsoids of revolution, with major radii 20 to 40 percent larger than the minor radii.

A simple explanation of the existence of deformed nuclei in these ranges is provided by the close-packed-spheron theory (*14*); it is that the inner core (of two or five spherons) in these ranges has an elongated structure, and that this elongation is imposed by the inner core on the two surrounding layers.

The most stable core configuration for an inner core of one spheron is *KM*, with an outer core of nine spherons. For icosahedral packing the outer core contains 12 spherons. These structures, which we may take as defining the limits of stability for a one-spheron inner core, have been discussed in the preceding section.

The upper limit of neutron number for one spheron as inner core is 90, corresponding to the icosahedral packing shown in Fig. 1. In the range beginning at about $N = 90$ we assign two spherons to the inner core. With *KM* ligation about each, as shown in Fig. 9, the core contains 26 neutrons; and with icosahedral ligation about each, also shown in Fig. 9, it contains 38 neutrons. These values correspond to the range for N from about 90 to 122 (Fig. 3).

Nuclei with an inner core of three spherons would have oblate deformation, rather than prolate. The packing is somewhat less satisfactory than for one, two, or four spherons, except for ligancy 10 (18 spherons in the outer core), which corresponds to 42 core neutrons, and thus lies in the *LN* core range. We conclude that the inner core contains 1, 2, or 4 spherons, in the range $N = 82$ to 126, and that only prolate deformation should occur.

An ellipsoidal nucleus with two spherons in the inner core has major radius greater than the minor radii by the radius of a spheron, about 1.5 f, which is about 25 percent of the mean radius. The amount of deformation given by this model is accordingly in rough agreement with that observed (*18*). In a detailed treatment it would be necessary to take into account the effect of electrostatic repulsion in causing the helions to tend to occupy the poles of the prolate mantle, with tritons tending to the equator.

In the region $N \geqq 140$ the inner core is a trigonal bipyramid of five spherons, surrounded by an outer core of 18 to 24 spherons (Fig. 10). The deformation is prolate, and about as great as for the region 90 to 120, in agreement with experiment.

The wave functions for the two inner-core spherons can, of course, be described as the symmetric and antisymmetric combinations of $1s$ and $1p_z$ functions. The Nilsson (*19*) treatment of neutron and proton orbitals in deformed nuclei is completely compatible with the foregoing discussion, which provides a structural interpretation of it.

Symmetric and Asymmetric Nuclear Fission

The foregoing considerations provide the basis for a discussion of the mechanism of nuclear fission.

Let us consider first the low-energy fission of the lighter fissionable elements, in the neighborhood of Pb^{208}. These elements (gold, thallium, lead, bismuth), when bombarded with particles such as 20-Mev deuterons, undergo symmetric fission, the distribution function of the products having a half width at half maximum of 8 to 15 mass-number units (*20*).

These fissioning nuclei (such as ${}_{84}Po_{127}^{211}$, formed by reaction of Bi^{209} and a deuteron) have a nearly spherical normal-state structure, resembling that of the doubly magic nucleus ${}_{82}Pb_{126}^{208}$, with an outer core of 16 spherons and an inner core of 4 spherons, shown in Fig. 6. The nucleus is excited, with vibrational energy about 25 Mev (for bismuth bombarded with 20-Mev deuterons). The vibrational deformation involves a change in the structure of the core, from a tetrahedral (nearly spherical) core of 20 spherons to a prolate ellipsoidal core with the same or nearly the same number of spherons.

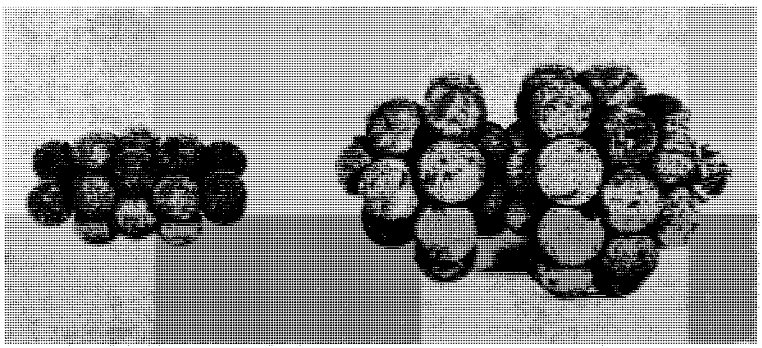
Fig. 12. (Left) An outer core of 21 spherons surrounding a linear inner core of four. (Right) The same core with a portion of the mantle, illustrating asymmetric fission.

The principles discussed in the foregoing sections strongly suggest that the deformed core has the structure shown on the left in Fig. 11. In the outer core there are rings of 3, 5, 5, and 3 spherons. The inner core consists of three spherons, in the interstices between pairs of rings. The central inner-core spheron has ligancy 12; it is surrounded by an icosahedron formed by the ten spherons of the two middle outer-core rings and the other two inner-core spherons. Each of these two inner-core spherons has ligancy 9; with its neighbors it constitutes a *KM* complex.

I assume that in the process of fission both the mantle and the core undergo splitting. The core could split between the two middle rings, which would result in symmetric fission.

In the process of fission the increasingly prolate deformation of the mantle could cause an equatorial fissure to occur in the mantle, as indicated on the right in Fig. 11. Before the fissure occurs there would be rings of spherons in the mantle between every adjacent pair of rings in the outer core. In the course of the vibration leading to fission the spherons of the mantle would be crowded toward the two poles. At the value of the reaction coordinate corresponding to the configuration shown at the right in Fig. 11 the nu-

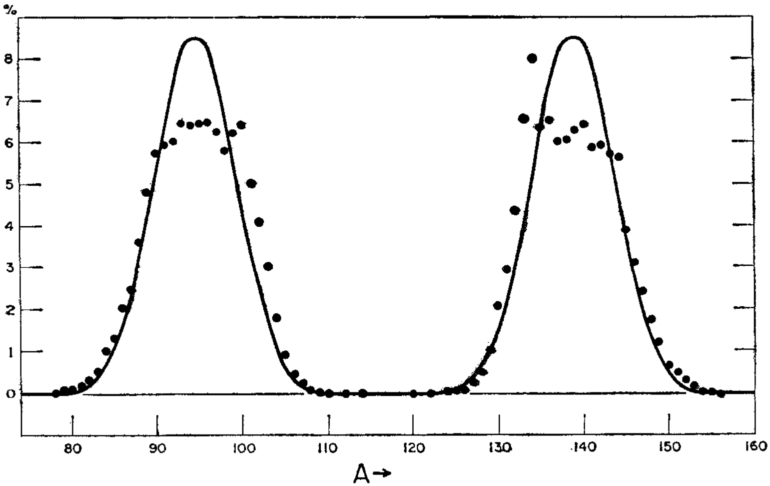

Fig. 13. Yields of nuclei in the fission of U^{235}, as a function of mass number. The points are averages of reported experimental values, and the curve is the result of a simple theoretical calculation described in the text.

cleus might be described as two smaller nuclei in contact; the ten spherons of the middle rings of the core of the original nucleus have become part of the mantles of the two daughter nuclei. This configuration would need only a small additional deformation to reach the saddle point in the energy surface.

The observed width of the distribution functions in mass number of the fission products indicates that the spherons that lie in the plane of the fissure are essentially randomly distributed between the two daughter nuclei, as discussed below for asymmetric fission.

A heavy fissionable nucleus, such as U^{236} (formed by combination of U^{235} and a neutron), undergoes asymmetric fission. This property can be related to the structure assumed by its core in the course of its prolate deformation. In its normal state the nucleus has an inner core of five spherons and an outer core of 20 spherons (Fig. 3), with a moderate prolate deformation, corresponding to the trigonal bipyramidal structure of the inner core (Fig. 10). The instability resulting from Coulomb repulsion of the protons leads to further prolate deformation and to fission, as described in the discussions based on the liquid-drop model. These discussions can be refined by consideration of the change in structure of the core with increasing prolate deformation of the nucleus.

To within its reliability of one or two units, the packing equation applies to ellipsoidal as well as to spherical nuclei. The more highly deformed core of ${}_{92}U_{144}{}^{236}$ assumed in the course of the fission reaction accordingly contains about 25 spherons. The structural principles discussed above lead to the assignment to this core of the structure shown at the left in Fig. 12. The outer core consists of five rings, containing 3, 5, 5, 5, and 3 spherons, with a linear inner core of four spherons, in the interstices of pairs of rings of the outer core. By applying the chart of Fig. 3 to protons, we identify the spherons of the outer core and the two central spherons of the inner core as tritons; the two end spherons of the inner core are dineutrons. The configuration of each end spheron of the inner core and its neighbors is the *KM* configuration, and that of each of the two others with its neighbors is the icosahedral configuration.

The spherons of the mantle, 22 helions and 25 tritons, may be described as forming four rings, in the grooves between pairs of rings of the outer core, and two caps, one at each end. The structure can be represented by the following diagram, where A represents the inner core, B the outer core, and C the mantle.

A: n^2 t t n^2
B: $3t$ $5t$ $5t$ $5t$ $3t$
C: 6α $5\alpha, 3\frac{1}{2}t$ $9t$ $9t$ $5\alpha, 3\frac{1}{2}t$ 6α
↑
Plane of fission

In this assignment the assumption is made that the 22 helions of the mantle occupy the end regions of the highly deformed nucleus, as a result of their strong Coulomb repulsion.

The greater stability of the core than of the mantle requires that fission occur along a plane between layers of the core. The number of layers is odd (five); accordingly the fission is not symmetric, as for the lighter fissionable nuclei (with four layers in the core), but is asymmetric.

The proposed mechanism of fission of U^{236} and other heavy fissionable nuclei is illustrated in Fig. 12. The nine tritons initially in the ring in the plane of fission crowd into the two end regions of the mantle, leaving a circular fissure, as shown in the figure. (This crowding is accompanied by the motion of one or more spherons from the poles of the mantle into the end regions of the core.) Each of the two outer-core rings of five spherons that determine the plane of fission may then be described as forming a part of the mantle of a daughter nucleus, and the large deformed nucleus may now be described as a smaller and a larger daughter nucleus in contact over the surface area of five or six spherons.

Eleven of the 25 core spherons of the parent nucleus thus become mantle spherons of the daughters (ten in the two rings of the outer core and one in the inner core), leaving 14 for the cores of the daughters. These cores are seen from Fig. 3 or Eq. 1, however, to contain about 16 spherons, over a range of partitions of the 144 neutrons between the two daughters. The process of fission thus involves the transfer of two (or perhaps three) spherons from the mantle to the two cores. This transfer could take place in three ways (2, 0; 1, 1; 0, 2) for two spherons and in four ways for three spherons. The partition between the two daughters of the nine tritons of the ring initially in the fission plane would be largely influenced by the nature of the two cores. We are thus led to a structural interpretation of alternative channels for the fission reaction, which may account for the observed fine structure in the distribution function of fission products; the observed peaks at $A = 100$ and 134 may be ascribed to the transfer of two spherons to the smaller core, to give fission products with cores of six and ten spherons.

Instead of attempting to introduce such refinements, I shall report the result of a very simple statistical treatment of the fission-product distribution function. The location of the plane of fission for U^{236} shown in the diagram is such as to assign 11α, $16\frac{1}{2}t$, and one dineutron to the lighter of the two daughter nuclei (assuming equal partition for the ten tritons in the fission plane). With one neutron promptly emitted by the light nucleus and 1.5 by the heavy nucleus, the average mass numbers are 94.5 and 139, in close agreement with experiment. The average charge of the light nucleus is 38.5, which is 1.2 larger than for constant charge/mass ratio. This difference has the correct sign but is larger than the observed value (about 0.8). The disproportionately large charge of the light fission products results from their larger share of the mantle.

The partition of the ten tritons in the fission plane is, of course, different for different fission channels. The curve in Fig. 13, corresponding to random distribution of the ten tritons, has been calculated with the de Moivre approximation to the binomial distribution function. The approximation to the experimental points (*21*) suggests that good agreement could be obtained by a more refined calculation involving consideration of the various channels for the fission reaction mentioned above.

The kinetic energy (*22*) of fission products of U^{236}, corrected for ionization defect, has the value 166.9 Mev, which is the Coulomb energy of the charges of pairs of daughter nuclei at the distance 18 f. This value is not in disagreement with the proposed mechanism of fission. The distance between the centers of the nuclei, considered as spheres, is 13 f, calculated with the formula $1.35\ A^{\frac{1}{3}}$ f for the contact radius. Coulomb repulsion causes the nuclei to be distorted, however, and, moreover, the helions, carrying much of the charge, are repelled to the opposite polar regions of the two mantles, thus causing the distance between the two centers of charge to be somewhat larger than 13 f.

There is no structure for an elongated core intermediate between that shown in Fig. 11, with three inner-core spherons, and that shown in Fig. 12, with four. The transition between these structures is calculated by use of Eq. 1, with $n_i = 22$, to occur at $n_t = 69$, that is, at $N = 138$. It is accordingly an expectation from the close-packed-spheron theory that, as observed, $_{90}\text{Ac}_{138}{}^{227}$ (formed by bombardment of Re^{226} with 11-Mev protons) gives a three-humped fission product distribution curve (*23*), which has been interpreted (*24*) as showing that both symmetric fission and asymmetric fission occur.

Asymmetric fission is observed in the spontaneous decomposition of $_{98}\text{Cf}_{156}{}^{254}$ and other very heavy nuclei. We may ask when the transition to symmetric fission would begin. The next elongated core, in the series represented in Figs. 11 and 12, would contain 31 spherons, and the transition to it should occur for 28 spherons in the core of the undistorted nucleus, that is, at $N = 163$ (calculated with use of Eq. 1). We conclude that $_{103}\text{Lw}_{163}{}^{266}$ and adjacent nuclei should show both asymmetric and symmetric fission.

Conclusion and Summary

The close-packed-spheron theory of nuclear structure may be described as a refinement of the shell model and the liquid-drop model in which the geometric consequences of the effectively constant volumes of nucleons (aggregated into spherons) are taken into consideration. The spherons are assigned to concentric layers (mantle, outer core, inner core, innermost core) with use of a packing equation (Eq. 1), and the assignment is related to the principal quantum number of the shell model. The theory has been applied in the discussion of the sequence of subsubshells, magic numbers, the proton-neutron ratio, prolate deformation of nuclei, and symmetric and asymmetric fission.

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*THE RESONATING-VALENCE-BOND THEORY OF SUPERCONDUCTIVITY: CREST SUPERCONDUCTORS AND TROUGH SUPERCONDUCTORS**

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The generally accepted theory of electric superconductivity of metals is based upon an assumed interaction between the conduction electrons and phonons in the crystal.[1–3] The resonating-valence-bond theory, which is a theory of the electronic structure of metals developed about 20 years ago,[4–6] provides the basis for a detailed description of the electron-phonon interaction, in relation to the atomic numbers of elements and the composition of alloys, and leads, as described below, to the conclusion that there are two classes of superconductors, crest superconductors and trough superconductors.

The resonating-valence-bond theory of the electronic structure of metals is based upon the idea that pairs of electrons, occupying bond positions between adjacent pairs of atoms, are able to carry out unsynchronized or partially unsynchronized resonance through the crystal.[4] In the course of the development of the theory a wave function was formulated describing the crystal in terms of two-electron functions in the various bond positions, with use of Bloch factors corresponding to different values of the electron-pair momentum.[5] The part of the wave function corresponding to the electron pair was given as

$$\Phi_k(1,2) = C\phi_{\mathbf{r}}(1,2) \exp (2\pi i \mathbf{P}_k \cdot \mathbf{r}/h), \qquad (1)$$

in which $\mathbf{r}$ is the radius vector from the origin to the point R in the crystal, $\phi_{\mathbf{r}}$ is the electron-pair-bond function in the region near R, $\mathbf{P}_k$ is the momentum vector corresponding to the three quantum numbers k, and C is the normalizing factor.

Some years later a more thorough discussion of the motion of pairs of electrons in a metal was given by Cooper,[7] as well as by Abrikosov[8] and Gor'kov,[9] who emphasized that the effective charge in superconductivity is $2e$, rather than e. The quantization of flux in units $hc/2e$ in superconducting metals has been verified by direct experimental measurement of the magnetic moments induced in thin films.[10] Cooper's discussion of the motion of electron pairs in interaction with phonons led to the development of the Bardeen-Cooper-Schrieffer (BCS) theory, which has introduced great clarification in the field of superconductivity.[2]

The BCS theory leads to the following equation for the critical temperature, T_c, for superconductivity:

$$kT_c = Ah\nu \exp(-1/\rho). \qquad (2)$$

In this equation ν is a phonon frequency, such that $h\nu$ is approximately $k\theta$, with θ the Debye characteristic temperature of the metal. The quantity ρ is the product of the density of electrons in energy at the Fermi surface, $N(0)$, and the electron-phonon interaction energy, V.

The coefficient A is somewhat uncertain; for example, the value 0.344 is given by Blatt[11] and the value 0.286 by Anderson.[12] In the following discussion I use the value $A = 0.30$. Equation (2) may then be written as

$$T_c = 0.3\theta \exp{(-1/\rho)}. \tag{3}$$

For lead, a representative superconductor, the observed values of T_c and θ are 7.19°K and 110°K, respectively, which lead to the value 0.37 for ρ; values 0.15 to 0.6 are found for other superconductors.

The Metallic Orbital and the Mechanism of Electric Conductivity.—In the resonating-valence-bond theory of metals it is required that most of the atoms have an extra orbital, the metallic orbital, which is necessary for unsynchronized resonance. The existence of the extra orbital, in amount 0.78 per atom, was discovered[13] in 1938 through the analysis of the observed values of the saturation magnetic moments of the iron-group transition metals and their alloys. In this analysis 8.22 of the nine dsp orbitals were found to be occupied by bonding electrons or by atomic electrons or electron pairs, leaving 0.78 orbitals per atom. The nature of the extra orbital was for some years not clear; in 1948 its function in permitting unsynchronized resonance was pointed out.[4]

The element tin may be used as an example. Gray tin, a nonmetallic form of tin, involves quadrivalent tin atoms, based upon the excited electron configuration $5s5p^3$. In this form of the element, which has the diamond structure, each atom forms single bonds with four surrounding atoms, at the corners of a regular tetrahedron. White tin, the metallic allotrope, is based upon the normal configuration of the tin atom, $5s^25p^2$. For this configuration the tin atoms are bivalent, and there is one extra orbital, the third $5p$ orbital. The presence of this extra orbital, unoccupied in the neutral tin atom, permits an electron pair to resonate into a bond position from an adjacent position, producing a negatively charged tin atom with three covalent bonds, electron configuration $5s^25p^3$, and leaving, in some other point in the structure, a positively charged tin atom, with electron configuration $5s^25p$ and forming only one bond. The ligancy of tin in white tin is 6. Because of the presence of the metallic orbital on the neutral and positively charged tin atoms the three bonds of Sn^- can resonate freely among the six bond positions, as can the two bonds of Sn and the single bond of Sn^+. The resonance energy of this unsynchronized resonance contributes greatly to the stability of metals. A metallic orbital is not needed for the anion, inasmuch as the assumption of an additional adjacent electron-pair bond would give a double negative charge, which is unstable.[14] A simple statistical argument leads to the conclusion that about half of the atoms in the crystal are neutral atoms, about one quarter are Sn^-, and about one quarter are Sn^+. The process of electric conductivity is described as involving the preferential motion of the positive charges and negative charges from atom to atom through the crystal under the influence of an electric field, and other characteristic metallic properties can similarly be described in terms of the resonance of the valence bonds.

Accordingly, the mechanism of conduction in metals is different from that for the ring currents in benzene, other aromatic molecules, and graphite, in which the atoms do not have the metallic orbital.[15, 16]

Electron-Phonon Interaction in Metals.—The effective radius of the neutral tin atom in metallic tin is the value corresponding to the valence 2, which with ligancy 6 leads to the average bond number $^1/_3$ for the six bonds. A different effective radius is expected for Sn$^-$, corresponding to valence 3 and average bond number $^1/_2$. The equation relating radius and bond number n, for no change in the nature of the bond orbitals, is[17]

$$R(n) = R(1) - 0.30 \text{ Å} \log n. \tag{4}$$

The change in effective radius of Sn$^-$ resulting from the change in bond number is -0.30 Å log $^3/_2$ = -0.053 Å and that for Sn$^+$ is 0.30 Å log 2 = 0.090 Å. In addition, the effective radius of Sn$^-$ is increased by the screening action of the added electron (decrease in effective nuclear charge), and that of Sn$^+$ is decreased by the decreased screening accompanying removal of an electron. These effects may be estimated as about ± 0.010 Å, for all atoms, by the use of screening constants.[18] In the tin crystal the charged atoms are under strain, tension for Sn$^-$ and compression for Sn$^+$.

Let us assume that a phonon is present in the crystal. In the compressed regions of the crystal, corresponding to the crest of the compressional waves of the phonon, the interatomic distances are decreased, and in the expanded regions, the troughs of the waves, they are increased. The strain is accordingly decreased for Sn$^-$ in the crests and increased in the troughs, and increased for Sn$^+$ in the crests and decreased in the troughs. As a result, the normal electronic state of the crystal in the presence of a phonon involves a larger concentration of Sn$^-$ in the crests and a larger concentration of Sn$^+$ in the troughs of the wave. The stability of the crystal is increased by this electron-phonon interaction, in that in the compressional regions the strain is essentially divided between Sn$^-$ and Sn, and in the expanded regions between Sn and Sn$^+$; the quadratic dependence of energy on strain leads to a smaller amount of strain energy than in the absence of the phonon, and the amount of resonance energy is nearly as great, because unsynchronized resonance can take place in the crests between the tin anions and neutral tin atoms (which have a metallic orbital), and in the troughs between neutral tin atoms and the cations.

Rough quantitative calculations of the energy of interaction of the electron pairs and the phonon can be made with use of the force constants for the bonds[19] and the changes in the position of the minimum in the potential functions for a bond, as given by the foregoing values of the change in effective radius.

Chest Superconductors and Trough Superconductors.—As additional examples I shall discuss other metals of the second long period of the periodic table, beginning with niobium, molybdenum, and technetium. The normal electron configurations of atoms of these elements are $4d^45s$, $4d^55s$, and $4d^55s^2$, respectively, followed by $4d^75s$ for ruthenium and $4d^85s$ for rhodium. The levels $4d$ and $5s$ have about the same energy for these elements, with $5p$ lying about $3eV$ higher. For the neutral niobium atom we expect quinquecovalence; that is, all five outer electrons are involved in bonding. We expect the valence 4 for Nb$^+$ and 6 for Nb$^-$, from the configurations d^3s and d^5s, respectively. These valences, together with the screening correction $-$ 0.010 Å for Nb$^+$ and +0.010 Å for Nb$^-$, lead to the values $\Delta R^+ = +0.019$ Å and $\Delta R^- = -0.014$ Å. Excess negative charge is accordingly expected to be associated with the crests of the phonons, and a deficiency of negative charge with the troughs. Inasmuch as it is electron pairs, carrying a negative charge, that travel with the phonons, the charge of a superconducting current in niobium metal is seen to travel with the crests of the waves. Niobium may be described as a crest superconductor.

The normal state of the neutral technetium atom, with configuration $4d^5 5s^2$, has five unpaired electrons, and might form five bonds, with Tc^+ (normal state $4d^5 5s$) forming six bonds and Tc^- (normal state $4d^7 5s$) forming four. These configurations and valences do not, however, provide a metallic orbital for Tc^+ and Tc. A $4p$ orbital might serve as metallic orbital, but only to an extent permitted by the promotion energy. I have assumed that for the elements Mo to Rh and their cations Tc^+ to Rh^+ one half of a $4d$ or $5s$ orbital is used as a metallic orbital and the remaining 5.5 orbitals are available for occupancy by unshared electron pairs. This assumption leads to the numbers of bonding electrons given in Table 1.

TABLE 1. *Calculation of T_c for superconductors of the second long period.*

	Y	Zr	Nb	Mo	Tc	Ru	Rh
				Configuration			
	ds^2, d^2s	d^2s^2, d^3s	d^4s	d^5s	d^5s^2	d^7s	d^8s
v^+	2	3	4	5	5	4	3
v	2.6	3.8	5	5.5	4.5	3.5	2.5
v^-	3.2	4.6	6	5	4	3	2
v_{av}	2.6	3.8	5	5.25	4.5	3.5	2.5
ΔR^+	0.024	0.021	0.019	0.003	−0.024	−0.027	−0.034 Å
ΔR^-	−0.017	−0.015	−0.014	0.023	0.025	0.030	0.039 Å
ρ calc.	0.065	0.178	0.371	−0.269	−0.402	−0.220	−0.103
T_c calc.	0.0001°	0.44°	8.12°	2.92°	9.98°	1.21°	0.007°K
T_c obs.	<0.07°	0.56°	9.1°	0.72°	10°	0.49°	<0.09°K

For yttrium and zirconium the values of the valence correspond to mixing of the normal configurations (ds^2, $v = 1$, for Y and d^2s^2, $v = 2$, for Zr) and the excited configurations (d^2s, $v = 3$, for Y and d^3s, $v = 4$, for Zr), which differ in energy by less than the energy of a single bond.

The calculated values of ΔR^+ and ΔR^- for the elements technetium to rhodium have signs interchanged from those of niobium. The excess negative charge is accordingly in the neighborhood of the troughs of the phonons, and these elements are trough superconductors. Molybdenum is also a trough superconductor; the positive value of ΔR^-, larger than that of ΔR^+, leads to excess negative charge in the troughs of the phonons.

The following simplified treatment is presented to illustrate some roughly quantitative aspects of the theory. The value of θ is taken to be constant, with $A\theta = 120°$. The interaction constant ρ is taken as $0.36\ v_{av}^3 \Sigma z_i p_i \Delta R_i$, in which p_i is the fraction of ions i in the crystal and ΔR_i is the change in radius. The quantity v_{av}^3, the cube of the average valence for the metal or alloy, is an approximate representation of the force constant k of the bonds, which enters linearly in the expression for V. The coefficient z has the value $+1$ for M^+ and -1 for M^-. The number 0.36 has been introduced to give agreement with the observed

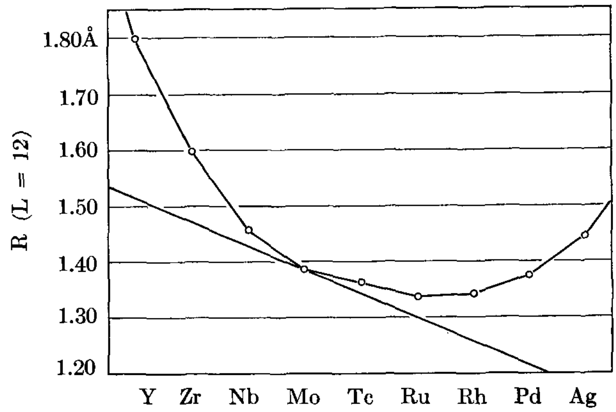


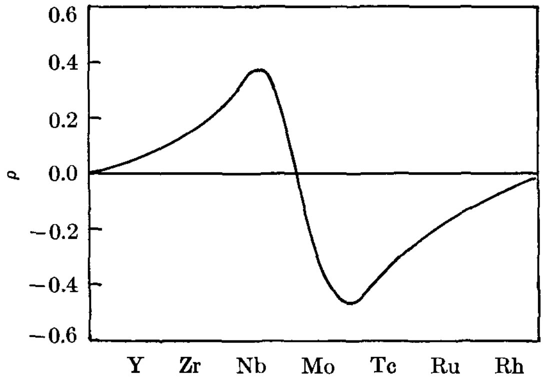
FIG. 1.—Values of the metallic radius for ligancy 12, represented by circles, for the elements yttrium to silver. The straight line represents the expected values for valence of other metals equal to the valence of molybdenum; that is, it shows the effect of increasing nuclear charge only.

value of T_c for technetium; no other arbitrary parameters are involved in the calculation.

The approximate correctness of the relative values of v_{av} given in the table is supported by the observed values of the metallic radii. Values of R for ligancy 12 are shown in Figure 1, with a straight line with slope that represents the change in radius with atomic number for constant valence and type of orbital, as given in Figure 3 of an earlier paper.[17] The points lie above the line by amounts that indicate a monotonic decrease in valence to both sides of molybdenum.

The calculated values of ρ are shown in Figure 2. Positive values (left of atomic number 41.7) correspond to crest superconductors, and negative to trough superconductors. Values of T_c calculated by introducing $|\rho|$ in equation (3) (with $\theta = 120°$) are represented by the curve in Figure 3, which applies to the elements and the alloys of adjacent elements. The calculation for the alloys was made by use of fractions p_i of $M^+{}_Z$, M_Z, $M^-{}_Z$, $M^+{}_{Z+1}$, M_{Z+1}, and $M^-{}_{Z+1}$ given by a probability function $\exp[-0.694(x - x_0)^2]$ (x = number of electrons)

FIG. 2.—Calculated values of ρ for the elements yttrium to rhodium and for binary alloys between adjacent elements.



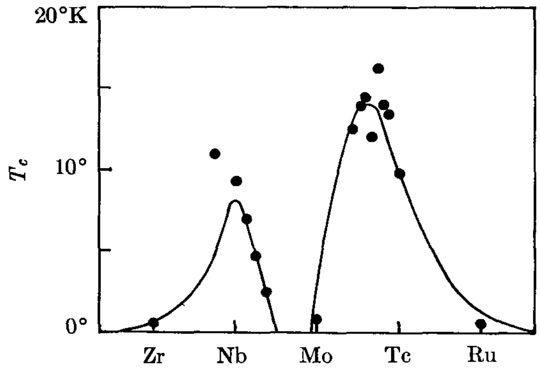


FIG. 3.—The curve represents the calculated values of the superconductivity critical temperature. The circles are the experimental values for the elements and for binary alloys between adjacent elements.

with center x_0 placed to correspond to the composition of the alloy. Experimental points for the five elements, one Zr-Nb alloy,[21] several Nb-Mo alloys,[22] and several Mo-Tc alloys[23] are seen to be in rather rough agreement with the calculated curve.

The gap in superconductivity between the fifth and sixth groups of the periodic table, discovered by Matthias,[24] is seen to correspond to the transition from crest to trough superconductivity. It does not require for its explanation the assumption[20, 25] that there are mechanisms of superconductivity other than the electron-phonon interaction.

The foregoing discussion leads to the conclusion that static deformations as well as phonons should be stabilized for superconducting metals by the change in effective radius associated with unsynchronized resonance of electron-pair bonds. Deformation from cubic to tetragonal symmetry, presumably the result of this interaction, has been reported for V_3Si at temperatures below 21°K[26, 27] and for Nb_3Sn at temperatures below 43°K.[28]

Discussion of other metals and alloys and of the isotope effect will be published later. I am grateful to Professor B. T. Matthias for having encouraged me to work on this problem.

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Influence of Valence, Electronegativity, Atomic Radii, and Crest-Trough Interaction with Phonons on the High-Temperature Copper Oxide Superconductors

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Several structural features, including electron transfer between atoms of different electronegativity, oxygen deficiency, and unsynchronized resonance of valence bonds, as well as tight binding of atoms and the presence of both hypoelectronic and hyperelectronic elements, cooperate to confer metallic properties and high-temperature superconductivity on compounds such as $(Sr,Ba,Y,La)_2CuO_{4-y}$.

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The theory of superconductivity based on the interaction of electrons and phonons was developed about thirty years ago.[1-4] In this theory the electron-phonon interaction causes a clustering of electrons in momentum space such that the electrons move in phase with a phonon when the energy of this interaction is greater than the phonon energy $\hbar\omega$. The theory is satisfactory in most respects.

In the resonating-valence-bond theory of metals the electronic structure of the metal is described in successive steps involving integrals of decreasing magnitude.[5-9] First, two electrons with opposed spins and occupying orbitals on adjacent atoms form a covalent bond, which may have some ionic character. Second, these covalent bonds resonate among the alternative positions in the metal. Third, because of the principle of approximate electroneutrality,[10] an atom can assume only resultant charges +1, 0, or −1, corresponding to M^+, M^0, and M^-. (This restriction explains why Fröhlich[2] decided that all metals are effectively univalent.) The wave function for such a structure, describing the resonance of bonding electron pairs among alternative interatomic positions, was formulated in 1949.[6]

The resonating-valence-bond theory is in many ways equivalent to the conventional band theory of metals, but it has the advantage that it permits far more easily the discussion of the dependence of the properties of a metal on the nature of the atoms of which it is composed. For example, in 1968 I pointed out that there are two classes of superconductors, crest superconductors and trough superconductors.[11] We may consider the hypoelectronic metal La as an example. It has valence $v=3$, ligancy $L=12$, and superconductivity temperature 6 K. Its metallic radius[12] for $L=12$ is 1.865 Å, which decreases to 1.650 Å for La^-, which has valence 4; accordingly La is a crest superconductor, with the La^- electrons riding the crests (higher density) of the phonon. The holes, M^+, tend to ride the troughs. If they moved as effectively as the electrons there would be no current. The rate of $M^-M^0 \rightarrow M^0M^-$ (electrons moving to the right on the crest of the phonon) is, however, greater than that of $M^+M^0 \rightarrow M^0M^+$ (holes moving to the right on the trough of the phonon) because the exchange integral is smaller for the motion of the hole as a result of the smaller size of M^+ than of M^-, which causes the holes to fall behind the electrons in following the phonons.

For a hyperelectronic metal, such as In ($T_c=3.4$ K, radius 1.550 Å, valence of In^0 3.56, of In^- 2.56, and of In^+ 4.56), the electrons ride the troughs and the holes ride the crests.

The compound La_3In has $T_c=10.4$ K. Because La is hypoelectronic and In is hyperelectronic, I expect electron transfer to take place to the extent allowed by the approximate electroneutrality principle.[13] The unit cube would then consist of 2 La, La^-, and In^+, with In^+ having no need for a metallic orbital and thus having valence 6 with the bonds showing mainly pivoting resonance among the twelve positions. The increase in valence of In and also of La (to $3\frac{1}{3}$) and the assumption of the densely packed $A15$ structure account for the decrease in volume by 14.3%. Because the holes are fixed on the In^+ atoms, only the electrons move with the phonon, explaining the increase in T_c.

The mechanism of superconductivity of the copper oxide compounds is different. In its oxides and other compounds, copper has three oxidation states, Cu^{I}, Cu^{II}, and Cu^{III}, the last occurring only rarely. Cu^{I}, in Cu_2O (cuprite), MCuO (M=Na,K,Rb), $LaCuO_2$, and other crystals, has 2 O atoms on opposite sides at about 1.85 Å, with 4 or more O atoms at a larger distance. Cu^{II}, in CuO (tenorite), Cu_4O_3 (paramelaconite[14]; linear O—Cu^{I}—O groups are also present), $CaCu_2O_3$, and other crystals, has 4 O nearby, at about 1.90 Å, with two others more distant. Cu^{III} is found in $M$$CuO_2$ (M=Na,K,Rb,Cs), $LaCuO_3$, and other crystals to lie at the center of a CuO_4 square with Cu—O bond length of 1.85 Å and with two other O atoms somewhat farther away. The volume per CuO_6 group decreases by two steps of about −10% as the oxidation state of Cu increases from I to III, as is expected for a hyperelectronic element.

Whereas cuprite is red, tenorite is black, showing that there is some electron mobility in this crystal: resonance of $2Cu^{II}$ to $Cu^{I}+Cu^{III}$.

The high-temperature superconductors such as $(Y,La,Sr,Ba)_2CuO_{4-y}$, with a structure resembling that of K_2NiF_4, differ from other copper-oxygen compounds in that the CuO_4 squares are condensed into infinite layers such that each O lies midway between two Cu. There are thus in the *a* and *b* directions infinite straight lines of alternating Cu and O atoms. I believe that this structure, in interaction with the layers of La and other metals, gives rise to superconductivity.

Cu and O differ in electronegativity by 1.6 units, corresponding to 47% ionic character. Each CuO_4 square, with four covalent bonds about 1.85 Å long, half covalent and half ionic, may be described as involving two pure covalent bonds resonating among the four positions. The bond orbitals of O are essentially $2p$, with only a small amount of *s* character. The *p* bonds make angles 90° with one another, not 180°. Hence in a sequence $\cdots O—Cu \cdots O—Cu \cdots$ there is always an alternation of one pure covalent bond and one "no-bond" (indicated by $\cdots$).

This sequence could be interrupted as an O swings an electron pair to form a bond to one of the four La nearby. Values of the electronegativity of Ba, Sr, La, and Y, 0.9 to 1.0, are so low that these atoms have a positive charge and the O atoms are O^{2-}, with a stable outer octet of electrons. This stability, however, does not prevent the movement of electron pairs along the string of atoms, in synchronism: $\cdots Cu—O \cdots Cu—O \cdots Cu —O \cdots$, the pair of electrons forming the bond on the left side of each O atom moves to the right side, still occupying the same *p* orbital but forming the new bond with its negative lobe.

Anderson pointed out[15] that resonance of covalent bonds in this way would lead to an insulator rather than a substance with metallic conductivity, but he has also stated recently that the doping of La_2CuO_4 with Sr or Ba shifts it away from the insulating state and permits the electron pairs to become superconducting pairs.[16] He describes the mechanism for superconductivity as predominantly electronic and magnetic, although weak phonon interactions may favor the state. I agree with this statement, but point out that other interactions are also involved.

In a line of atoms with an alternation of bonds and no-bonds there are only two structures, each extending the length of the line. The probability of resonance is very small. If, however, some O atoms were missing, so that vacancies interrupted the sequences, there would be the possibility of unsynchronized resonance. Moreover, there is some dismutation of $2Cu^{II}$ to $Cu^{I}+Cu^{III}$. Cu^{I} differs from Cu^{III} in having an additional pair, which it can pass on to the next Cu^{III} by donating it to the back lobe of a *p* orbital of O as the electron pair occupying the front lobe moves onto the next Cu^{III}, converting it to Cu^{I}. Somewhat similar processes involving Cu^{II} can also occur. If the segments are short enough, the amount of unsynchronized resonance can become so great as to make the conducting state more stable than the insulating state, as is the case with metals. Suitable doping may be required.

Interactions with the La (Ba,Sr) atoms are also essential for high-temperature superconductivity. As in other cases, electron transfer is expected from the hyperelectronic atoms (Cu) to the hypoelectronic atoms (La, Sr,Ba). The distances between La atoms, 3.81 and 3.95 Å, are only a little greater than that in La metal, 3.73 Å. The extra electrons transferred to La from Cu are not required for La—O bonds, because O retains its full complement of 8 electrons in its completed *L* shell. Accordingly these transferred electrons are used in forming covalent bonds that resonate among the La-La and La-Cu positions and confer electronic conductivity on the substance, making it a metal. This conductivity is increased by the resonance along the $O—Cu \cdots O—Cu$ lines of atoms, and superconductivity is probably achieved through interaction with a phonon.

Whatever may be the mechanism of superconductivity, it is certain that the value of the critical temperature T_c is increased as the amount of scattering of the electrons by phonons decreases; that is, as the strength of the electron-phonon interaction becomes smaller. The crest-trough theory of this interaction led me years ago to the conclusion that this result could be achieved by combining a crest and a trough superconductor. La (also Sr, Ba, Y, etc.) is a crest superconductor—the extra electron causes tighter binding and greater local density, the phonon crest; whereas Cu would be a trough superconductor—extra electrons would cause a decrease in bonding and in local density.

Tight binding and low atomic weight favor high values of T_c. Sc might accordingly be more effective than Y. I think that no other hyperelectronic element can compete successfully with Cu. Ag and Au have the right oxidation states but are too heavy and too loosely bound. No other hyperelectronic element has a good range of oxidation states.

The observation reported in the press that a green cuprate when heated explodes to give a black powder can be understood. The explosion results from the exothermic release of oxygen to give the metallic oxygen-deficient substance. The release of energy is caused by the extra stability resulting from the increase in valence from electron transfer and the energy of unsynchronized resonance characteristic of metals.

The individual structural features of the high-temperature superconductors are found in other substances. A substance with alternating metal-salt layers is Ag_2F, with sequence $\cdots FAgAgFAgAgF \cdots$. Resonance between a covalent bond and a no-bond is found in B ($v=3, L=6$) and in metals and organometallic clusters. Hyperelectronic-hypoelectronic electron transfer occurs in many alloys, leading to contraction and increase in the Debye constant. The copper oxide superconductors are the only substances known that incorporate all of these features.

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Apparent icosahedral symmetry is due to directed multiple twinning of cubic crystals

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Recently the announcement was made of the remarkable discovery of intermetallic compounds with approximate composition MAl_6 ($M = Cr$, Mn, Fe) that formed crystals or pseudocrystals with icosahedral symmetry, as shown by the shape of the small nodules and by their electron diffraction patterns[1]. I have found it hard to believe that any single crystal with 5-fold axes could give reasonably sharp diffraction patterns, resembling those given by crystals, and I have not been convinced to the contrary by the theoretical discussions of this possibility that have been published[2–7]. I therefore set myself the task of predicting how a molten alloy of Mn (or Cr or Fe) and Al might react to sudden cooling. I have discovered that such an alloy on sudden cooling could form a metastable cubic crystal with a large cube edge, about 26.7 Å, with the unit cube containing about 1,120 atoms (possibly a few more), and that these crystals would show ordered multiple growth such that 20 of them, roughly tetrahedral in shape, grow out from a central seed in such a way as to produce an aggregate with approximately icosahedral symmetry.

The task of predicting a reasonable structure for this alloy was carried out with no information about the powder X-ray diffraction pattern except that one group of investigators had said that it could not be indexed by any Bravais lattice. The prediction of the structure was made entirely on the basis of knowledge of the effective radii of metal atoms and the principles determining the structure of metals and intermetallic compounds.

The transition metals form icosahedral complexes with Al; the crystal WAl_{12}, for example, is discussed in refs 8, 9. The effective radii[8] (for ligancy 12) of Mn and Al are 1.268 and 1.429 Å, respectively, with ratio 0.89, corresponding closely to the value 0.902 for a regular icosahedron. Two MAl_{12} icosahedra might condense, with elimination of Al atoms, by sharing a corner, an edge or a face. Two icosahedra sharing an edge could easily eliminate another Al atom to share a face. I accordingly assumed that each MAl_{12} icosahedron would share four faces with surrounding icosahedra, leading to the composition MAl_6. The four M—M vectors from each icosahedron to its neighbours are directed towards the corners of a regular tetrahedron. Moreover, when two icosahedra share a face, they are related by a plane of symmetry (the plane of the shared face). The other three faces of each icosahedron can be shared in either the eclipsed conformation or with a twist of 40°. The eclipsed conformation of tetrahedral bonds leads, with only slight deformation (reduction of the angle from 109.47°, the tetrahedral value, to 108°, the value for a pentagon), to pentagonal rings and then, when continued, to pentagonal dodecahedra of 20 icosahedra.

These structures are reminiscent of those of the rare-gas hydrates, which involve tetrahedrally hydrogen-bonded water molecules with the eclipsed relative orientation. The hydrate with a unit cube 12 Å on edge, containing 46 H_2O molecules, has 2 pentagonal dodecahedra and 6 tetrakaidecahedra in the unit[10], whereas the one with unit cube 17 Å on edge, containing 136 H_2O molecules, has 16 pentagonal dodecahedra and 8 hexakaidecahedra in the unit[11]. I selected the latter because of its larger number of dodecahedra.

Replacement of each water molecule by an $MnAl_{12}$ icosahedron with shared faces leads to an infinite framework with 136 Mn and 816 Al atoms in the unit cube. This framework is similar to the framework of covalently bonded carbon atoms in a diamond crystal, with one body diagonal of each pentagonal dodecahedron in place of each C—C covalent bond.

I was able to make a moderately reliable prediction of the edge of the unit cube for the proposed MAl_6 structure. I assumed the Al—Al distance along the edges of the MAl_{12} icosahedron to be 2.864 Å, as in metallic Al. The distance between centres of icosahedra sharing a face is then 4.329 Å, 1.568 times the hydrogen-bond length in the 17-Å hydrate, with $a_0 = 17.0$ Å. With this factor the predicted value of the cube edge a of the alloy is 26.7 Å.

I obtained from D. Shechtman a copy of an X-ray diffractometric record, made with CuKα radiation in the US Bureau of Standards. This pattern shows 7 Si peaks (several with $\alpha_1\alpha_2$ splitting), 6 Al peaks (somewhat broader, indicating small crystallite size) and 22 other, rather broad, peaks, corresponding to the compound $MnAl_6$. I found that all 22 peaks could be indexed with a cubic unit of structure. Moreover, the indicated value of the edge of the cubic unit of structure, 26.73 Å, turned out to be in good agreement with my predicted value, 26.7 Å. All of the observed diffraction maxima are those expected for spherically symmetrical groups about the diamond points 000, $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, and so on.

The fact that the structure that I formulated for this alloy from chemical arguments with no knowledge about the X-ray diffraction diagram was found later to agree quantitatively with that diagram has convinced me that the structure is correct. I emphasize that I formulated only one structure, and that the X-ray diagram was not involved in any way in its formulation. The probability of chance agreement of the lattice constant to 0.1 Å and of adherence to the selection rules for intensities is surely less than 1 in 1,000.

The approximate intensity rules are given by the assumption of spherically symmetrical aggregates of atoms about the positions of the carbon atoms in diamond. They are that the reflections with *h*, *k* and *l* all even and their sum divisible by 4 should be the strongest, those with *h*, *k* and *l* all odd should be next, and those with *h*, *k* and *l* all even with sum not divisible by 4 the weakest. Table 1 verifies this prediction; the seven strongest reflections are of the first type, and none of the third

Table 1 Analysis of X-ray diffraction pattern of icosahedrally twinned cubic crystals of $MnAl_6$

h k l	*d* (Å)	*a* (Å)	Intensity*
4 4 4	3.850	26.68	7
8 0 0	3.341	26.73	2
7 3 3	3.299	27.00	1
7 7 5	2.405	26.67	1
9 7 3, 11 3 3	2.269	26.75	3
7 7 7, 11 5 1	2.209	26.78	4
12 2 2	2.168	26.73	100
12 4 0	2.116	26.77	3
10 8 2	2.060	26.70	150†
15 1 1	1.7728	26.71	0.5
14 6 0	1.7554	26.74	1
12 12 4	1.5314	26.70	0.2
16 8 0	1.4946	26.74	7
16 8 4	1.4604	26.77	2
20 4 0	1 3075	26.67	1
15 11 9	1.2930	26.72	1
20 6 2	1.2765	26.78	21
24 4 0	1.0994	26.75	6
24 4 4	1.0856	26.77	5
20 12 12	1.0208	26.78	1
23 11 7, 25 7 5	1.0108	26.72	1
24 8 8	1.0077	26.74	1
	Average 26.73		

* All intensity values from 5 to 150 are those assigned by Shechtman and Blech[2]. For most peaks the values of *d* are calculated from the values of 2θ printed on the diffractometer record. The exceptions are the weak reflections 4, 10, 11, 12 and 16.

† This very strong peak is about twice as broad as the peak with $d = 2.168$ Å. It is probably broadened by unresolved adjacent reflections 991 and 993.

type appears.

The absence or very low intensity of 111, 311, 331, 333 and 511 indicates that clusters of atoms, perhaps 13–20, occupy the centres of the hexakaidecahedra, around $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ and so on. There are also smaller clusters, probably of four atoms, inside the pentagonal dodecahedra, increasing the number of atoms in the 25.73-Å cube to between 1,120 and 1,176. The composition of the alloys may be changed from MAl_6 by these additional atoms.

An X-ray powder photograph taken with a focusing camera and X rays monochromatized by crystal reflection would probably show more than 100 powder lines, providing a more rigorous text of the proposed structure. Accurate values of predicted intensities of the lines will become available only after coordinates have been assigned to all of the atoms, a formidable task with such a complicated structure. This task is now being attempted (S. Samson, personal communication).

A further complication is that an icosahedron sharing four faces loses its symmetry operations of the second sort and becomes chiral, D or L. The eclipsed configuration described above requires that D and L alternate. Hence, in a ring of five icosahedra one DD or LL bond must occur, with a strain in the ring of 40°, which is a rotation of 4° per shared face in each icosahedron. The space-group symmetry is thus changed from that of diamond to a subgroup.

Although I knew about the work of Samson in determining the structures of $NaCd_2$, Cu_4Cd_3 and β-Mg_2Al_3, I did not recognize until after my MAl_6 structure had been formulated that they have essentially the same structure. The delay resulted in part from the fact that in his descriptions of the structures Samson emphasized the Friauf polyhedra (ligancy 16 of the central large atom) rather than the icosahedra[12–15]. I made an X-ray diffraction study of $NaCd_2$ in 1922 (ref. 16), but the structure was so complicated that I could not determine it then or during the next four decades, after which Samson was successful[13]. The edge of the unit cube is 30.56 Å, with between 1,120 and 1,190 atoms, not all of which were located by Samson. The structure contains 568 icosahedra, 124 Friauf polyhedra and 428-495 unidentified or others[12,13]. A complete structure determination was made by Samson for Cu_4Cd_3: edge of unit cube 25.87 Å, 1,124 atoms, 568 icosahedra, 124 Friauf polyhedra[14], and a partial determination for β-Mg_2Al_3, edge of unit cube 28.24 Å, 1,192 atoms, 624-672 icosahedra[15]. The lattice constants differ from the value for $MnAl_6$ by amounts determined by the relative sizes of the atoms.

The first complex intermetallic compound found to have large clusters of atoms with local icosahedral symmetry was $Mg_{32}Al_{49}$, which has 162 atoms in a body-centred cubic unit[17]. The unit cube contains 98 icosahedra, 20 Friauf polyhedra and 44 others.

This compound gives an indication of the extent to which structures with local icosahedral symmetry can develop. It contains icosahedral groups of 117 atoms, a central atom with surrounding shells of 12, 32 and 72 atoms, the last being shared with surrounding groups (ref. 8, p. 428). The developing strain restricts the icosahedral complex to three shells of atoms around the central one. The hypothesis that I propose for the growth of a 20-fold twin of the MnAl alloy is that the seed is a pentagonal dodecahedron. It is surrounded by a shell of 12 dodecahedra, sharing faces, then by 32 (12 sharing faces with the inner 12, 20 sharing corners and with a body diagonal directed radially), and then by 72 (12 sharing faces with the next inner 12, 60 combining tetrahedrally with the next inner 20). At this point, the strain of attempting to fill space with pentagonal dodecahedra becomes great enough to disrupt the 12 outer dodecahedra, introducing additional atoms. The 20 tetrahedral groups of 4 dodecahedra continue to add dodecahedra in the way found in the 17-Å hydrate, and the twin of 20 pyramid-shaped cubic crystals with cube edge 26.73 Å develops.

The individual cubic crystals sometimes grow at equal rates, filling the spaces between them. Each assumes the shape of a trigonal pyramid, with the outer edges 5% longer than the radial edges. The multiple twin then has the macroscopic appearance of an icosahedron.

This postulated mechanism fixes the orientation of the 20 cubic crystals. Each crystal has a body diagonal extending out from a 3-fold axis of the seed dodecahedron and the other 3-fold axes lie in the planes of symmetry of the seed dodecahedron. A diffraction photograph of the twin would be the superposition of the diffraction photographs of the individual crystals that intercept the beam. I have not been able to make a thorough analysis of the published electron diffraction patterns because of lack of information about the conditions in which they were made, but my partial analysis indicates that the patterns are compatible with the proposed structure. The proposed structure also accounts for the dimensions of the pentagonal rings observed in electron micrographs of the alloys.

I conclude that this successful analysis of the diffraction pattern settles the question of the nature of the 'icosahedral' MAl_6 alloys. They are multiple twins of a cubic crystal. The validity of this conclusion is strengthened by the fact that the value of the cube edge given by the diffraction pattern is almost exactly equal to that which I predicted, without any knowledge of this pattern, on the basis of purely chemical arguments. Crystallographers can now cease to worry that the validity of one of the accepted bases of their science has been questioned.

I thank Dr D. Schechtman for cooperation in providing me with the X-ray diffraction pattern and for other information, and Professor Barclay Kamb for pointing out to me that an icosahedron becomes chiral when it shares its faces. This investigation was supported in part by a grant from the Japan Shipbuilding Industry Foundation.

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So-called Icosahedral and Decagonal Quasicrystals Are Twins of an 820-Atom Cubic Crystal

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It is proposed that a molten alloy may contain a 104-atom cluster with icosahedral symmetry and largely icosahedral packing. The cluster may be described as involving twenty interpenetrating Friauf polyhedra. On rapid freezing these clusters form cubic crystals related to the β-W structure. The structure is compatible with x-ray and neutron powder diffraction patterns, the single-crystal precession x-ray patterns of CuLi$_3$Al$_6$, the electron diffraction photographs, and the high-resolution electron micrographs.

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The discovery by Shechtman *et al.*[1] that a rapidly cooled alloy with composition MnAl$_6$ and some other alloys seem to have icosahedral symmetry has aroused great interest, with about 500 papers having been written on this subject during the last two years, many of them dealing with Penrose tiling, six-dimensional space, and other efforts to explain the observations. Decagonal quasicrystals have also been reported.[2,3] The few efforts to discuss the phenomena in terms of twinning[4-6] have been largely ignored.

I suggested last year[6] that an icosahedral or decagonal seed orders twenty or ten cubic crystals into orientations such as to give the twinned clusters icosahedral or decagonal point-group symmetry. The structure that I proposed, on the basis of arguments about icosahedral packing of larger atoms (Al) about smaller ones (Mn), was the 1168-atom face-centered-cubic NaCd$_2$ structure[7-10] with cube edge 26.73 Å. This structure accounted reasonably well for the x-ray powder pattern, but it was pointed out[11,12] that other large units might also account for this pattern and that I had not provided a satisfactory discussion of the electron-diffraction (ED) patterns and the high-resolution electron micrographs (HREM's).

During the past year I made considerable progress with the 26.73-Å unit, but kept having difficulties. One problem was that a sequence of ED diffraction maxima on essentially all the ED photographs had surely, on the twinning hypothesis, to be $hh0$ rather than $h00$, because the cubic crystals are oriented with their body diagonals and symmetry planes coincident with the threefold axes and symmetry planes of the icosahedral seed, and $hh0$ of the 26.73-Å cube could not give the correct ED spacings if the scale published by Shechtman and Blech[13] were correct. I suggested to these authors and also to Bendersky[2] that there was an error by the factor $3^{1/2}/2$ in their scales. They kindly sent me calibrating ED's proving that my suggestion was wrong. The alternative was that the error lay in my value of the cube edge, and I soon found that a primitive unit cube with edge length 23.36 Å and containing about 820 atoms is in complete agreement with the high-resolution x-ray powder diffraction pattern reported by Bancel *et al.*[14] The longest interplanar distances, 3.850, 3.349, and 2.856 Å correspond, respectively, to the indices 6 1 0, 6 3 2, and 7 3 3; the other values also agree with this unit. The unit also accounts for the neutron diffraction patterns,[15,16] including one strong line (2.622 Å, 8 4 0) that does not appear on the x-ray pattern.

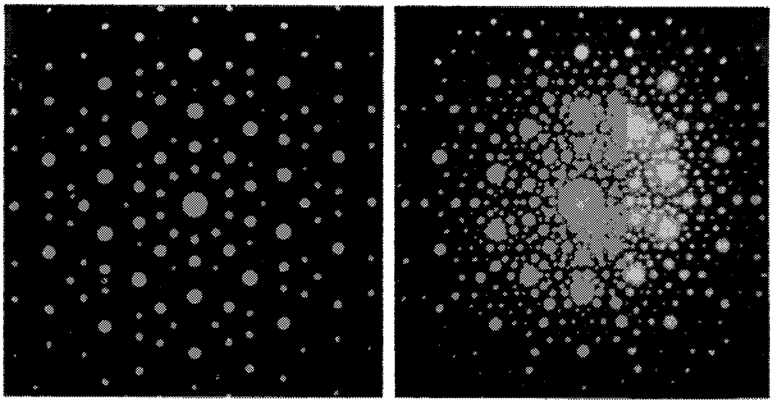
The single-crystal x-ray photographs of the CuLi$_3$Al$_6$ decagonal quasicrystals sent to me before publication by Bartges *et al.*[17] were of great help to me in substantiating the 820-atom cubic structure. Diffractions 5 5 0, 8 8 0, 13 13 0, and 16 16 0 are seen as the principal features on the fivefold axis, threefold axis, and twofold axis precession x-ray photographs.

It is of interest that this is the most complicated structure to have been reported for an intermetallic compound. It has 820 atoms in the Bravais unit, nearly three times as many as the NaCd$_2$ structure.

Representative ED photographs with the beam along a fivefold axis (kindly given to me by Dr. K. K. Fung[3]) are shown in Fig. 1. Analysis of the spots on the meridional (P-P) plane of symmetry is given in Table I. All of the spots are orders of $hh0$, with the stronger ones representing the first six terms of the Fibonacci series, as is expected from the icosahedral packing of the atoms in the assigned structure (described below).

There are only three equatorial spots. Each of the three can be accounted for by double diffraction (of 3 3 0, 5 5 0, and 8 8 0, with the factor for R of $1.9021 = 2\sin 72°$). By vector addition it is seen that the other spots can be accounted for by multiple diffraction of $hh0$.

Whereas only $hh0$ can diffract with the beam along a fivefold axis of the icosatwin because of the tilt of the cubic crystals, any plane in the zone $1\bar{1}0$ of the decatwin can diffract because the seed orients the cubic crystals with this zone axis parallel to the fivefold axis of the twin. It is seen from Fig. 1(b) that the meridional spots of decagonal FeAl$_6$ are the same as for icosahedral MnAl$_6$, representing orders of $hh0$, but that there are many more equatorial spots, eleven instead of three. Indices are assigned in Table II; some spots involve double



(a) (b)

FIG. 1. Fivefold ED photographs of icosahedral $MnAl_6$ (left) and decagonal $FeAl_6$ (right) (Ref. 3).

diffraction. Inspection of Fig. 1 (vector addition) shows that all of the spots between the symmetry planes can be accounted for by multiple diffraction or primary diffraction (the two strongest, spacings 2.565 and 1.835 Å, have indices 1 1 9 and 3 3 12).

I have analyzed many other ED photographs, with similar success in accounting for the observed patterns with the 23.36-Å unit.

Recognition that the crystals have a cubic unit with edge 23.36 Å required that I reconsider the nature of their structure. The relative sizes of Mn and Al indicate icosahedral packing. This packing was first reported by Friauf[18] for the copper atoms in the 24-atom face-centered compound $MgCu^2$ and then by other investigators for some of the atoms in α-Mn, β-Mn, and β-W. In 1950, I recognized that the 39-atom cubic structures of $Mg_3Cu_6Al_5$ and Mg_2Zn_{11} (Samson[19,20]) could be obtained from a centered icosahedron surrounded by a shared shell of 32 atoms, and I used this idea to predict the structure of $Mg_{32}(Al,Zn)_{49}$. This structure was refined by Bergman, Waugh, and Pauling[21,22] who pointed out that the central position may not be occupied. Samson[23] has emphasized that the structure may be described as involving a complex of twenty interpenetrating Friauf polyhedra (Fig. 2).

This complex is especially appealing as a unit in a very rapidly quenched alloy. The $Mg_{32}(Al,Zn)_{49}$ structure, with its outer 72-atom shell shared, would be slow to form, but a packing of the 104-atom complexes of Fig. 2 into a crystal without sharing atoms could form rapidly. The cube edge 23.36 Å corresponds to eight of these complexes in the unit. One simple way of arranging them is the NaCl structure, with two orientations alternating; it is ruled out because it is face centered. The other way, the β-W structure (two atoms at 000, $\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}$, 6 at $\frac{1}{2} \pm \frac{1}{4}\,0,\curvearrowleft$), is not ruled out. With this structure each complex C_1 at 000 or $\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}$ is surrounded icosahedrally by twelve complexes C_2 of the second sort at 13.06 Å, and each C_2 has four C_1 at this distance, two C_2 at 11.68 Å, and twelve C_2 at 14.31 Å, its coordination polyhedron being a hexagonal antiprism with two polar caps. The three distances 11.68, 13.06, and 14.31

TABLE I. The meridional (P-P) diffraction maxima of the $MnAl_6$ icosatwin fivefold-axis ED photograph (Ref. 3). Values of intensity, I; radius, R; observed and calculated interplanar distances, d_{obs} and d_{calc}; and indices. Scale $Rd = 75.6$ mm Å, $a_0 = 23.36$ Å.

	I	R (mm)	d_{obs} (Å)	d_{calc} (Å)	hkl
1	vvvw	9.1	8.3	8.26	220
2	w	14.0	5.40	5.51	330
3	s	22.8	3.32	3.304	550
4	vs	36.6	2.066	2.065	880
5	vvw	45.5	1.662	1.652	10100
6	vvvw	50.5	1.497	1.502	11110
7	s	59.2	1.277	1.271	13130
8	w	73.2	1.033	1.032	16160
9	vvw	81.8	0.924	0.918	18180
10	w	95.6	0.791	0.787	21210

TABLE II. The equatorial (D-D) diffraction maxima of the $FeAl_6$ decatwin fivefold-axis ED photograph (Ref. 3). Values of intensity, I; radius, R; observed and calculated interplanar distances, d_{obs} and d_{calc}; and interpretation. Scale $Rd = 72.6$ mm Å, $a_0 = 23.36$ Å.[a]

	I	R (mm)	d_{obs} (Å)	d_{calc} (Å)	Interpretation[b]
1	m	7.0	10.3	10.14	$d(006)$, $d(550)$, 18°
2	m	11.5	6.29	6.300	$d(006)$, $d(006)$, 36°
3	s	18.5	3.91	3.893	$d(006)$
4	m	22.9	3.157	3.150	$d(0012)$, $d(0012)$, 36°
5	m	25.6	2.824	2.833	$d(550)$, $d(550)$, 72°
6	ms	30.3	2.386	2.384	$d(448)$[c]
7	m	37.1	1.949	1.947	$d(0012)$
8	s	41.7	1.734	1.737	$d(550)$, $d(550)$, 144°
9	s	49.6	1.458	1.460	$d(0016)$
10	s	60.6	1.193	1.192	$d(8816)$[c]
11	s	68.0	1.063	1.062	$d(0022)$

[a] The value of a_0 is uncertain. If Rd were the same as for Fig. 1(a), a_0 would be 24.4 Å.

[b] The factor for double diffraction by equivalent planes at 36° is τ, the golden number, with retention of orientation (D-D stays D-D). At 72° the factor is 1.756 and at 144° it is 1.9021, with rotation P-P to D-D or the reverse.

[c] Crystals rotated by $\pm 36°$ diffract $h\,h\,2h$ at $\pm 0.7°$ from the D-D plane.

Å correspond, respectively, to about six, seven, and eight effective shell thicknesses. The distance along the cube edges, 11.68 Å, involves the sharing of pairs of atoms between C_2 and C_2, the distance 13.06 Å involves the juxtaposition of two five-rings rotated by 36° relative to one another, and the distance 14.01 Å involves the juxtaposition of pairs of hexagons to form a dicapped hexagonal prism, as found by Samson[24] in the 184-atom face-centered-cubic crystal $Mg_3Cr_2Al_{18}$ (cube edge 14.53 Å). The eight 104-atom complexes lose twelve atoms by the sharing of pairs between C_2 and C_2, giving 820 in the unit cube. This number leads to atomic volume 15.5 Å^3 and to density 3.31 g ml^{-1} for $MnAl_6$, in agreement with the observed values[25,26] 3.287 ± 0.038 and 3.26 ± 0.06 g ml^{-1}. If the intercluster icosahedra and hexagonal prisms were centered, the calculated density would be 6% larger and unacceptable; it is accordingly to be concluded that these polyhedra remain empty, perhaps because of such low activity of single atoms as to decrease their availability during the process of very rapid freezing of the melt.

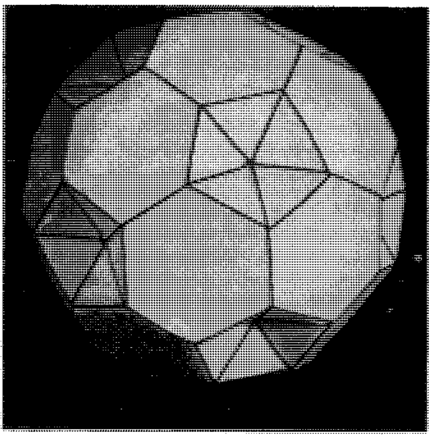


FIG. 2. A complex of twenty Friauf polyhedra, with icosahedral symmetry (Samson, Ref. 23). This complex contains 104 atoms, if the central icosahedral position is not occupied. Most of the atoms show approximate icosahedral ligancy; twenty atoms, at the centers of the Friauf polyhedra, have ligancy 15 or 16. The complex was first identified in $Mg_{32}(Al,Zn)_{49}$. In the cubic crystals that form the icosatwins and decatwins these complexes are packed in such a way as to approximate an icosahedral arrangement of twelve complexes about a central one, the structure being similar to that of β-W.

This structure, based on the space group $O_h^3 Pm3n$, involves about fifty atomic positional parameters, for which approximate values can be estimated from the $Mg_{32}(Al,Zn)_{49}$ parameters. Refinement of the structure would be laborious.

The structure factor for the 104-atom complex with almost perfect icosahedral symmetry determines the intensities of the diffraction maxima, in correspondence with the inverse relationship between intensity in reciprocal space and the atom-pair vectors in real space that was discovered fifty years ago by Patterson.[27] The icosahedral nature of the clusters in the cubic crystal explains the appearance of the Fibonacci numbers and the golden ratio.

I conclude that the evidence in support of the proposal that the so-called icosahedral and decahedral quasicrystals are icosatwins and decatwins of cubic crystals is now convincingly strong. I point out that there is no reason to expect these alloys to have unusual physical properties.

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