CHARLOTTE ROBERTS AND HER TEXTBOOK ON STEREOCHEMISTRY

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In 1892 Charlotte Fitch Roberts, a young woman of 33 and an associate professor of chemistry at Wellesley College, was given leave from her teaching duties for graduate work at Yale University. She received her Ph.D. in 1894—the first in chemistry given to a woman by Yale. Her dissertation was a notable analytical and expository work in which she surveyed the relatively new field of "Chemistry in Space" or "Stereochemistry." Published in 1896 as a 189-page monograph, *The Development and Present Aspects of Stereochemistry,* it formed a substantial addition to the English language literature on a subject where most of the primary publications were in German or French, and it served as an advanced textbook for a number of years (1). However, within little more than two decades the field caught up with it and, indeed, passed it by. The development by G. N. Lewis, Irving Langmuir, J. J. Thomson, and others of the electronic theory of chemical bonding, and its rapid acceptance among chemists, made the theoretical speculations Roberts's book presented of little more than historical interest (2). As with other replaced theories, the practicing chemist saw little reason to pay them any attention. However, as a concise record of ideas current 100 years ago about the three-dimensional structure of organic compounds, and apparently the only such record written by an American chemist to that time, the book is still of historical interest (20).

Roberts's studies in stereochemistry probably began about nine years before she went to Yale. In 1885-86 she had spent a year at Cambridge University where she attended lectures by the Scottish chemist, Sir James Dewar. Though perhaps now remembered more for his later work on the liquefaction of gases, Dewar also carried out a considerable amount of research in organic chemistry and contributed his share to the development of ideas of molecular structure (3). For Roberts, although she made no original contributions to the area, stereochemistry was to remain a major interest throughout her life. During the 1890s, at the time she was writing her monograph, experimental observations were being turned out by European chemists at an ever-increasing rate, but after the grand generalizations of van't Hoff and Le Bel in the 1870s, theory had failed to keep pace; the field was without any coherence or unity. Despite the confusion, however, Roberts's last chapter, with its summary of current ideas, demonstrates that some of the working hypotheses then being put forward have interesting correspondences with more modern concepts.

Being a textbook in chemistry, the work makes rather dry reading for the non-chemist historian concerned with women's contributions to science. An introductory chapter summarizes the background and the state of the field by the mid-1890s. Topics discussed include the discovery of isomerism, starting with Pasteur's work on optical isomerism in the tartaric acids in the 1860s and that of Wislicenus on the lactic acids in the 1870s. Roberts relates how this led directly to ideas of different arrangements of atoms in space and to the concept of geometrical form in molecules. The story continues through the critical work of Le Bel and van't Hoff and the introduction of the idea of the tetrahedral distribution of the valencies of the carbon atom, with the representation of linked carbon atoms as tetrahedrons having the carbons at the centers and one solid angle in common (4). Van't Hoff's hypothesis of free rotation about single carbon-carbon bonds is covered, Victor Meyer's suggestion of limited rotation in certain special cases (such as the di-

Charlotte Fitch Roberts, 1890. Photo by Partridge (Courtesy of Wellesley College Archive)

carboxylic acids) is discussed, and the troublesome problem of multiple carbon-carbon bonds gone into at some length (5). From this follows a stereochemical explanation for the isomerism observed in compounds such as maleic and fumaric acids.

Chapter 2 amplifies these topics, presenting further illustrations and applications. Chapter 3 deals with the structure of aromatic compounds, detailing the arguments and conflicting evidence brought forward *pro* and *con* in support of the various representations of benzene, including those suggested by Kekulé, Claus, Dewar and Armstrong (7). Claus's diagonal formula had the advantage over Kekulé's of limiting the number of possible disubstitution products to three. On the other hand, it also predicted that the formation of addition products would require the breaking of single bonds. As to Dewar's suggestion, Roberts commented that it seemed to have no advantage over Kekulé's and had the disadvantage of containing two different kinds of carbon atom, which should give rise to two mono-substitution products; further, the formation of a hexa-addition product required the breaking of a single bond. Armstrong's "centric" formula was an attempt to explain "the unwillingness of benzene to form addition compounds," the "energy" being "directed toward the center of the molecule instead of holding together any two particular atoms" (8). To a modern chemist, it appears to be a groping towards an explanation for the properties which would later be seen as associated with the stable π-cloud of benzene. The stereochemical problems presented by

Charlotte Fitch Roberts c 1900(?) (Courtesy of Wellesley College Archive)

THE

DEVELOPMENT

AND

PRESENT ASPECTS

OF

STEREO-CHEMISTRY.

BY

CHARLOTTE F. ROBERTS, PH.D.

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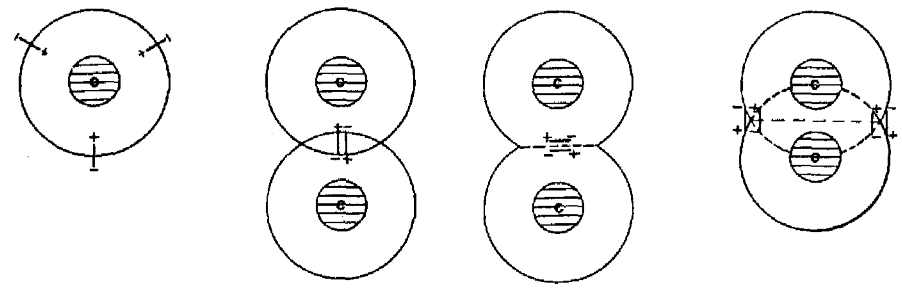
1896.

organic compounds containing nitrogen merited a chapter to themselves, the varying valence of nitrogen being one unresolved difficulty and isomerism in compounds containing a carbon-nitrogen double bond, especially the oximes, another.

A short chapter on the relation of stereochemistry to optical activity and to crystallography completed the literature survey, and led to Roberts's final and perhaps most interesting chapter, summarizing speculations about fundamental questions concerning atomic structure and the nature of valence. The major outstanding questions she posed as follows (9):

> Is [valence] an inherent property of the atom, or is it first called into existence by the approach of other atoms? Has it definite location in the atom, is it exerted in certain definite directions, is it to be considered as originally to be divided into parts in the atoms; or is it more of the nature of other attractive forces, an undivided whole, until the near approach of other atoms causes it to be divided among them? In what does the difference of valence in different elements consist? Does it correspond to the difference in different magnets, a difference in the amount of attractive force; or to a difference in the motions of the atoms, perhaps a different number of vibrations in a unit of time; or to a difference in the number of certain particular parts of the atom which we may call valence places? What do we mean by double and triple linking between two carbon atoms, and what conceptions of valence can explain the fact that doubly linked carbon atoms are not held to-



(a) (b_1) (b_2) (c)

Meyer and Riecke's representation of the carbon atom with surrounding ether envelope in the surface of which are embedded electrical dipoles: (a) isolated carbon atom (the fourth dipole is hidden behind the central carbon); (b_1) and (b_2) carbon atoms joined by a single bond; (c) carbon atoms joined by a double bond (14).

> gether with twice the strength of two singly linked atoms, and triply linked with three times that strength?

Stereochemistry had raised these questions but had failed to provide many answers. There seemed, however, to be little doubt that valence had direction, which further implied, given a geometric form for an atom, that there must be definite "valence places" on the atom. Hence valence and atomic form or shape would seem to be linked. Van't Hoff's conception of the carbon atom as the center of a tetrahedron with attractive forces concentrated in the four solid angles explained many situations, but ran into difficulties when doubly or triply linked carbon atoms had to be accommodated. Lossen, Wislicenus, von Baeyer and others all contributed their ideas to the problem of multiple linkage, but difficulties remained (10).

In 1888 Victor Meyer and Eduard Riecke had published an electrical explanation of valence, taking an approach which organic chemists had tended to avoid (11), although the idea that there was a close and definite relationship between atoms and electric charge went back to the electrochemical research of Michael Faraday in the 1830s and even earlier (12). Meyer and Riecke pictured the carbon atom as surrounded by a spherical "ether envelope," of diameter several times larger than the atom, the surface of the envelope being the "seat of valence," and each of the four valences being an electrical dipole freely rotatable in the ether envelope (13). Thus, in the figure, single bonds are represented in (b_1) and (b_2), and double bonds in (c), the electric dipoles lined up as in (b_1) representing the situation where there was free rotation about the carbon-carbon axis, while (b_2) depicted restricted rotation—as, for instance, in the dioxime of benzil. In (c) rotation about the carbon-carbon axis was forbidden. This picture of overlapping "envelopes" is remarkably suggestive of the later concept of orbital overlap.

Roberts ended on a cautious note (15):

> Granting, then, the existence of inherent valence-places, there is still diversity of opinion as to whether these are caused by a qualitative difference of matter at these points, or whether they are the results of a polar condition either in the atom itself or its ether envelope; and in regard to this point stereochemistry has nothing to say. Having thrown down the postulate of the existence of valence-places, stereo-chemistry withdraws, having apparently no facts to offer in explanation of the cause and nature of such places. These subjects seem at present to be left largely to the domain of pure speculation, though there is an undoubted and proved connection between electricity and valence which cannot be overlooked in any explanation of the latter.
>
> It is plain, then, that stereochemistry offers no distinct and definite representation of an atom. It only emphasizes certain attributes of the atom, and has already been very fruitful in stimulating speculations concerning atomic structure and valence. Whether any one of the theories now before the public, or one yet to be evolved, will ever receive experimental verification enough to be yielded universal acceptance, and thus give a definite conception of the atom or not, time alone can tell. . . .

Roberts had as a model for her work van't Hoff's *Stéréochimie,* the revised and expanded, but still remarkably concise, third edition of *La Chemie dans l'Espace*. Published in Paris in 1892, it presented in a style that was clear and lively a review of experimental data and current theories. To some extent she followed van't Hoff's general organizational scheme, while giving considerably more space to work carried out by other authors. An English translation of van't Hoff's monograph appeared in 1898, two years after Roberts's book, and was most favorably reviewed in the *Journal of the American Chemical Society* (16). Indeed, it was seen as becoming a standard textbook in stereochemistry. Strangely enough Roberts's book, which covered much the same ground, was not mentioned in the review. Another important work in the same area, the *Handbuch der Stereochemie*, edited by C. A. Bischoff, came out in two volumes in 1894 and 1895, the second volume—from Roberts's point of view the more important—appearing too late to be consulted by her before her monograph went to press. Being nothing short of an encyclopedic reference work of research relating to practically all aspects of stereochemistry, it hardly took the place of a textbook. However, it and the translation of van't Hoff's book may to some extent have overshadowed Robert's contribution. Both the European works had the advantage of being written by acknowledged experts in the field.

Charlotte Roberts taught at Wellesley College from 1880 until her death in 1917, progressing from an assistantship to full professor and head of the chemistry department by 1896, when she was still in her 30s. Beyond five papers on analytical methods written while a graduate student of Frank Gooch at Yale (1892-94), she published little experimental research, and the monograph is clearly her most significant contribution to the chemical literature (17, 18). She had three study leaves in Europe over the course of her career and spent some time in van't Hoff's laboratory in Berlin in 1899-1900, but would appear to have been concerned mainly with keeping abreast of current developments in chemistry rather than attempting any research of her own.

Indeed, with poor facilities and equipment in their laboratories and heavy teaching loads, few of the turn-of-the-century women chemists at small women's colleges like Wellesley carried out experimental work after completing their graduate degrees, even when granted study leaves. Roberts, perhaps as a result of the handicaps she faced, clearly turned her attention to studies of the development of ideas in chemistry rather than attempting laboratory work. By about 1905 she had become interested in the very beginnings of modern chemistry and its evolution from alchemy. She joined the English Alchemical Society, and during her last two study leaves (1905-06 and 1912-13) spent some of the time she had in Europe investigating the life and work of the later alchemists, particularly Paracelsus, the 16th century Swiss alchemist and physician sometimes called the father of experimental chemistry. This historical research was still in progress at the time of her death and unfortunately none of it appears to have been published.

Roberts grew up in Greenfield, Massachusetts, and first entered Wellesley as an undergraduate in 1876, the year the college opened. After receiving her B.A. in 1880 she stayed on as an assistant in the chemistry department and became instructor two years later. Following her year in England, she was promoted to associate professor and taught for six years before going to Yale to study for her Ph.D. In 1917, at the age of 58, she died suddenly at her home in Wellesley of a cerebral hemorrhage. Popular with her students and well-liked by her colleagues, she was remembered especially for her lively and fun-loving personality; among her special pleasures were her activities in the college theater group, in capacities ranging from author to manager and actor. Wellesley was her home for most of her adult life, and her career there almost coincided with the first 40 years of the college's existence. The Charlotte Fitch Roberts endowed professorship in chemistry commemorates her name (19).

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8. Reference 1, p. 70.
9. *Ibid*, p. 155.
10. See, for instance, W. Lossen, "Ueber die Lage der Atome im Raum," *Ber.*, **1887**, *20*, 3306-3310; J. Wislicenus, "Ueber die Lage der Atome im Raum. Antwort auf W. Lossen's Frage," *ibid*, **1888**, *21*, 581-585; Adolf von Baeyer, "Ueber Polyacetylenverbindungen," *ibid*, **1885**, *18*, 674-681, 2269-2281.
11. V. Meyer and E. Riecke, "Einige Bemerkungen über das Kohlenstoffatom und die Valenz," *ibid*, **1888**, *21*, 946-956, 1604, 1620.
12. Jöns Jacob Berzelius, in his *Essai sur la théorie des proportions chimiques et sur l'influence chimique de l'électricité*, Mequignon-Marvis, Paris, 1819, had proposed that chemical combination between atoms involved neutralization of opposite electrical charges (electrical dipoles). See C. A. Russell, *The History of Valency*, Leicester University Press, Leicester, 1971, especially pp. 261-269, and J. R. Partington, *A History of Chemistry*, Vol. 4, Macmillan, London, 1964, pp. 160, 169.
13. Reference 1, p. 183.
14. *Ibid.*, pp. 952-3, 955.
15. *Ibid.*, 1, p. 189.
16. J-H. van't Hoff, *The Arrangements of Atoms in Space*. Second revised and enlarged edition with a preface by Johannes Wislicenus, and an appendix, "Stereochemistry Among Inorganic Substances," by Alfred Werner. Translated and edited by Arnold Eiolart. Longmans, Green and Co., London and New York, 1898. Reviewed by Thomas H. Norton, *J. Am. Chem. Soc.*, **1898**, *20*, 386.
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18. Probably Roberts's only other publication was a joint paper with her student Louise Brown, "The Action of Metallic Magnesium on Aqueous Solutions," *J. Am. Chem. Soc.*, **1903**, *25*, 801-809, a painstaking piece of work carried out with the simplest of materials and equipment.
19. Biographical information about Roberts came from the following articles: E. L. Burrell, "Charlotte Fitch Roberts," *Wellesley Alumnae Quarterly*, **1918**, *2(2)*, 80-81; Anon., "Charlotte Fitch Roberts," *Wellesley College News*, 13 Dec., 1917. It is a pleasure to thank Wilma R. Slaight and Jean N. Berry, Wellesley College Archives, for providing copies of these.
20. Editor's Note: The American chemist, Robert Bowne Warder, had actually published a 25-page review of recent developments in stereochemistry in 1890 as his address to the chemical subsection of the American Association for the Advancement of Science the year he served as its chairman. See R. B. Warder, "Recent Theories of Geometrical Isomerism," *Proc. Am. Assoc. Adv. Sci.*, **1890**, *39*, 111-136. However, Robert's monograph appears to have been the first book-length review in English. Its most likely English language successor would have been the 1914 monograph, *Stereochemistry* (Longmans, London) written by the British chemist and erstwhile author of detective novels, Alfred W. Stewart.

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