BOOK REVIEWS

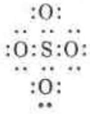
FRITZ EPHRAIM'S INORGANIC CHEMISTRY. Fourth English Edition. By P. C. L. THORNE AND E. R. ROBERTS. Nordeman Publishing Company, Inc., New York, N. Y. Pp. xii and 921. Figs. 95; 1943. Price: $8.75.

The first German edition of this book, which was published by Ephraim in 1922, introduced several innovations. The results of the modern investigations of atomic and crystal structure were taken into account in a systematic way. Much attention was paid to the complex or coordination compounds. A given chemical compound was described together with compounds to which it shows significant interrelations, rather than, as had been customary, in a chapter devoted to one of the elements involved. For instance, calcium carbide is treated not with other calcium or carbon compounds but under the heading "carbides, silicides, and borides: intermetallic compounds." In this way a great deal of information has been presented as concisely as possible. These characteristics and the quality of presentation earned for the numerous German and English editions a leading place among modern textbooks of advanced inorganic chemistry.

The new English edition contains some additions to the broad factual material. Much emphasis has been placed on the electronic interpretation of the structure of inorganic compounds. The authors met a difficult situation in this respect, for widely divergent points of view have been applied to this problem since the appearance of the first edition. In order to arrive at a consistent presentation it would have been necessary either to discriminate among the different theories or to show the connecting links between them. One example, of interest to the mineralogist, namely, the electronic structure of silicates, may be chosen to show how the authors dealt with this problem.

In view of the emphasis on the interrelations between the individual substances, one would expect that the structure of orthosilicate ion $(SiO_4)^{4-}$ be treated in a way analogous to that of the sulfate ion $(SO_4)^{2-}$. The latter is considered in the book from two very different points of view. On p. 231, SO_4^{2-} is derived, as in the former editions, from S^{6+} and four O^{2-} ions and is chosen as an example of a strong deformation of an easily polarizable anion by a strongly polarizing cation. It should be pointed out, that the polarizing power of the ions increases with increasing ionic charge and with decreasing size and the values given on this page for 19 cations and 8 anions run parallel with their (active) polarizing ability and not, as is stated, with their (passive) polarizability. As the measure of the latter, the ionic refraction has to be considered, which for ions of noble gas character of a given charge increases with increasing size.

On p. 575, one finds in the present edition for the first time another description of SO_4^{2-} ion based on the "resonance" considerations of L. Pauling which are reproduced throughout the book in connection with many other compounds. Since these resonance formulas are also given in great detail in the new book by the mineralogist P. Niggli, which is reviewed below, it is not out of place to explain their origin and purpose. The idea of single, double, and triple bonds, which originated in the chemistry of carbon compounds, has been represented by G. N. Lewis (1916) by one, two, and three pairs of electrons respectively shared by the bonded atoms.



$$\begin{array}{ccccc} & & :\ddot{\mathrm{O}}: & & \\ :\underset{..}{\ddot{\mathrm{O}}} & : & \underset{..}{\ddot{\mathrm{S}}} & : & \underset{..}{\ddot{\mathrm{O}}}: \\ & & :\underset{..}{\mathrm{O}}: & & \end{array}$$

The formula proposed for SO_4^{2-} on the basis of this covalent theory is reproduced here. This formula was in agreement with another aspect of the theory, an octet of electrons around each atom, and was considered as a satisfactory scheme until Pauling arrived at the conclusion that the internuclear distance S—O does not correspond to the value this formula led him to expect. The latter expectation is based on the postulate of the additivity of "covalent radii." According to this, a single-bond S—O distance should be exactly the sum of half of the S—S distance in the S_8 molecule and of half of the O—O distance in H—O—O—H. Since the distance in SO_4^{2-} is shorter than this sum, a dynamic electron distribution is assumed, such that part of the four S—O bonds have part of the time a "double bond character" represented by four electrons. It is known that the carbon-carbon distance in $H_2C=CH_2$ is shorter than in H_3C-CH_3. There are many possible structures which can be written in this way for SO_4^{2-}; seven of them take up half of p. 575. None of them is supposed to have any reality but the whole is regarded as a "resonance hybrid." This scheme can hardly be considered a simple one and since it is not possible to estimate the contribution of the single resonating structures to the hybrid without arbitrariness, the main goal of the whole method, namely, a quantitative explanation of the S—O distance, cannot be achieved.

The authors do not make any attempt to correlate the SO_4^{2-} treatments on pp. 231 and 575. Furthermore, in spite of the analogy between SO_4^{2-} and SiO_4^{4-}, the discussion of the internal structure of the silicates on p. 826 ff. has little in common with either of the two descriptions of SO_4^{2-}. The formulas $(SiO_3)^{2-}$, $(Si_2O_7)^{6-}$ of the German edition of 1934 are replaced by $(SiO_3)^{II}$, $(Si_2O_7)^{VI}$, etc. On the other hand, while in the 1934 edition the binding within these complexes is represented throughout as Si—O and is called in the English 1939 edition binding of Si and O *atoms*, in the present edition the statement is made that according to the results of W. L. Bragg the silicates have to be regarded as consisting of Si^{4+} and O^{2-} *ions*. Consequently in the subsequent text, Si- and O-atoms are replaced by Si- and O-ions. This constitutes an improvement; unfortunately the remaining text has been left without change, which leads to contradictions. For instance the statement that oxygen neighboring two Si^{4+} "has no free valency and hence is fully saturated towards other ions, the linkage being homopolar as is the linkage of carbon in organic chains" is inconsistent with the assumption of ionic binding as well as with the facts. In the chain structure of enstatite ($MgSiO_3$) the O^{2-} with two Si^{4+} neighbors are *not* "fully saturated," they are approached by one Mg^{++}, although at a distance of about 0.3 Å larger than the distance between Mg^{++} and O^{2-} when the latter has only one Si^{4+} neighbor. These facts can be easily explained from the point of view of polarization and tightening of O^{2-} by adjacent cations but can not be understood from the homopolar (covalent) point of view or on the basis of the idea of definite ionic radii.

The polarization of O^{2-} by Si^{4+} is not mentioned in connection with the structure of silicates although on p. 231 the polarizing power of Si^{4+} is expressed by the high value 26 as compared with the polarizing power of F^- 0.6 which according to p. 39 deforms the K^+ in KF appreciably. The undersigned agrees fully with the statement on p. 39 that "the polarization, distortion and alteration in volume of the ion due to the presence of adjacent ions alters its properties." If so, is it justified to give in the table on p. 36–37 apparent radii of Si^{4+} (0.39 Å) and of S^{6+} (0.34) derived from the experimental distances Si—O and S—O by subtraction of a *constant* value for O^{2-}? This procedure must appear still less appropriate if one realizes that the free O^{2-} is not stable and can exist in compounds only due to the stabilizing influence of adjacent positive ions. It is therefore understandable that the degree of tightening of O^{2-}, which can be measured by the very sensitive optical refraction, depends to a high degree on the surrounding electric fields. Thus it appears most natural to compare the S—O distance in SO_4^{2-} with the Si—O distance in the analogous SiO_4^{4-} and not with the S—S and O—O distances in S_8 and H_2O_2. Since S^{6+} must attract and tighten O^{2-} stronger than does Si^{4+}, one can understand that in SO_4^{2-} the distance, the molar refraction and dispersion are smaller than in SiO_4^{4-}. Thus the assumption of many resonating forms is not necessary for the explanation of the properties of SO_4^{2-}. It deserves to be stated in this connection that the additivity of "covalent radii" is not generally true even in cases which are usually considered as closely analogous: although diamond, silicon and SiC all have the same crystal structure, the Si—C distance (1.883) is smaller by 0.060 Å than the arithmetic mean of the C—C (1.541) and the Si—Si (2.346) distances.

The valence bond theory which originated in the chemistry of carbon compounds has been known for a long time to encounter serious difficulties in the cases of many inorganic compounds. It suffices to mention here B_2H_6 which has a composition analogous to C_2H_6 although boron is tri- but carbon tetra-valent. The attempt to make this theory more satisfactory by introduction of electron pairs and octets and the newest additional assumptions strongly emphasized in the present edition, like resonance, one-electron, three-electron and even no-electron bonds do not improve the situation. (See the following review). Thus it is difficult to avoid the conclusion that the very foundations of the theory of covalency have to be revised and that considerations based on it should be taken with reserve.

The experimental facts, however, are presented in the book in a reliable and interesting way and the newest edition of Ephraim can be warmly recommended in this respect. The carefully prepared index of 33 pages adds to the value of the volume as a reference book.

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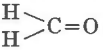
GRUNDLAGEN DER STEREOCHEMIE. By Paul Niggli. Lehrbücher und Monographien aus dem Gebiete der Exakten Wissenschaften. Chemische Reihe. Volume I. Verlag Birkhäuser, Basel. Pp. 283, Figs. 207. 1945. Price: 32.50 Swiss francs.

The well known mineralogist and crystallographer explains in the introduction the purpose of presenting in this volume the Principles of Stereochemistry. He distinguishes three periods in the development of this branch of chemistry.

1. Van't Hoff postulated that the four valences of a carbon atom are directed from the center to the corners of a tetrahedron. Thus he fixed the directions of the hypothetical valence forces and not the real position of the atomic centers. In many cases when the carbon has only three adjacent atoms, e.g., in  $\begin{matrix}H\\H\end{matrix}\!>\!C{=}O$ or two, e.g., in $O{=}C{=}O$, the valence tetrahedron does not show a direct relation to the atomic positions but can be correlated with them if appropriate assumptions are made. However, in the case of benzene, difficulties arise.

2. Alfred Werner introduced the purely geometric idea of the coordination number of an atom as the number of its nearest neighbors. In the case of the complex compounds, the coordination number is often higher than the normal valency. Werner's distinction between principal and secondary valences did not find justification in the experimental facts.

3. The results of the *x*-ray analysis of crystals have shown that even in such simple compounds as NaCl, one must strictly distinguish between valency and coordination number. This made it necessary, according to Niggli, to develop a stereochemistry which in the first instance investigates systematically all the geometrically possible forms and only then discusses the forces which are responsible for the stability of some selected configurations. This plan has been followed by the author and his associates in a series of papers and the present book gives a review of the results obtained.

The titles of the book's four main chapters and some subtitles will indicate the questions which the author intends to answer.

I. Symmetry relations within configurations of points:
   A. General concepts. Equivalent points. . . . Isomers and formulas expressing the symmetry. . . . Symmetry of vibrations within a given configuration.
   B. Molecular configurations.
   C. One-, two-, and three-dimensional configurations in crystals.
   D. Formulas for configuration of points in crystals.
II. Structural groups within configuration of points.
   A. Homogeneous groups (formed by one kind of points).
   B. Regular heterogeneous groups within A_mB_n.
   C. Structural groups within A_mB_n with variable coordination numbers of a given component.
   D. Structural groups of multiple heterogeneity.
III. Chemical combination of atoms.
   A. Formation of ions and electron pair bond.
   B. Hydrogen bond. One- and three-electron bond.
   C. Relations between the different kinds of binding. Resonance.
IV. Stereochemistry as the study of group formation of atoms.
   A. Molecular configurations in the broader sense. . . . Heteropolar covalent molecules with one positive center. . . . Isomerism. Polymerism. . . . Pseudocrystalline State. . . . Anions of pyro- and poly-acids.

B. Crystalline configurations. . . . Salt-, molecular- and metallic crystals. . . . Complexity of the kinds of binding in crystalline compounds. . . . The concept of type in stereochemistry.

In the purely geometrical Chapters I and II, the interrelations are discussed in a systematic and exact way. The 147 figures, most of them of remarkable clearness, help considerably in the understanding of the text. Several symbols are introduced which characterize the geometric relations.

One of the goals of such a thorough and critical analysis of the geometrical relations should be to assist the physicist and chemist in the choice between existing theories of interatomic forces and to prepare a foundation for the further development of this problem. Chapter III in which one could expect a discussion of this kind contains merely a report on some current views of electronic structure without any attempt to show their relation to the problems of stereochemistry.

The discussion starts on p. 169 with the very appropriate example of CO_2. As the first possibility, the formulation $O^{2-}C^{4+}O^{2-}$ is given and it is stated that the assumption of a complete transfer of electrons from C to O which this formula is commonly thought to indicate, is not adequate. Therefore several covalent resonance formulas (see preceding review) are discussed. A new method of presentation of groups of shared and unshared electrons by numbers instead of points is described. However, the question which is sterochemically of main interest, how the combination of all these resonating forms can lead to the linear structure of CO_2, is not mentioned and would be indeed difficult to answer. The same applies to the internuclear distance. The next example is SO_4^{2-} for which, as in Ephraim, seven covalent forms are reproduced but without explanation of the observed tetrahedral form. Even for $SiCl_4$ twelve covalent forms fill p. 182 although this compound is known to give chloride ions with great ease when in contact with water. This alone would be sufficient to justify the formula $Si^{4+}(Cl^-)_4$. Naturally, due to the strong polarizing field of Si^{4+}, the Cl^- in this compound are tightened to a higher degree than in Na^+Cl^-, as has been unambiguously shown by the molar refraction data. It can furthermore be shown that the formulations $Si^{4+}(Cl^-)_4$ and $S^{6+}(O^=)_4$ explain the tetrahedral shape of these groups. The equilibrium positions of the anions Cl^- and O^{2-} around the central cation are the result of the attraction exerted by the latter and the repulsive forces between the anions themselves. Consequently the anions tend to occupy positions as far as possible from each other, and these are given by the corners of a regular tetrahedron. In a similar way the linear structure of CO_2 follows at once from the formula $O^{2-}C^{4+}O^{2-}$. Naturally the O^{2-}, although its electronic shell is assumed in this formulation to have the quantum configuration of the neon atom, is still more strongly deformed and tightened by the intense field of the small C^{4+} than it is in the silicates by the larger Si^{4+}. Thus from the electric point of view, the formula $O^{2-}C^{4+}O^{2-}$ does not mean a complete transfer of electrons from C to O. Due to the ionic polarization, such complete transfer does not take place even in the typically ionic molecules like NaCl.

The individuality of the two O^{2-} as a definite quantum state is strongly supported by the fact that CO_2 adds a third O^{2-} in an alkaline solution with greatest ease to become a symmetrical planar carbonate ion with OCO angles of 120°. The structure $C^{4+}(O^{2-})_3$ is in best accord with the properties of CO_3^{2-}. Its larger C—O distance as compared with CO_2 is due to the additional repulsion of the third O^{2-}.

Thus the "carbon atom" as such does not have four valences aiming at the corners of a tetrahedron and it is logical to assume that CF_4 has a tetrahedral structure due to the repulsion of the $4F^-$ surrounding C^{4+}. Finally in Be_2C, which has the fluorite structure, each C is surrounded by 8 Be and the idea of four carbon valences represented by four bonds fails completely. The only possible formulation is $(Be^{++})_2C^{4-}$. The main reason why Niggli did not arrive at all these conclusions which relate the geometry of molecules and crystals with their physics and chemistry is that he followed the trend of the last decade in strongly overemphasizing the covalent point of view. On pp. 218–19 the polarization of ions is mentioned but the author does not make use of the applications of this concept to crystal structure which is due especially to V. M. Goldschmidt. Niggli denotes (p. 224) crystallized NaCl as being held by "true" ionic binding, but ScN by covalent binding. However, the fact that ScN has NaCl structure with the coordination number six is much better understood when one ascribes to it the structure $Sc^{3+}N^{3-}$. The polarization of the ions in ScN is naturally much stronger than in NaCl but it is still stronger in $Al^{3+}N^{3-}$ which causes the ions to have the coordination number four, and is extremely strong in $B^{3+}N^{3-}$ with the coordination number three.

On the other hand Niggli recognizes clearly that one has to distinguish strictly between the experimental coordination scheme and the hypothetical valence scheme. Thus he recommends (p. 168) calling the angle of 180° in CO_2 the angle between coordination directions and not the "valence angle." It is of interest to note that for representing the valence scheme of CO_2 the author uses in Fig. 149 the classical spatial diagram with two double bonds and not the resonance structures discussed on pp. 170–172. On p. 203 Niggli writes: "it is not yet possible to see whether it is justified to ascribe to the resonance forms such great importance as is done by Pauling." The reader may be helped in answering this question by the present reviews as well as by the fact that the resonance forms given on p. 180 for B_2H_6 with one-electron bonds have been recently generally abandoned. The undersigned considers the formula

$$\begin{array}{ccccc} H^- & & H^- & & H^- \\ & B^{3+} & & B^{3+} & \\ H^- & & H^- & & H^- \end{array}$$

as the best representation of this molecule, which for many years was an enigma of the covalent theory.

Chapter IV is a combination of the points of view of geometric character with those pertaining to the nature of chemical binding. It contains many facts of interest for the crystallographer as well as for the chemist. The praise of the figures of Chapter I and II cannot be fully extended to those in Chapter IV. Many of them are photographs of models and some contain such a large number of spheres representing the atoms and wires indicating axes as well as bonds that they can hardly help in the understanding of the structures.

The text does not contain specific references to the literature, which however are given at the end of the book in three parts, each arranged alphabetically. Not all authors' names mentioned in the text are to be found in the references.

The main value of the book consists in the extension to molecules of the exact geometric relations developed during the last thirty years in the field of atomic structure of crystals.

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RÖNTGENOGRAPHISCH—ANALYTISCHE CHEMIE. MÖGLICHKEITEN UND ERGEBNISSE VON UNTERSUCHUNGEN MIT RÖNTGENINTERFERENZEN IN DER CHEMIE. By E. BRANDENBERGER. Lehrbücher und Monographien aus dem Gebiete der Exakten Wissenschaften. Chemische Reihe. Volume II. Verlag Birkhäuser, Basel. Pp. 287, Figs. 120; 1945. Price: 28.50 Swiss francs.

According to the author the book is a counterpart to that of P. Niggli reviewed above and is intended to deal with the methods and possibilities of chemical and especially stereochemical investigations by means of *x*-ray diffraction. The titles of the eight main chapters and a few subtitles indicate the general content of the book.

I. The nature of the crystals. Molecular and crystalline compounds.
II. Methods of *x*-ray investigation of crystalline substances.
III. Crystalline and amorphous phases.
IV. *X*-ray diffraction patterns as criterion of crystalline types—Methods of determination of crystalline types by *x*-rays.
V. Roentgenographic analysis of mixtures and exploring of the composition of complex systems.
VI. *X*-ray and electron diffraction patterns as criterion of the state of the crystal—in respect to particle size, mosaic structure, texture, condition of the surface, etc.
VII. *X*-ray diffraction as means of investigation of transformations and chemical reactions in solid state.
VIII. *X*-ray diffraction as criterion of the constitution of solids (determination of crystal structure by *x*-rays). General procedure of a crystal structure determination. . . . Crystal-chemical characterization of atoms and ions and their importance for crystal structure determinations. . . .

As can be seen, the author deals with many sided applications of *x*-ray diffraction in crystals to chemical problems. The *x*-ray spectra of the elements as a means of qualitative or quantitative chemical analysis are not treated, as the title of the book "Roentgenographic—analytical chemistry" might lead one to expect. The subtitle given above "Possibilities and Results of Investigations by X-ray Diffraction in Chemistry" comes closer to the content of the book. The selection of the topics is very appropriate and their presentation instructive and interesting. Paper, print and figures are excellent. The references to the literature are given in an original way. At the end of each of the Chapters II to VI follows a list of references including the full title of the papers involved. Chapter VII contains such a list after each of the four subdivisions. For instance, on pp. 176–197 are treated "tarnishing and analogous processes." In the text, no author's name is given in this section; however, pp. 198–199 contain 29 references. Their order is neither alphabetical nor chronological but after each title a short explanation is given concerning the method of investigation the paper is suppose to illustrate. The paper of W. H. Taylor, "The structure of analcite" is characterized as "Example of investigation by *x*-ray diffraction of a dehydration process and of a base exchange." Thus the book can serve as a guide for the selection of appropriate methods of investigation. In view of the increasing importance of the applications of *x*-ray methods it should prove to be very useful.

It deserves mentioning that the implications of Table VI, in which ionic radii are given with two decimal places, do not conform to the present knowledge and to the critical remarks in the book of Niggli (pp. 225–226) about the lack of exact additivity of internuclear distances. For instance, 1.12 Å is given as the radius of Hg^{2+} for the coordination number six. This value was derived in 1926 on the assumption of additivity from an approximate evaluation of the Hg^{2+}—F^- distance in HgF_2. However, the coordination number of Hg^{2+} in HgF_2 is not six but eight. In the molecular structure of $HgCl_2$, Hg^{2+} has six neighbors, but the octahedron formed by the six Cl^- is far from regular, the Hg^{2+}—Cl^- distances being 2.23, 2.27, two at 3.34 and two at 3.63, which by subtraction of 1.81 for Cl^- would give for Hg^{2+} values between 0.42 and 1.82 Å. Obviously, due to the high polarizability of Cl^- and Hg^{2+} and the high polarizing power of Hg^{2+} the ions interpenetrate each other strongly and are far from spherical. A similar situation is found in $HgBr_2$ and in cinnabar. A definite "radius" of Hg^{2+} for the coordination number six does not apply to any compound of known structure. It would have been more instructive and more exact to give the present experimental value 2.40 Å of the internuclear distance in HgF_2 and the above facts about $HgCl_2$ than a hypothetical radius of Hg^{2+}.

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THE ART OF GEM CUTTING by H. C. DAKE AND R. M. PEARL. Pp. 128, figs. 55, 6″×9″, paper. Mineralogist Publishing Company, Portland, Oregon. 1945, Price $1.50.

The Art of Gem Cutting is designed primarily for the "amateur" gem stone cutter and is an extension of an earlier edition first issued in 1938. Following a brief description of gem cutting as a hobby, the methods for cabochon and facet cutting are given in detail in parts I and II. The fundamentals of the scientific aspects of gemology are discussed in part III. Part IV is entitled Special Lapidary Technic and includes short articles by H. L. Luoma, E. P. Van Leuen, Ralph Dietz, and E. F. Montgomery. This inexpensive publication contains much useful information and should appeal greatly to the amateur gem cutter.

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