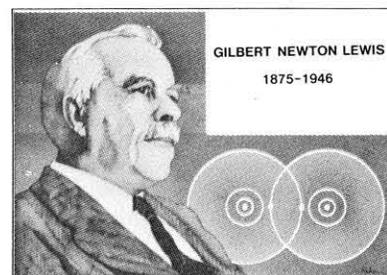


G. N. Lewis and the Chemical Bond

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My first knowledge of Gilbert Newton Lewis came from reading his paper on "The Atom and the Molecule," published in 1916 in the *Journal of the American Chemical Society* (1). During the year 1919-20 I had a full-time job as instructor in quantitative analysis in the Oregon Agricultural College. At the beginning of 1919 I had not returned to the college, because of lack of money, and I was pleased when I had the opportunity to teach the courses in quantitative analysis. My office was in the chemistry library, where copies of the *Journal of the American Chemical Society* and of other journals were available. My teaching load was very heavy, but I had some spare time to read the journals, and when I ran across the 1919 papers by Irving Langmuir (2) I read them with great interest, and also read G. N. Lewis' paper. I spoke on the subject of the electronic theory of valence in the chemistry seminar that year—chemistry seminars were rare, only about one each year. In 1922, when I received my degree of Bachelor of Science in Chemical Engineering, I was offered and accepted an appointment as teaching fellow in the California Institute of Technology. In September of that year, in the middle of the train ride from Oregon to Pasadena, there was a stopover of a few hours in the Bay area. I went to the chemistry building, Gilman Hall, and found a young chemist, Roy Newton, at work in a laboratory on the first floor. He was good enough to talk to me for about half an hour about the work that he was doing and about the nature of graduate work in chemistry. I did not see Lewis at that time, nor did I see any other person in the building—perhaps it was Saturday.

I first met Lewis in 1924, when my wife and I went to Berkeley to see my old friend Lloyd Alexander Jeffress, who had got me interested in chemistry when we were both 13 years old. It is my recollection that I talked with Lewis about the work that I was doing on the determination of the structure of crystals by the X-ray diffraction method, and that I got his permission to say in my application to the National Research Council for a fellowship to begin in July of 1925 that I would do the work in Berkeley. It turned out, however, that I did not go to Berkeley; instead I resigned the fellowship in the middle of the 1925-26 year, after having spent the first few months in Pasadena, in order that I might go immediately to Europe on a Guggenheim fellowship.

In 1928 Lewis spent a day or two in Pasadena. I learned about 50 years later that he had come to offer me a job, but that Arthur A. Noyes, the Chairman of the Division of Chemistry and Chemical Engineering in the California Institute of Technology, had persuaded him not to do so.

For five years, beginning in the spring of 1929, I spent one or two months each year in Berkeley as visiting lecturer in physics and chemistry. During these extended visits to Berkeley I had the pleasure of talking with Lewis for many hours, in his office, his home, and his Marin County country place. My lectures were largely on new ideas about the chemical bond and molecular structure based in part on the theory of quantum mechanics and in part on the empirical analysis of the properties of substances. Lewis was, of course, intensely interested in the work. I am now, in retrospect, rather surprised that he and I did not write a paper together. So far as I can remember, our discussions led to some clarifi-

cation of the new ideas, but not to the discovery of anything significant.

G. N. Lewis' 1916 paper introduced the theory of the shared electron pair chemical bond and revolutionized chemistry. Comparison is often made of G. N. Lewis' paper and the paper by W. Kossel (3) that was published in the same year. Kossel's paper (133 pages) was much longer than Lewis' (22 pages). Even so, I think that Kossel's paper represented no significant contribution. Much of it is nonsense. He gave a long discussion of electrostatic valence, but nothing about covalence, although he suggested electronic structures for some molecules in which the electrons were related to two nuclei. He mentioned the suggestion by Niels Bohr that in the hydrogen molecule two electrons occupy the same circular orbit in a plane perpendicular to the midline between the two nuclei, and he suggested that in the nitrogen molecule the two nuclei, each with a pair of K electrons, are held together by 10 electrons moving in the same circular orbit in the plane midway between the nuclei and in the plane perpendicular to the internuclear line. On the other hand, the two papers that Irving Langmuir published in the *Journal of the American Chemical Society* in 1919, comprising 84 pages, contained many significant

VALENCE

and

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BY

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contributions and additions to the theory of the shared electron pair chemical bond. For some reason Lewis was antagonistic to Langmuir, and in my opinion did not give him proper credit. In his 1923 book "Valence and the Structure of Atoms and Molecules" (4), Lewis mentions that after publishing his 1916 paper he had intended at a later time to present in a more detailed manner the various facts of chemistry that made necessary his radical departures from the older valence theory. He then continued (5)

This plan, however, was interrupted by the exigencies of war, and in the meantime the task was performed, with far greater success than I could have achieved, by Dr. Irving Langmuir in a brilliant series of some twelve articles, and in a large number of lectures given in this country and abroad. It is largely through these papers and addresses that the theory has received the wide attention of scientists.

It has been a cause of much satisfaction to me 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. Here and there he has been tempted to regard certain rules or tendencies as more universal in their scope than I considered them in my paper, or than I now consider them, but these questions we shall have a later opportunity to discuss. 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.

G. N. Lewis' main contribution to chemistry was the idea that the chemical bond (named the covalent bond by Langmuir) is at all times a pair of electrons held jointly between two

atoms. Lewis also, after having placed the eight electrons of what Langmuir called the octet (s^2p^6) at the corners of a cube, suggested that the electrons are in pairs at the corners of a tetrahedron. In this way he could ascribe to the acetylene molecule a structure with a triple bond, three shared electron pairs lying at the corners of the common face of the two carbon tetrahedra. Lewis discussed the partial ionic character of covalent bonds by writing that the electron pair is midway between two identical atoms but may be shifted toward one or another of a pair of non-identical atoms.

Langmuir (6) contributed the important idea of the electroneutrality principle—that atoms in a molecule hold electrons to such an extent as to keep the electric charge of each atom close to zero. In applying the electroneutrality principle he did not, however, make any correction for the shift of electric charge resulting from partial ionic character. He showed, using the electroneutrality principle, that a transition metal may have high covalence, such as 8 for nickel in nickel tetracarbonyl, to which he assigned a structure with a double bond between the nickel atom and each of the carbon atoms of the carbonyl groups. He introduced the concept of isosterism, pointing out that molecules with an equal number of nuclei and an equal number of total electrons in general have very nearly the same structures. He concluded that CO_2 , N_2O , NCO^- , NNN^- , and other such molecules are linear. The linearity of the trinitride ion and the cyanate ion was shown later by Sterling Hendricks and me through our X-ray diffraction studies of potassium trinitride, sodium trinitride, and sodium cyanate. Langmuir also reached the remarkable conclusion that the nitrous oxide molecule has the linear structure NNO rather than NON . In his discussion of the Heusler alloys, which contain manganese, copper, and small amounts of arsenic, aluminum, or other elements and are ferromagnetic, he stated that "Copper has too many electrons. It gives one to manganese to make the atom like the iron atom." This statement shows remarkable insight.

Langmuir, however, was wrong in some of his ideas. He regarded quartz as containing SiO_2 molecules similar to the molecules of carbon dioxide, and said that the hardness is the result of the leaking of residual silicon-silicon forces. Lewis, in fact, had made a similar suggestion in his 1916 paper. Only in 1923 did Lewis realize that the silicon atoms are held together by bridging oxygen atoms.

Langmuir also assigned to the P_4 molecule a ring structure containing alternating single and double bonds. He overlooked the possibility of a tetrahedron with only single bonds between the phosphorus atoms. Similarly, his structure for P_4O_6 involves a square of phosphorus atoms held together by single bonds, with two oxygens attached to each of two phosphorus atoms and one to each of the other two—not a very sensible structure.

In his 1923 book Lewis discussed early suggestions about the electronic structure of molecules that had been made by Kossel, Stark, and others, especially A. L. Parson, a student who in 1915 published an interesting paper entitled "A Magneton Theory of the Structure of the Atom." Parson considered the electron as a rotating ring of negative electricity that accordingly possessed a magnetic moment and could be called a magneton. Lewis says that it was he who suggested to Parson that the magnitude of the magnetic moment to be assigned to such a spinning electron was constant, whereas Parson had considered it to be variable. Parson and Lewis thus anticipated by 25 years the discovery that the electron has a spin and a magnetic moment. Lewis, however, then rejected the idea, writing, "This idea has not proved fruitful, and it seems unlikely, although perhaps not impossible, that an electron possesses any magnetic properties except when it is a part of an atom or a molecule."

Lewis felt an indebtedness to Werner, writing that "His 'Neuere Anschauungen auf den Gebiete der anorganischen Chemie' (1905) marked a new epoch in chemistry; and in at-

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tempting to clarify the fundamental ideas of valence, there is no work to which I feel so much indebtedness as to this of Werner's." However, in his discussion in 1923 of the types of coordination postulated by Werner (octahedral, tetrahedral, square planar), Lewis did not make any mention of the results of the study of crystals containing these coordination complexes that had been published during the preceding two years by Roscoe G. Dickinson and R. W. G. Wyckoff, who had verified the octahedral arrangement in crystals such as K_2SnCl_6 and K_2PtCl_6 , the square arrangement in K_2PdCl_4 and K_2PtCl_4 , and the tetrahedral arrangement in $K_2Zn(CN)_4$ and $K_2Cd(CN)_4$. No X-ray work was being done at that time in the College of Chemistry at Berkeley, and Lewis seems not to have been following the developments in X-ray crystallography.

G. N. Lewis was remarkable in his originality. I was much impressed in the early 1920's when I read his paper announcing the discovery of the O_4 molecule. He had asked why the paramagnetism of oxygen dissolved in liquid nitrogen decreased as the concentration of the oxygen increased. He was able to show that he could account for the experimental values of the magnetic susceptibility of solutions of oxygen in nitrogen by the assumption that there is an equilibrium between paramagnetic molecules of dioxygen and the diamagnetic molecules of tetraoxygen, O_4 . From the values of the paramagnetic susceptibility he was able to evaluate the standard Gibbs free energy change and the enthalpy change for the reaction.

As I think about the history of the chemical bond, I ask myself why some of the discoveries that were made in the quantum-mechanical era of the 1930's were not discovered earlier. The electronegativity scale of the elements is an example. It was formulated in 1933 through the analysis of the decrease in enthalpy accompanying reactions in which single bonds between like atoms are converted to single bonds between unlike atoms, such as $\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \rightarrow HCl$. The basic idea, attributed to quantum mechanics in 1933, is that the partial ionic character of a bond makes it more stable, with lower energy, than a pure covalent bond between the unlike atoms. This idea is, in a sense, not a quantum mechanical idea; we might well have concluded before quantum mechanics was developed that if the actual bond is a covalent bond with partial ionic character it must be more stable than the pure

covalent bond, because if it were less stable the molecule would have a structure involving pure covalent bonds between the unlike atoms. The necessity for making a correction in the heats of formation of compounds involving reaction of dioxygen or dinitrogen (O_2 or N_2) with single-bonded elements to form single-bonded products is a complication, but chemists knew even before quantum mechanics that the bonds in these molecules are not single bonds and that the molecules might have greater stability than single-bonded molecules have. Langmuir formulated the electroneutrality principle, but did not make much use of it, and Lewis ignored it. The reason may well be that the principle does not work very well unless the partial ionic character of bonds is taken into account, and until the electronegativity scale was developed it was not possible to discuss the partial ionic character in a satisfactorily quantitative way. Moreover, Lewis did not make use of the theory of resonance, which had not yet been formulated in 1923 but which might have been proposed, as was done by Robert Robinson and C. K. Ingold in 1926, in the theory that Ingold called mesomerism. Lewis in 1923 expressed some concern that a structure of the carbonate ion in which one oxygen atom is held by a double bond and two by single bonds seems, as had been stated by Latimer and Rodebush (in Berkeley) three years before (7), to be in contradiction with the apparent trigonal symmetry of the ion in calcite as shown by X-ray diffraction. The idea that the double bond resonates among the three positions apparently did not develop in Lewis' mind at that time.

Gilbert Newton Lewis showed himself to be one of the great chemists of the 20th century through his work in chemical thermodynamics and other fields, as well as through his formulation of the basic principle of the chemical bond—the idea that the chemical bond consists of a pair of electrons held jointly by two atoms.

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