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The Traité of the Third Chemical Revolution

A Tribute to "Valence and the Structure of Atoms and Molecules"

1. Introduction

In 1995 I published a paper arguing for a threerevolution model of the history of modern chemistry. Paralleling the three distinct levels of discourse used in present-day chemistry (1, 2):

1. The macroscopic or molar level (simple substances, compounds, solutions, and heterogeneous mixtures).

2. The atomic-molecular level (atoms, ions, and molecules).

3. The subatomic or electrical level (electrons and nuclei).

I argued that there had also been three distinct chemical revolutions, each marked by a 20-year period during which chemists had made significant progress in gaining access to each of these levels:

1. The first chemical revolution of 1770-1790, leading to a clarification of the concepts of simple substances and compounds and the roles of heat (caloric) and conservation of mass in both changes of state and chemical reactions.

2. The second chemical revolution of 1855-1875, leading to self-consistent atomic weights, compositional molecular formulas, the valence concept, the periodic law, and classical structure theory.

3. The third chemical revolution of 1904-1924, leading to the modern electronic theory of chemical bonding and reactivity.

The first of these revolutions was largely the product of the labors of Antoine Lavoisier and a few collaborators. The second was the product of more than a half dozen chemists, including Cannizarro, Williamson, Frankland, Odling, Wurtz, Couper, Kekulé, and van't Hoff, whereas the third was shared with the science of physics and was the joint product of the work of dozens of chemists and physicists.

Historians have long agreed that the fruits of the first revolution were first summarized in Lavoisier's classic 1789 text, *Traité élémentaire de chimie*. If asked to select a similar representative book for both the second and third revolutions, I would nominate Lothar Meyer's 1864 monograph, *Die modernen Theo*-



Figure 1. The title page to Valence and the Structure of Atoms and Molecules by G. N. Lewis.

rien der Chemie und ihre Bedeutung für chemische Statik, as characteristic of the second revolution; and G. N. Lewis' 1923 monograph, Valence and the Structure of Atoms and Molecules (figure 1), as characteristic of the third revolution – whence both the title of my talk this morning and of my choice of topic for a symposium devoted to "Great Chemistry Books of the 20th-Century" (3).

2. The Author

Before looking at *Valence and the Structure of Atoms and Molecules* in detail, I should tell you a little about the life of its author (4). Gilbert Newton Lewis (figure 2) was born in 1875 in Weymouth, Massachusetts, and raised in Lincoln, Nebraska. Initially home schooled, he began his higher education at the University of Nebraska but transfered to Harvard in 1892, where he

completed in rapid succession his AB (1896), AM (1898) and Ph.D (1899) degrees in chemistry – the latter for work done under the supervision of Theodore Richards on the electrochemistry and thermochemistry of zinc and cadmium amalgams.

Lewis served as an instructor at Harvard from 1898 to 1903, with the exception of a year (1900) spent in Germany working in the laboratories of Ostwald at Leipzig (figure 3) and Nernst at Göttingen. In 1904, apparently fed up with his slow rate of promotion at Harvard, he accepted a position as the Superintendent of Weights and Measures at Manila in the Philippine Islands, but within a year was back in the United as an instructor at MIT, where he rapidly advanced through the academic ranks, becoming Assistant Professor in 1907, Associate Professor in 1908, and full Professor in 1911. The next year he accepted a position as Professor and Permanent Dean of the College of Chemistry at the University of California-Berkeley, where he remained until his death in 1946 at age 70.

3. The Book

Valence and the Structure of Atoms and Molecules was published in 1923, the same year as Lewis' equally



Figure 2. Gilbert Newton Lewis (1875-1946) about the time he wrote his classic paper on the electron-pair bond.



Figure 3. A young Lewis (far left on landing) during an afternoon coffee and *pfannkuchen* break in Ostwald's laboratory at Leipzig, c. 1900.

famous thermodynamics text (of which I will say more during the afternoon session of the symposium) by the Chemical Catalog Company of New York as part of its new "American Chemical Society Monograph Series." It is a slim volume of only 172 pages with a dark blue cover, and is divided into 14 chapters. As admitted by Lewis in the preface, it is essentially a semi-popular progress report on the current status of the electronpair model of the covalent bond, which Lewis had introduced seven years earlier in his classic 1916 paper, "The Atom and the Molecule," and which had since been extensively elaborated by Irving Langmuir (figure 4) in a series of papers published between 1919 and 1921 (5):

I take it that a monograph of this sort belongs to the ephemeral literature of science. The studied care which is warranted in the treatment of the more slowly moving branches of science would be out of place here. Rather with the pen of a journalist we must attempt to record a momentary phase of current thought, which may at any instant change with kaleidoscopic abruptness.

It is therefore not unlikely that some of the things said in this book may soon have to be unsaid, but I trust that these may be matters of detail rather than of essence. During the seven years that have elapsed since my previous publication concerning the structure of the molecule and the nature of the chemical bond, I have found little need of subtracting from the views there set forth, although there is now much to add.

Indeed, Langmuir's more recent work had so eclipsed Lewis' original paper, that the concept of the

shared electron-pair bond was being widely attributed to Langmuir alone, and the desire to reclaim credit for his idea may well have motivated Lewis to take the time to write the monograph even while submerged in the details of his thermodynamics text. A measure of just how influential Langmuir's modifications of Lewis' original work had become may be found in the fact that much of our current vocabulary used in connection with the Lewis model, such as the terms "covalent bond" and "octet completion," is actually due to Langmuir rather than to Lewis (6).

Though the American Chemical Society heavily advertised the book (figure 5) in the *Journal of Industrial and Engineering Chemistry*, the only review I could locate appeared in the same journal in early 1924. Written by Saul Dushman of the Edison Lamp Works (figure 6), it provided a chapter by chapter synopsis which accurately summarized the major conclusions of the book, indicating that Dushman fully understood the details of Lewis' model, but ended with what appears to have been a bit of veiled sarcasm, no doubt reflecting the fact that Dushman had been a colleague of Langmuir at General Electric (7):

... the reader will be impressed with the fact that throughout the book Professor Lewis presents largely his own views or those of men associated with him. But perhaps this personal touch adds to the interest of the



Figure 4. Irving Langmuir (1881-1957).



Figure 5. A rather detailed full-paged ad for the Lewis book from *The Journal of Industrial and Engineering Chemistry* for 1923. Note the selling price of \$3.00.

monograph, especially in view of the contributions made by the author to the progress of physical chemistry.

4. Conceptual Innovations

This book is the source of so many of our current ideas on the electronic theory of bonding and reactivity – many of which are mentioned almost nonchalantly by Lewis in passing – that it would be impossible for me, in the time alloted, to review and analyze each of them in detail (8). In lieu of such an analysis, let me instead list a few of the most significant of these innovations using Lewis' own words:

1. The shared electron-pair bond:

... the chemical bond is at all times and in all molecules merely a pair of electrons held jointly by two atoms.

2. The continuity of bond type and polarization:



Figure 6. Saul Dushman (1883-1954).

Great as the difference is between the typical polar and nonpolar substances, we may show how a single molecule may, according to its environment, pass from the extreme polar to the extreme nonpolar form, not "per saltum," but by imperceptible gradations as soon as we admit that an electron may be the common property of two atomic shells.

3. The relationship between bond polarity and electronegativity:

The pair of electrons which constitutes the bond may lie between two atomic centers in such a position that there is no electrical polarization, or it may be shifted toward one or the other atom in order to give to that atom a negative, and consequently to the other atom a positive charge. But we may no longer speak of any atom as having an integral number of units of charge, expect in the case where one atom takes exclusive possession of the bonding pair and forms an ion ... Let us consider once for all that by an [electro] negative element or radical we mean one which tends to draw toward itself the electron pairs which constitute the outer shells of all neighboring atoms, and that an electropositive group is one that attracts to a less extent, or repels, these electrons.

4. The inductive effect:

Such a simple explanation accounts satisfactorily, in the main, for the observed strength of organic acids and bases. We have already discussed the case of chloroacetic acid ... The substitution of one methyl hydrogen by chlorine produces a greater pull upon the electrons of the methyl carbon, and thus causes a displacement which seems to occur throughout the molecule, finally pulling the electrons away from the hydrogen and permitting greater dissociation of the hydrogen ion. The substitution of a second and third chlorine heightens the effect... It need only be borne in mind that although the effect of such a displacement of electrons at one end of a chain proceeds throughout the whole chain, it becomes less marked the greater the distance, and the more rigid the constraints which hold the electrons in the intervening atoms.

5. The proton acid-base definitions:

The definition of an acid or base as a substance which gives up or takes up hydrogen ion would be more general than the one we used before [i.e. the Arrhenius definitions].

6. The Lewis acid-base definitions:

A basic substance is one which has a lone pair of electrons which may be used to complete the stable group of another atom, and ... an acid substance is one which can employ a lone pair from another molecule in completing the stable group of one of its own atoms.

7. The limitations of the octet rule:

The striking prevalence of molecules in which each atom has its full quota of four electron pairs in the outermost shell has led Langmuir to attempt to make the octet rule absolute, and he even proposes an arithmetical equation to determine, in accordance with this rule, whether a given formula represents a possible chemical substance. I believe that in his enthusiasm for this idea he has been led into error, and that in calling the new theory the "octet theory" he overemphasizes what is after all but one feature of the new theory of valence. The rule of eight, in spite of its great significance, is less fundamental than the rule of two, which calls attention to the tendency of electrons to form pairs.

8. The electronic interpretation of free radicals:

I called particular attention to the remarkable fact that when we count up the electrons which are comprised in the valence shell of various types of molecules, we find that of the some hundred thousand known substances, all but a handful contain an even number of such electrons. It is therefore an almost universal rule that the number of valence electrons in a molecule is a multiple of two ... odd molecules which form an exception to the rule of two may be said in the best sense of the old adage to prove that rule, for they form a class of substances with very singular properties. With the exception of nitric oxide, everyone absorbs light in the visible part of the spectrum, and most of them are intensely colored. In so far as they have been investigated, they prove to be highly paramagnetic. They are very reactive and attach themselves to a great variety of substances.

9. The coordinate bond and the structures of oxyanions:

It had always been supposed that the atom of oxygen in every one of its compounds is tied to another atom or atoms by two bonds. In applying the new idea of the bonding pair of electrons it became evident that many of the difficulties of the old-fashioned graphical formula, such as Werner pointed out, were at once dispelled if oxygen in many of its compounds, and especially in the oxygen acids, were assigned a single bond. In this way the artificial distinction which had previously been made between the oxygen acids and the halogen acids disappeared.

10. The importance of the hydrogen bond:

It seems to me that the most important addition to my theory of valence lies in the suggestion of what has become known as the hydrogen bond. The idea was first suggested by Dr. M. L. Huggins, and was also advanced by Latimer and Rodebush ... This suggestion is that an atom of hydrogen may at times be attached to two electron pairs of two different atoms, thus acting as a loose bond between these atoms.

Of these concepts, some, such as the Lewis acidbase definitions (9) and the hydrogen bond (10), have since become the subject of entire monographs. Others, such as Lewis' comments on the limitations of the octet rule and the use of single-bonded oxygen in the structures of oxyanions have continued to be the subject of controversy. Thus the 1950s and 1960s saw a reversion to the 19th-century double-bonded oxygen formulas for the oxyanions and acids based largely on bond-length arguments, thus requiring that these species be treated as examples of octet expansion, along with the more classic examples, such as PF5 and SF6, originally cited by Lewis to illustrate the limitations of the octet rule. However, quantum mechanical calculations by Weinhold et al have since shown that Lewis' original formulation of the oxyanions using singlebonded oxygen ligands and no octet expansion is actually the more accurate of the two competing models (11).

Likewise, repeated quantum mechanical calculations over the last 50 years have been virtually unanimous in discounting the importance of d-orbitals and octet expansion for compounds of the main-block elements, opting instead for the use of either no-bond single bond resonance or the use of various 3c-4e bonding schemes (12). In other words, in direct contradiction to Lewis' original conclusion, the octet rule or the rule of eight has proved to be a more rigorous bonding principle than the rule of two when narrowly interpreted in terms of localized 2c-2e bonds. As usual, most Freshman chemistry textbooks continue to propagate the wrong answer to both of these issues.

5. Prose Style

As may be seen from the above quotes, in keeping with Lewis's passing reference to "the pen of a journalist," the entire monograph is written in an informal first person singular style, and aspects of this style are also apparent in many of Lewis' other books and published papers. This may in part be a reflection of how these contributions were produced, since, according to the testimony of his former colleagues, Lewis, after moving to Berkeley, would dictate his carefully crafted sentences to his personal assistant, while vigorously pacing back and forth in the departmental conference room and puffing on a series of large, evil smelling, Manila cigars.

Indeed, *Valence* is such a treasure trove of the "Lewis style" in technical writing that I cannot resist quoting a few additional examples:

1. From the opening paragraph of Chapter 1:

The concept of a granular structure of matter had been a favorite among philosophers for centuries, and at the beginning of the nineteenth century it was prevalent among scientists and laymen. "Pound St. Paul's church into atoms, and consider any atom," Boswell quoted Johnson as saying a decade earlier.

I can still recall how delighted I was as an undergraduate chemistry major on first reading this opening. The idea that the author of an advanced chemistry monograph could actually be literate and begin his book with a reference to Boswell's *Life of Samuel Johnson* was something of a revelation to me and one which was quite at odds with my previous experiences with the chemical literature.

2. On the contributions of Irving Langmuir to "The

New Theory of Valence" discussed in Chapter 6:

It has been a cause of much satisfaction to me to find that in the course of this series of applications of the new theory, conducted with the greatest acumen, Dr. Langmuir has not been obliged to change the theory which I advanced ... The theory has been designated in some quarters as the Lewis-Langmuir theory, which would imply some sort of collaboration. As a matter of fact Dr. Langmuir's work has been entirely independent, and such additions as he has made to what was stated or implied in my paper should be credited to him alone.

In other words, with respect to Langmuir, what was of value was not original and what was original was not of value.

3. From Chapter 5 on the impact of Werner's coordination theory:

"Neuere Anschauungen auf dem Gebiete der anorganischen Chemie" (1905) marked a new epoch in chemistry; and in attempting to clarify the fundamental ideas of valence, there is no work to which I feel so much personal indebtedness as to this of Werner's. While some of his theoretical conclusions have not proved convincing, he marshaled in a masterly manner a great array of facts which showed the incongruities into which chemists had been led by the existing structural formulae of inorganic chemistry.

4. From the concluding section of the book on "The Future of Quantum Theory:"

In that old American Institution, the circus, the end of the performance finds the majority of spectators satiated with thrills and ready to return to more quiet pursuits. But there are always some who not only remain in their seats but make further payment to witness the even more blood-curdling feats of the supplementary performance.

Our own show is now over, and I trust that the majority of readers who have had the patience to reach this point will now leave the tent, for what I am about to say is no longer chemistry, nor is it physics, nor perhaps is it sense.

6. The Legacy

Lewis' comment about the ephemeral nature of his monograph ultimately proved correct, since no updated second edition was ever called for, though a German translation by Gustav Wagner and Hans Wolff of the



Figure 7. The title page of the 1927 German translation of Lewis' monograph.

University of Würzburg did appear in 1927 (figure 5) in which the translators took a qualified exception to Lewis' original characterization (13):

The supposition expressed by Lewis in his preface that, because of rapid developments in physical and chemical research, his book would soon be superseded has proved to be unfounded – at least with respect to the major portion dealing with chemistry. Although the physical introduction, as a result of the rapid development of atomic physics, naturally no longer represents the current state of the science, it still suffices for a complete understanding of the chemical aspects.

Nevertheless the translators supplemented Lewis' original bibliography by adding numerous updated references to their translation in the form of page footnotes.

Somewhat ironically, 1927 also saw the publication of the book that would ultimately supersede even the chemical aspects of Lewis' monograph – *The Electronic Theory of Valency* by the British chemist, Nevil Sidgwick, who had made some significant advances in applying the Lewis model to the chemistry of transition metal complexes and who would also coin the term "coordinate bond." And, as is the way of all science, Sigwick's book would eventually be displaced, in turn, by the publication in 1939 of the first edition of Linus Pauling's monograph – *The Nature of the Chemical Bond*.

However, it was precisely its ephemeral nature as a report of "research in progress," coupled with its popular journalistic depiction of a key moment in the development of the chemical bond, that eventually converted *Valence* into a valuable and highly readable historical document, and which, in my opinion, entitles it to the status of the "Traité of the Third Chemical Revolution." In recognition of its new status as a classic of chemistry, *Valence* was reprinted by Dover Books in 1966 with a new introduction by Kenneth Pitzer.

Many of the ideas propounded in this delightful monograph form the foundations of the electronic theory of bonding as it is still taught in both Freshman chemistry and introductory organic chemistry, and, as such, it can still be read with great profit, not only by historians of chemistry, but by teachers of undergraduate chemistry as well.

8. References and Notes

1. An invited lecture given at a symposium organized by the Bolton Society on classic 20th-century chemistry textbooks held at the 230th National Meeting of the ACS in Washington, DC, on 29 August 2005.

2. W. B. Jensen, "Logic, History and the Chemistry Textbook: III. One Chemical Revolution or Three?," *J. Chem. Educ.*, **1998**, 75, 961-969.

3. G. N. Lewis, *Valence and the Structure of Atoms and Molecules*, The Chemical Catalog Co: New York, NY, 1923.

4. For biographical background, see A, Lackman, Borderland of the Unknown: The Biography of Gilbert Newton Lewis, One of the World's Great Scientists, Pagent Press: New York, NY, 1955 and E. S. Lewis, A Biography of a Distinguished Scientist: Gilbert Newton Lewis, Mellen Press: Lewiston, NY, 1998.

5. For specific quotes, see reference 3, pp. 9, 68, 78, 83, 86, 97, 109, 139, 141-142, 162-163.

6. For the role of Langmuir in the development of the shared electron-pair bond, see R. Kohler, "Irving Langmuir and the 'Octet' Theory of Valence," *Hist. Stud. Phys. Sci.*, **1974**, *4*, 39-87; and R. Kohler, "The Lewis-Langmuir Theory

of Valence and the Chemical Community," *Hist. Stud. Phys. Sci.*, **1975**, *6*, 431-438.

7. S. Dushman, "Review of 'Valence and the Structure of Atoms and Molecules'," J. Ind. Eng. Chem., **1924**, 16, 104.

8. For historical background to many of these concepts, see R. Kohler, "The Origin of G. N. Lewis's Theory of the Shared Pair Bond," *Hist. Stud. Phys. Sci.*, **1971**, *3*, 343-376.; R. Kohler, "G. N. Lewis's Views on Bond Theory," *Brit. J. Hist. Sci.*, **1975**, *8*, 233-239; A. Stranges, *Valence and Electrons, The Development of the Theory, 1900-1925*, Texas A&M University Press: College Station, TX, 1982; and W. B. Jensen, "Abegg, Lewis, Langmuir and the Octet Rule," *J. Chem. Educ.*, **1984**, *61*, 191-200.

9. See, for example, W. Luder, S. Zuffanti, *The Electronic Theory of Acids and Bases*, Wiley: New York, 1946, W. B. Jensen, *The Lewis Acid-Base Definitions: An Overview*, Wiley: New York, NY, 1980.

 See, for example, G. C. Pimentel, A. L. McClellan, *The Hydrogen Bond*, Freeman: San Francisco, CA, 1960; G.
A. Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford University Press: New York, 1997.

11. L. Suidan, J. K. Badenhoop, E. D. Glendening, F. Weinhold, "Common Textbook and Teaching Misrepresentations of Lewis Structures," *J. Chem. Educ.*, **1995**, *72*, 583-586.

12. W. Kutzelnig, "Chemical Bonding in Higher Main Group Elements," *Angew. Chem. Int. Ed.*, **1984**, *23*, 272-295.

13. G. N. Lewis, *Die Valenz und der Bau der Atome und Moleküle*, Vieweg: Braunschweig, 1927, p. vi.

Update

For updates on the history of the debate over octet expansion and its current quantum mechanical status, see:

1. F. Weinhold, C. Landis, *Valency and Bonding*, Cambridge University Press: Cambridge, 2005, Chapter 3.

2. W. B. Jensen, "The Origins of the Term 'Hypervalent'," J. Chem. Educ., **2006**, 83, 1751-1752.

For a recent and entertaining account of the rivalries and conflicts between Lewis and other physical chemists of his generation, see:

1. P. Coffey, *Cathedrals of Science: The Personalities* and Rivalries that Made Modern Chemistry, Oxford University Press: London, 2008.