CONTRIBUTIONS OF X-RAY STUDIES OF CRYSTAL STRUCTURE TO ORGANIC CHEMISTRY[1]

WHEELER P. DAVEY

School of Chemistry and Physics, The Pennsylvania State College, State College, Pennsylvania

THE CARBON ATOM

Ever since the first structural formula was written, it has been the creed of organic chemists that the properties of the materials with which they work must be attributed to the shapes and sizes of their component atoms and to the arrangement of those atoms in space. Structural formulas represent hypothetical configurations of atoms which are consistent with the results of chemical and physical experiments. Because these structural formulas show an atomic configuration in only two dimensions, they have been universally recognized as being only workable fictions which, however well they may represent the chemical properties of substances, have no necessary relation to the true positions of the atoms in the molecules. In a few cases, attempts have been made to include the third dimension. Outstanding examples of this are found in the three-dimensional formulas assigned to methane and ethane on the basis of a tetrahedral carbon atom, and in the stereo-formulas of the three kinds of tartaric acid. Even such formulas have been recognized as being only figures of speech which do not necessarily correspond to the actual configuration of the atoms in space. The x-ray study of crystal structure is gradually laying the foundation for a new set of three-dimensional structural formulas. These are of such a sort, and are backed by such strong experimental evidence that we feel justified in accepting them as representing a close approximation to reality.

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[1] Delivered before the Division of Organic Chemistry of the American Chemical Society at the Seventy-third Meeting, Richmond, Virginia, April 14, 1927.

The arrangement of carbon atoms in diamond (1) (2) (3) is well known. This arrangement is easiest accounted for on the basis of a tetrahedrally shaped carbon atom (4) (5). The arrangement of atoms in graphite (2) (6) (7) (8) (9) (10) is such that the "domains" (5) or "packing shapes" of the carbon atoms are to be regarded as being very nearly tetrahedral. This is in complete agreement with all the chemical evidence, and we may consider the organic chemist's picture of a tetrahedral carbon atom to be on a sure foundation. There is no clue, however, as to whether the four valence electrons of the carbon atom are "attached" at the vertices of the tetrahedral atomic domain, or at the centers of the faces, (fig. 1). The reason for this lies in the fact that the angles subtended at the center by the vertices of the tetrahedron are the same as the angles subtended by the face-centers, 109° 28′. It is only a matter of words, therefore, whether we say that the four valence electrons have mean positions at the centers of the faces of a given tetrahedron, or whether we say that their mean positions lie at the vertices of a second tetrahedron inscribed in the first so that the four vertices of the second tetrahedron coincide with the centers of the four faces of the first. The essential thing is that carbon atoms pack in crystals practically as though they were tetrahedra, i.e., they have four points 109° 28′ apart which can not be distinguished from each other. The distance of closest approach of carbon atoms in diamond is 1.54×10^{-8} cm. In graphite it is 1.50×10^{-8} cm. In order to make certain of the illustrations in this

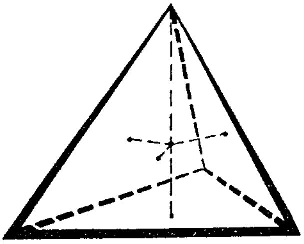

FIG. 1. TETRAHEDRAL SHAPE OF THE CARBON ATOM

article (figs. 4, 7, 8, 9 and 10) appear more stereoscopic, the carbon atoms will be represented by circles the radii of which correspond to 0.75 × 10^{-8} cm. The interpretation of these circles in terms of tetrahedra will in all cases be sufficiently obvious.

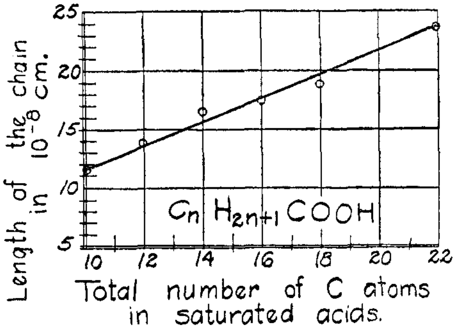

FIG. 2. LENGTHS OF MOLECULES OF SATURATED FATTY ACIDS (MÜLLER)

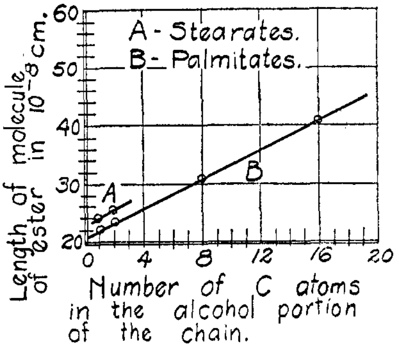

FIG. 3. LENGTHS OF MOLECULES OF ESTERS OF PALMITIC AND STEARIC ACIDS (SHEARER)

THE PARAFFIN SERIES

The ordinary structural formulas for the paraffins, and for the acids and esters derived from them, show the carbon atoms as lying along a straight line. Such a picture is not consistent with the x-ray data. For each of the saturated fatty acids and their esters, the x-ray diffraction patterns show three dimensions. Two of these are, within experimental error, identical for all the compounds so far tested (11) (12) (13) (14) (15) (16).

The average numerical values are 4.1 and 3.7×10^{-8} cm. The third dimension varies rather systematically with the number of carbon atoms in the molecule. The interpretation of all this is taken to be that all the saturated acids, and their esters, in the paraffin series have essentially the same cross section, but that the length of the "chain" depends upon the number of carbon atoms in it. The cross section is greater than would be expected on the basis of a straight chain of carbon atoms each 1.5×10^{-8} cm. in "diameter." It is hard to imagine that the hydrogen atoms (the smallest in the whole list of elements) could account for the discrepancy in cross section. It seems necessary to assume that the carbon chain is in zig-zags. This assumption is strengthened by the fact that the chains are considerably shorter than the distances calculated by multiplying the "diameter" of carbon by the number of carbons in the chain. The lengths found experimentally by Müller (11) for the chains of various acids are given in figure 2.[2]

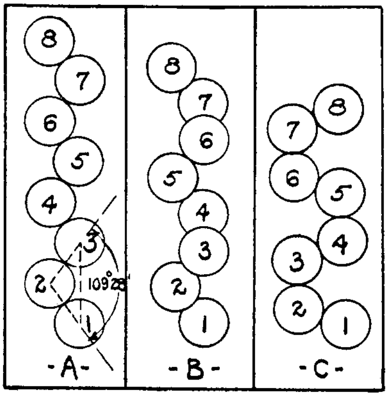

FIG. 4. THEORETICALLY POSSIBLE CARBON CHAINS (MÜLLER AND SHEARER)
A corresponds to the saturated alcohols. C corresponds to the free saturated acids.

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[2] Langmuir (17) measured the lengths of the molecules of palmitic and stearic acids in terms of their spreading on water. His values are 11 per cent higher than those of Müller by x-ray methods. Adam's values (18) for myristic and behenic acids are 13 per cent higher. This is perhaps as close agreement as might be expected because of the experimental conditions inherent in the water spreading method.

Similar data by Shearer (12) for the lengths of the molecules of various esters of palmitic and stearic acids are given in figure 3. The data show that the increase in the length of the alcohol averages $1.22^5 \times 10^{-8}$ cm. for each CH_2 group. This is to be contrasted with an average increase of 1.02×10^{-8} cm. per CH_2 group for the free fatty acids of figure 2.

Müller and Shearer (13) have investigated the effect of possible configurations of carbon atoms on the length of the chain. Their three simplest cases are shown in figure 4. In A all the carbon atoms lie in one plane. The arrangement is identical with that chain of atoms in diamond in the 1 1 0 plane which runs parallel to the 1 0 0 plane. Since the atoms are tetrahedral in shape, the angle 1 2 3 is taken as 109° 28′. The distance 1 2 or 2 3 is equal to the "diameter" of carbon, i.e., 1.50×10^{-8} cm. The vertical length along the chain which is contributed by each carbon atom is half the distance 1 3. It is

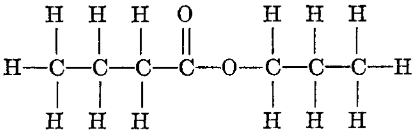
$$1.50 \times 10^{-8} \sin \frac{109^\circ\ 28'}{2}$$

or 1.22×10^{-8} cm. This agrees with the experimental value for the average increase per carbon atom for the alcohols, as measured in the esters of saturated acids. It is therefore assumed that the carbons in the chains of saturated alcohols have the configuration of figure 4A. It should be noted that the model requires all the carbons to produce the same increment in length. This agrees with Figure 3 which gives, on a single straight line, data for both odd and even numbered alcohols.

B of figure 4 represents a spiral of tetrahedral carbon atoms. It is evident that it does not represent the experimental facts for the increment in length per atom is 1.12×10^{-8} cm. which is about half way between the correct values for the alcohols and for the saturated fatty acids. Although this configuration is theoretically possible for carbon atoms, it does not appear in either diamond or graphite.

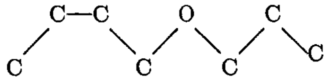
C of figure 4 shows a third possible configuration which actually occurs in diamond. Atoms 1, 2 and 3 are related to each other as in figure 4A. Atoms 4, 5, and 6 are also like the corresponding atoms in figure 4A but atom 4 is joined on to a different tetrahedral face of 3 in C than in A. Each pair of atoms contributes 2.0×10^{-8} cm. to the length of the chain. The average increment in length per atom, 1.0×10^{-8} cm. is within experimental error identical with the average increment per atom for the saturated fatty acids of figure 2. Of each pair of atoms in figure 4 C, one contributes 1.5×10^{-8} cm. and the other contributes 0.5×10^{-8} cm. This again agrees with the experimental facts, for if the lengths of the odd numbered acids were plotted in figure 2 their graph would have been parallel to the length of the even numbered acids, but a little above it. "The difference between the acids containing an odd and an even number of carbon atoms is interesting. It is well known that similar differences are found in their melting points. Also the even-numbered acids are common in nature, whilst the odds are very rare. It would therefore appear that there is a stronger tendency to add two carbon atoms to the acid chain than only one (13)."

The x-ray investigation of the paraffin series, in so far as structural formulas are concerned, may be illustrated in terms of an ester like propyl butyrate. The ordinary structural formula is



$$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-O-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$$

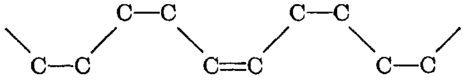
If the interpretation of Müller and Shearer is correct, the carbons should be written



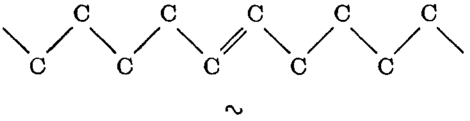
The end carbons have three H atoms attached at angles 109° 28′ from the line joining the end carbon to its next neighboring carbon. In the same way the hydrogen atoms of the CH_2 groups would be one above and one below the plane of the paper at angles determined by the tretrahedral carbon atom. The additional oxygen atom of the carboxyl group would likewise not lie in the plane of the paper.

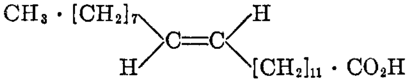
There is one other important result of the x-ray investigation of the fatty acids that deserves mention. The x-ray data show that both the saturated and the unsaturated acids have their molecules in pairs as though the two CO-OH groups were in contact. In other words the natural state of these acids, when free from water, is one of association, with *n* equal to 2. In this connection it is interesting to remember that the molecular weight of acetic acid, measured in terms of the depression of the freezing point of benzene is *twice* the formula wieght. There is no x-ray evidence for any association of the esters.

Portion of the Carbon Chain of Erucic Acid.



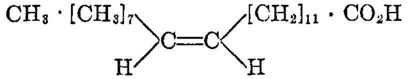
Portion of the Carbon Chain of Brassidic Acid.





$$\begin{matrix} CH_3\cdot[CH_2]_7 & & H \\ & C=C & \\ H & & [CH_2]_{11}\cdot CO_2H \end{matrix}$$

Ordinarily called Erucic Acid,
Actually Brassidic Acid.



$$\begin{matrix} CH_3\cdot[CH_3]_7 & & [CH_2]_{11}\cdot CO_2H \\ & C=C & \\ H & & H \end{matrix}$$

Ordinarily called Brassidic Acid,
Actually Erucic Acid.

Fig. 5

Very little is known, from the x-ray standpoint, of the unsaturated fatty acids. Müller and Shearer have investigated the

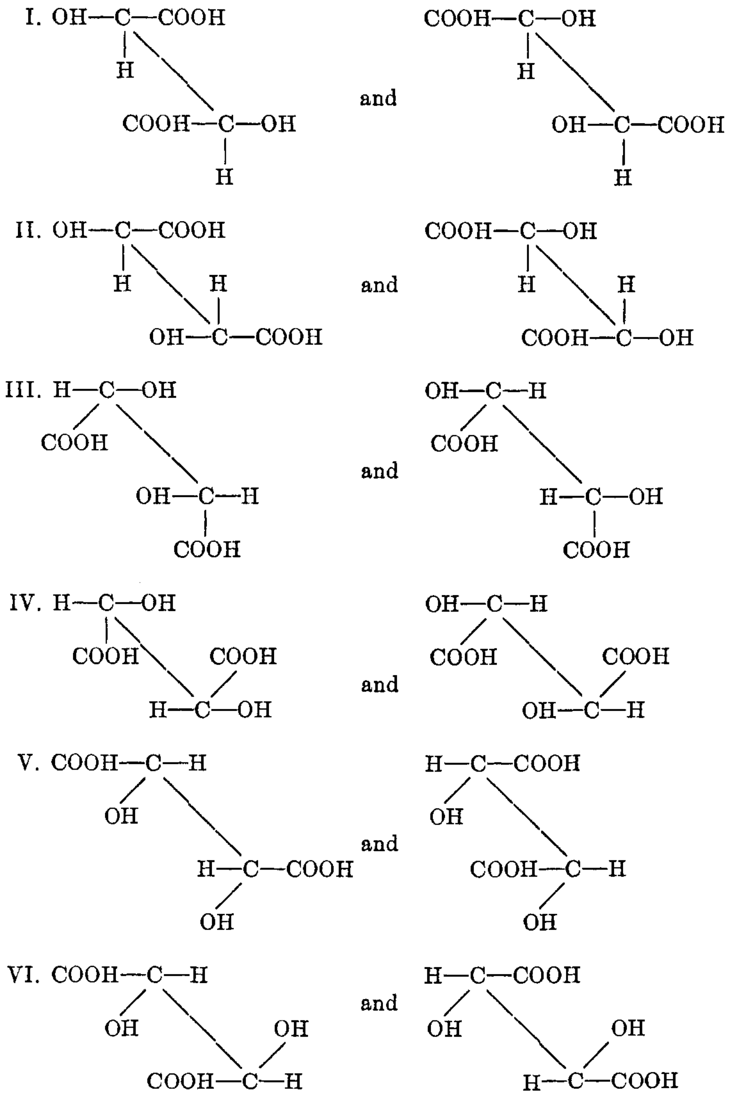


FIG. 6. POSSIBLE MOLECULAR STRUCTURES OF DEXTRO- AND LAEVO-ROTARY TARTARIC ACID PERMITTED BY THEIR CHEMICAL PROPERTIES (ASTBURY)

two isomers, erucic acid and brassidic acid. Each of these contains 22 carbon atoms. There is one double bond, similarly placed, in each acid. The x-ray results are consistent with the structural formulas of figure 5. Since the material ordinarily known to organic chemists as brassidic acid has a chain 12 × 10^{-8} cm. longer than the chain of the substance which they call eruric acid, it is evident that the structure corresponding to figure 4A is the brassidic acid. As is brought out in figure 5, this requires that the ordinary structural formulas for these two acids be interchanged.

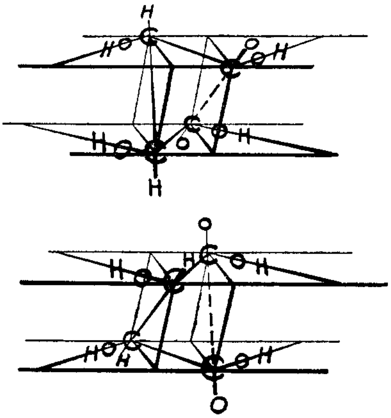


FIG. 7. MOLECULAR STRUCTURE OF DEXTRO- AND LAEVO-TARTARIC ACID (ASTBURY)

According to the latest data (19) available on the saturated hydrocarbons, their chains are like those of the alcohols except that they are stretched in the ratio $\frac{1.3}{1.2}$. The reason for this stretching is not yet clear.

Since almost every elementary text-book in organic chemistry gives so-called stereo-formulas for dextro- and laevo-tartaric acid it will be interesting to see what the real stereo-formulas are. The possible relationships between the atoms permitted by the chemical properties of tartaric acid are shown in figure 6. Astbury's analysis of the crystal structure (20) is shown in figure 7.

The second arrangement in figure 6 is the two-dimensional counterpart of figure 7. It is assumed that the spiral arrangement of carbon atoms is a characteristic of the tartaric acid molecule, but that the spiral arrangement of OH groups is imposed by the crystal. In solution, then, the OH radicals would be free to set themselves at other angles to the carbon atoms, and these new angles need not be rigorously constant, at least in very dilute solutions. All this is consistent with the data to date on the optical activity of tartaric acid.

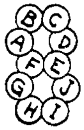


FIG. 8. RING STRUCTURES OF DIAMOND AND GRAPHITE (BRAGG)

THE BENZENE SERIES

The structure of the benzene ring has been a subject for controversy among organic chemists for some time. From the standpoint of x-ray studies, much of this controversy is practically without meaning. W. H. Bragg has pointed out (21) that both diamond and graphite are made up of rings each of which contains six carbon atoms. One such ring alone might be assumed to have the structure of a benzene ring. Two with a common side might represent the carbons in naphthalene, etc. In diamond and graphite, these rings can be studied without the possibility of complications from the atoms of other elements. In figure 8, atoms A B C D E F alone would represent a benzene ring, while A B C D E F G H I J would represent a naphthalene ring. It is seen that the rings resemble hexagons except that they are puckered so that three of the atoms lie on one level and the other three on a parallel but higher level. The difference between this and the ordinary hexagon may be illustrated as follows. Let two equilateral triangles be laid on top of each other in such a way that one is 180° from coincidence with the other. The six corners form a perfect hexagon. Now let one of the triangles be raised up off the other, but let the planes remain parallel. The six corners now form a puckered hexagon. In naphthalene, the hydrogen atoms attached to A, G, J and D of the ring of figure 8 are called the alpha hydrogens. Those attached to B, C, H and I are called the beta hydrogens.

In terms of Morse's theoretical work (22) and the fragmentary work of Broome (23), Bragg has also proposed a slightly different model of the benzene ring. This need not be discussed here, however, as the new model seems not to have been used in the investigation of crystal structures, and anyway it would make little difference in the end result. The model discussed in this paper is consistent with the work of Dickinson and Bilicke on beta-benzene-hexaldehydes (24). The height[3] of the puckered hexagon, i.e., the distance from the center of C to the center of E in figure 8, is 2.45 × 10^{-8} cm. The width is 2.87. In the case of benzene we lack sure experimental data on which to base

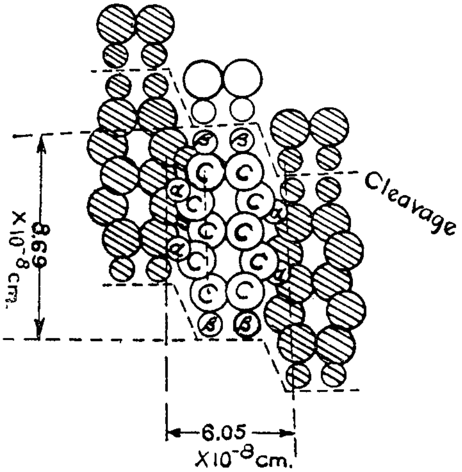


FIG. 9. THREE NAPHTHALENE MOLECULES AND PARTS OF OTHERS (BRAGG)

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[3] As the structural formula is usually written, this would be the width. The new terminology is employed to make the discussion fit better with the model of the crystal.

any calculations. For naphthalene and anthracene, however, the experimental data are well known (20). Remembering that the "radius" of carbon is to be taken as 0.75×10^{-8} cm., the height of the naphthalene molecule, exclusive of the beta hydrogens is $2\ (2.45) + 2\ (0.75) = 6.40 \times 10^{-8}$ cm. The width, exclusive of the alpha hydrogens is $2.87 + 2\ (0.75) = 4.37 \times 10^{-8}$ cm. The experimental values for the height and width of the naphthalene molecules, including the hydrogen, are 8.69 and 6.05×10^{-8} cm. This leaves $\frac{2.29}{2} = 1.14 \times 10^{-8}$ cm. for the beta hydrogens at each end and $\frac{1.68}{2} = 0.84 \times 10^{-8}$ cm. for the alpha hydrogens on each side. Figure 9 shows that in the crystal of naphthalene the alpha hydrogens lie between the carbons of adjacent molecules. They are well crowded, probably by powerful electrostatic forces. The beta hydrogens lie next to the beta hydrogens of adjacent molecules. A repulsive force is to be expected which increases the distance. The measured over-all height includes, of course, half the vacant space at each end of the molecule. For anthracene, the beta hydrogens on each end have 1.16×10^{-8} cm. and the alpha hydrogens on each side have 0.83×10^{-8} cm. These are almost identical with the corresponding spaces allowed for the alpha and beta hydrogens in naphthalene, thus giving additional evidence of the corrections of the stereo-formulas described above.

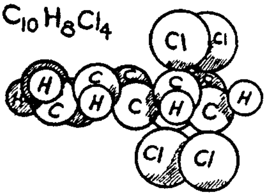

FIG. 10. A MOLECULE OF NAPHTHALENE TETRACHLORIDE (BRAGG)

The new stereo-formulas also receive considerable support from Bragg's investigation of naphthalene tetrachloride (25). The molecule is shown in perspective in figure 10. The increase in the thickness of the molecule in passing from naphthalene to naphthalene tetrachloride is almost exactly the diameter of two chlorine atoms.

CELLULOSE

X-ray investigations show (25) (26) (27) (28) that cellulose contains orthorhombic crystals each of which is built up of four units of $C_6H_{10}O_5$. This does not mean, however, that the formula for cellulose is $C_{24}H_{40}O_{20}$. For instance, there are three SiO_2 units in an elementary crystal of quartz, but the arrangement of atoms in the crystal makes it very evident that silicon dioxide is composed of elbow-shaped molecules whose formula is SiO_2. Similarly, in the case of cellulose, the value of n in the formula $(C_6H_{10}O_5)\ n$ must be found by a study of the arrangement of atoms in the crystal. Such a study by Sponsler and Dore (28) indicates that n is unity. It is perhaps only fair to say that their work is so far without convincing confirmation.[4]

Further studies (16) show that all cellulose compounds except the diacetate (rayon) are crystalline. It seems, too, that the swelling of cellulose in water consists chiefly in pushing the individual crystals further apart from each other.

There are many other ways in which the x-ray analysis of crystal structure has been of value to the organic chemist. Studies of the packing of organic molecules in crystals not only lead to information of the sort taken up in this paper, but also give a better understanding of many of the physical properties of organic substances. Studies of stretched and unstretched rubber, of gelatin, and of shellac (16) should prove of great importance to the practical chemist. To take up all of these aspects in detail would require a considerable fraction of a book. The writer has therefore limited himself to the narrow field of the stereo-structure of typical organic molecules, in the hope that the contributions of x-ray studies to such a fundamental field will seem important enough to warrant organic chemists in looking up the rest in the literature.

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[4] Note added in reading the proof: In this connection see Houser, Ind. Eng. Chem. **21**, 124 (1929).

REFERENCES

(1) W. H. AND W. L. BRAGG: Nature, **91**, 557, (1913).
W. H. AND W. L. BRAGG: Proc. Roy. Soc., London, **89**, 277, (1913).
(2) HULL: Phys. Rev., **10**, 661, (1917).
(3) W. H. BRAGG: Proc. Phys. Soc. Lond., **33**, 304, (1921).
(4) W. H. BRAGG: Nature, **114**, 862, (1924).
W. H. BRAGG: J. Franklin Inst., **198**, 615, (1924).
(5) DAVEY: Chem. Reviews, **2**, 349, (1926).
DAVEY: Gen. Elec. Rev., **29**, 274, (1926).
(6) DEBYE AND SCHERRER: Physik Z., **17**, 277, (1916); **16**, 291, (1917).
(7) ASAHARA: Sci. Papers, Inst. Phys. Chem. Research (Tokyo), **1**, 23, (1922).
(8) WEVER: Ergebnisse Physiol., **4**, 81, (1922).
(9) HASSEL AND MARK: Z. Physik., **25**, 317, (1924).
(10) BERNAL: Proc. Roy. Soc., London, **106**, 749, (1924).
(11) MÜLLER: J. Chem. Soc., **123**, 2043, (1923).
(12) SHEARER: Ibid., **123**, 3152, (1923).
(13) MÜLLER AND SHEARER: Ibid., **123**, 3156, (1923).
(14) TRILLAT: Compt. rend., **180**, 1329, 1485, 1838, (1925).
(15) TRILLAT: Ann. phys., **6**, 1, (1926).
(16) See also, WYCKOFF: The Structure of Crystals, 381. Chemical Catalog Co., (1924).
See also, CLARK: Applied X-Rays, N. Y. McGraw-Hill, (1927), 153, etc.
(17) LANGMUIR: Proc. Nat. Acad. Sci., **3**, 251, (1917).
(18) ADAM: Proc. Roy. Soc., London, **101**, 452, (1922).
(19) MÜLLER AND SAVILLE: J. Chem. Soc., **127**, 599, (1926).
(20) ASTBURY: Proc. Roy. Soc., London, **102**, 506, (1923).
(21) W. H. BRAGG: Proc. Phys. Soc., London, **34**, 33, (1921); J. Chem. Soc., **121**, 2766, (1922).
(22) MORSE: Phys. Rev., **22**, 525, (1923).
(23) BROOME: Physik. Z., **24**, 125, (1923).
(24) DICKINSON AND BILICKE: J. Amer. Chem. Soc., **5a**, 764, (1928).
(25) W. H. AND W. L. BRAGG: X-Rays and Crystal Structure, Harcourt, Brace and Co.
(26) HERZOG, JANCKE, POLANYI: Z. Physik, **3**, 196, 343, (1920).
(27) HERZOG: Cellulose-chemie, **2**, 101, (1921).
(28) SPONSLER AND DORE: Fourth National Colloid Symposium Monograph, 174, (1926).