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VALENCE[1]

THE theory of valence is one of the most important theories of chemistry. Scarcely any other except the atomic theory, with which it is inseparably connected, has been so fruitful in results which have led to industrial applications and also to the development of chemical knowledge. In spite of these results, which no one can dispute, the theory is more or less in disrepute, especially among physical chemists and students and teachers of inorganic chemistry. In many of our elementary text-books structural formulas are used so sparingly that they make no impression on the student and in some of them they are not even mentioned.

This attitude is due, in part, to a reaction from the overemphasis given to the subject at a time when nearly all chemists were working on the structure of organic compounds. It is due, also, to confused and conflicting ideas about the philosophy of science.

Some have gone so far as to claim that speculations and hypotheses form no part of genuine science. To such persons science is only an orderly description of phenomena which we can see and handle, which we can weigh and measure and connect by mathematical processes. An attempt to acquire knowledge about atoms and electrons and molecules, so long as they remain beyond the direct cognizance of our senses, may be interesting but to followers of this school such attempts form no part of science.

To an organic chemist the achievements in the determination of the structure of carbon compounds demonstrate the falsity of such a claim. It may be remarked, in passing, that

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[1] Address of the chairman and retiring vice-president of Section C—Chemistry, American Association for the Advancement of Science, Baltimore, December 27, 1918.

the philosophy of science referred to easily leads to the conclusion that the discovery of new facts is of supreme value in science and that one is doing good scientific work when he adds a few facts to our already unwieldy accumulation of knowledge, whether the facts discovered have any valuable relation to fundamental principles or not.

Another school of philosophers contends that the number of explanations which will fit any given set of natural phenomena is infinite, and that, for this reason, any explanation which we use, as for instance, the Copernican system or the atomic theory, is purely a product of our imagination and that it is hopeless ever to arrive at a system which shall actually correspond to the realities of the universe. This, if I understand him correctly, was the point of view held by Poincaré. It is only a step from this to the conclusion that there is no reality outside of our own minds, for, surely, if we can never attain to a knowledge of realities outside ourselves, for all practical purposes such realities do not exist.

A more true philosophy of science, as it seems to me, recognizes the intimate connection between speculation, hypothesis and theory on the one hand and the accurate study of phenomena on the other. Neither is complete or sufficient alone. Science advances most rapidly by what may be called a "cut-and-try" method. Speculation alone led to the useless dialectics of the school-men. A study of phenomena alone leads to an almost equally barren accumulation of facts for which we have no earthly use. It is inconceivable that chemistry, or indeed, that science as a whole could have made the progress that it has during the last century if Dalton, or some one else, had not given us the atomic hypothesis as a key for the study of chemical phenomena.

The subject of valence furnishes a particularly good illustration of the methods by which science advances. The positive achievements of the theory are so great that no one can doubt that there is some reality in the relations of atoms which corresponds to the theory. At the same time our knowledge is so vague and indefinite at many points that we must consider the theory as still very unsatisfactory and in need of further development.

Ernst von Meyer has pointed out with some truth that the theory of valence is implied in the Law of Multiple Proportions. A somewhat more definite approach was made when Graham demonstrated the polybasic character of phosphoric acid. His results were expressed, however, in the old dualistic formulas in which one, two or three molecules of water of hydration in the acid were considered as replaced by one, two or three molecules of a metallic oxide. When Liebig introduced the idea that acids are compounds of hydrogen the notion of polybasic acids became still more definite and the fact that an atom of antimony may replace three atoms of hydrogen while an atom of potassium replaces only one was given a clear statement. During the same period the discovery of the chloroacetics acids by Dumas and the development of the theory of types by Gerhardt and others gave greater precision to our knowledge of the replacement of one atom by another and it became evident that in such replacements one atom of oxygen may take the place of two atoms of chlorine.

Thus far the rudiments of the idea of valence had been developed only on the basis of the replacing power of different atoms. In 1852 Frankland went a step further and introduced the more exact conception of a definite, though variable, combining power for different atoms. Using the atomic weight 8 for oxygen he gives the formulas NO_3, NH_3, NI_3, NS_3; PO_3, PH_3, PCl_3; SbO_3, SbH_3, $SbCl_3$; AsO_3, AsH_3, and NO_5, NH_4O, NH_4I; PO_5, PH_4I, etc., to show that the elements nitrogen, phosphorus, arsenic and antimony combine with either three or five atoms of other elements. He also pointed out that when an atom of tin is combined with two ethyl groups in tin ethyl, $Sn(C_2H_5)_2$, it will take up only one atom of oxygen, giving the compound, $Sn(C_2H_5)_2O$, while an atom of tin alone will combine with two atoms of oxygen to form stannic oxide, SnO_2.

A few years later Couper and Kekulé, quite independently of each other, developed clearly the idea that carbon compounds are held together in chains by attractions between the atoms and that the structure of the molecules of such compounds is directly dependent on the valence of the atoms of which they are composed.

In the same year, 1858, at Genoa, Cannizzaro revived the hypothesis of Avogadro and Ampère and gave such convincing evidence of its truth that it was soon accepted by the leading chemists of the world. This introduction of a correct system of atomic and molecular weights aided greatly in the very rapid development of structural organic chemistry. We can still imagine with what enthusiasm the chemists of that day seized the key to nature's mysteries which the doctrines of valence and of the linking of atoms had given them and applied them to the solution of problems of structure and of synthesis. Only a few years before the thought of definite, accurate knowledge of this kind would have seemed the dream of a hair-brained visionary.

Chemistry is primarily an experimental science. New theories make their way slowly and speculations which are not forced upon us by incontrovertible facts have met with little favor. At the time when the theory of valence made itself indispensable as a guide to the investigation of carbon compounds the older electrochemical theory had practically disappeared and no theory for the cause of the attraction between atoms received more than passing attention. It was tacitly assumed that some sort of attraction between atoms held them bound together but even such necessary terms as "single bonds" and "double bonds" or "linkages" were used with reserve by many chemists.

During the forty years following the publication of the papers by Couper and Kekulé the theory was amplified in only one important detail. The original theory considered only the sequence of atoms in compounds. While there may have been occasional thoughts about arrangements in space, chemists were very reticent in expressing them. In 1874, however, van't Hoff proposed an explanation of the relation between the structure of optically active compounds and the arrangement of their atoms, based on the fundamental proposition that four univalent atoms or groups combined with a given carbon atom are arranged symmetrically about the center of the atom. From the same starting point he postulated the supposition that two carbon atoms connected by a double union can not rotate independently about the points of union. The first hypothesis gave a satisfactory explanation for optically active compounds and it is impossible now for any one to question the fact that a compound which is optically active in solution must contain a central atom or group around which four or more atoms or groups are arranged in an asymmetric fashion. Incidentally it may be remarked that the discovery of compounds in which the asymmetric atom is nitrogen or sulfur or tin demonstrates that the principle of valence is general in its application and is not simply of value for carbon compounds.

The use of van't Hoff's principle in the explanation of the isomerism of such compounds as fumaric and maleic acids was equally successful.

In 1885 Bayer gave the following statement of the well-established principles used in explaining the structure of carbon compounds·

1. Carbon is usually quadrivalent.
2. The four valences are alike.
3. The valences are symmetrically directed in space from the center of the carbon atom.
4. Atoms attached to the four valences do not easily exchange places—van't Hoff's principle.
5. Carbon atoms may be united with one, two or three valences.
6. The compounds may be either open chains or rings.

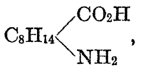
Baeyer proposed a seventh principle:

7. The directions in which the valences are exerted may be diverted from the normal angle of the tetrahedron, which is 109° 28′,

but the tension which results renders the compound less stable.

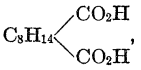
He explained in this manner the extreme instability of acetylene compounds and the ease with which additions are made to double unions; also, the instability of rings of three carbon atoms in comparison with those of four or five atoms. This so-called "tension theory" has been very suggestive and useful.

An interesting confirmation of the ease with which rings containing six atoms are formed and evidence that rings containing seven atoms are not so natural was discovered, almost by accident, by Mr. Potter and myself a few years ago. Aminocamphonanic acid, usually written,



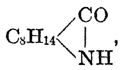
$$C_8H_{14}\Big\langle\begin{matrix}CO_2H\\NH_2\end{matrix},$$

is a compound in which the carboxyl and amino groups are separated by three carbon atoms. It is derived from *d*-camphoric acid,



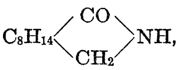
$$C_8H_{14}\Big\langle\begin{matrix}CO_2H\\CO_2H\end{matrix},$$

and we should expect it to have a right handed rotation for polarized light. Both the free acid and its anhydride,



$$C_8H_{14}\Big\langle\begin{matrix}CO\\|\\NH\end{matrix},$$

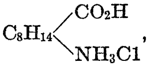
are, however, left-handed in rotation. The anhydride of its homologue, *α*-aminocampholic acid,



$$C_8H_{14}\Big\langle\begin{matrix}CO\\CH_2\end{matrix}\Big\rangle NH,$$

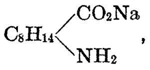
is also a lævo compound.

The hydrochloride of aminocamphonanic acid,



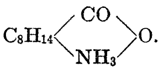
$$C_8H_{14}\Big\langle\begin{matrix}CO_2H\\NH_3Cl\end{matrix},$$

has the right-handed rotation which would be expected of the free acid. If we add to a solution of the hydrochloride one mol of sodium hydroxide, liberating the free acid, the rotation of the solution changes, from right-handed to left-handed. The addition of a second mol of sodium hydroxide, forming the sodium salt,



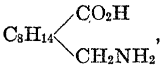
$$C_8H_{14}\Big\langle\begin{matrix}CO_2Na\\NH_2\end{matrix},$$

again causes a right-handed rotation in the solution. Similar relations were found for a number of allied compounds. The only simple explanation which is apparent is that the free acid has the cyclic structure,



$$C_8H_{14}\Big\langle\begin{matrix}CO\\NH_3\end{matrix}\Big\rangle O.$$

The homologue,



$$C_8H_{14}\Big\langle\begin{matrix}CO_2H\\CH_2NH_2\end{matrix},$$

on the other hand, is a dextro compound and both its hydrochloride and its sodium salt are right-handed, indicating that the free acid, which would require the formation of a ring of seven atoms to form a cyclic salt, does not form such a salt.

These relations seem to establish, also, the quadrivalence of nitrogen in ammonium salts. It seems impossible to reconcile this with Werner's idea that the fourth hydrogen of the ammonium group remains combined with the acid radical in such salts.

In 1899 Thiele proposed his theory of partial valences to account for the addition of bromine, hydrogen, or two other atoms or groups to the end carbon atoms in conjugated double unions, which have the structure $>C=CH-CH=C<$. The compound formed has the structure $>CX-CH=CH-CX<$. This relation always reminds me of two bar magnets in which the north pole of one is in contact with the south pole of the other $\boxed{N\ S\,|\,N\ S}$. At the center of such a system no attraction will be exerted but the free ends will exert their usual attraction. While this is an analogy rather than an explanation, and is also rather closely related to Thiele's idea, it seems to me better than that which he has expressed. If we attach any definite meaning of localized attraction to the term valence it is difficult to conceive of the valence as being divided, as seems to be implied in the term, "partial valence."

Werner in discussing this point, and also in discussing the Walden inversion and other topics, rejects the idea of localized attraction and prefers the notion of a general attraction of the atom as a whole. But a general attraction seems hard to reconcile with the fact that it is never satisfied by more or less than four univalent atoms or groups.

In 1887 Arrhenius proposed his theory of electrolytic dissociation, or, as it is better called, of ionization. The attention of chemists was once more directed to the intimate relation between electrical forces and chemical affinity. About ten years later J. J. Thomson demonstrated the existence of electrons as definite units of negative electricity having a mass eighteen hundred times smaller than that of the hydrogen atom. Almost at the same time the first discoveries of radioactive elements were made and as these were developed Rutherford brought out his theory of the disintegration of atoms. It soon became evident that atoms are not homogeneous, indivisible particles, as had been more or less tacitly supposed but that they must be complex aggregates of electrons and much more dense material with a positive charge. J. J. Thomson made an attempt to account for the properties of atoms by supposing a uniform positive sphere into which electrons found their way and distributed themselves in accordance with their attraction for the positive matter and their repulsion for each other. In contrast with this Bohr, Rutherford and others have assumed a very dense central nucleus, with a positive charge, about which electrons are in very rapid rotation. Experimental evidence based especially on the scattering of helium atoms which are shot through a thin film of gold or other metals has given very positive evidence in favor of atoms with a central nucleus. Some progress has been made in the discussion of the relation between the spectra of some of the elements and the revolving electrons of their atoms.

While physicists have been busy with studies of radioactivity and have reached some rather positive conclusions about atoms, which are certainly dynamic, rather than static, chemists have been busy with the applications of the new electro-chemistry in its relation to the electron theory. It is evident that in ionization a positive univalent ion has lost an electron and a negative ion has gained one. Chemists have usually been very reticent about the fate of these electrons when ions unite but it seems rather certain that some atoms still retain their position or negative character in their compounds. This was first definitely pointed out for nitrogen trichloride, in which the chlorine is positive, as contrasted with nitrosyl chloride, NOCl, in which it is clearly negative.

The evidence for the existence of positive chlorine in nitrogen trichloride and of negative chlorine in nitrosyl chloride is usually stated to be that the trichloride hydrolyzes to ammonia and hypochlorous acid while nitrosyl chloride hydrolyzes to nitrous acid and hydrochloric acid. Recent experiments, not yet published, have shown that dry ammonia and chlorine react with the formation of the trichloride and also that a dry solution of the trichloride reacts with dry hydrochloric acid to form ammonium chloride and chlorine. These facts seem to prove that the trichloride is formed by the addition of chlorine to ammonia, forming chloroammonium chloride, $NH_3Cl^+Cl^-$, followed by the splitting off of hydrochloric acid, and a repetition of the process till all of the hydrogen is gone. On the other hand, the decomposition of the trichloride by hydrochloric acid is caused by the addition of the acid, giving trichloroammonium chloride, $NCl_3H^+Cl^-$, followed by the splitting off of a positive and a negative atom of chlorine, as free chlorine. Under suitable conditions these reactions may be practically quantitative in either direction.

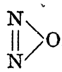
The close analogy between these reactions and those which take place in the substitution of chlorine for hydrogen in methane or in benzene is very striking and recalls Michael's theory that addition compounds are at first formed in such cases. The idea which is partly new is that such additions are always of two atoms or groups, one of which is positive and the other negative. Also that atoms may form unstable compounds of higher valence when one of the new valences is positive and the other negative. The instability of such compounds is due to the fact that they contain two atoms or groups of opposite sign.

This is closely related to Abegg's contravalences, according to which the non-metallic elements, in particular, exhibit maximum positive and negative valences the sum of which is eight. Thus sulfur has a negative valence of two in hydrogen sulfide and a positive valence of six in sulfur trioxide and in sulfuric acid. But sulfur very readily assumes three negative valences, in such compounds as triethyl sulfonium iodide, $(C_2H_5)_3SI$, in which it has also assumed one positive valence. We may assume that methane, in a similar manner forms with chlorine the compound $CH_4Cl^+Cl^-$, which at once splits off hydrochloric acid.

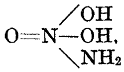
It seems worth while to remark that we have much need of revising our conception of the non-metallic elements as being *negative* elements. This is based on the fact that the halogens when univalent form their most stable compounds as negative atoms and also because nitrogen, sulfur and similar elements form very stable negative groups, such as SO_4, NO_3, etc. We are a little apt to forget that oxygen forms the negative part of these groups and that nitrogen and sulfur are *positive* in them. Some apparent anomalies in the laws for the orientation of substituting groups in benzene derivatives are easily explained when these facts are kept in mind.

It will have been noticed that very much importance is attached, above, to additions and decompositions in which the two groups or atoms added or split off are of opposite sign. Nef, Michael and others have often emphasized the importance of reactions of this type but at a time when an accurate consideration of the positive or negative character of the atoms or groups involved was not in vogue.

Some of our ideas need revision, as it seems to me, in this regard. Let us take the commonly accepted formula of nitrous oxide,

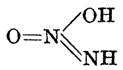


The compound is formed by the decomposition of ammonium nitrate. This would almost certainly begin by the splitting off of hydrogen and NO_3, giving ammonia and nitric acid. Besides recombining to ammonium nitrate part of the ammonia would add itself to the nitric acid, giving



$$O{=}N{\begin{smallmatrix}OH\\-OH,\\NH_2\end{smallmatrix}}$$

Such a compound would lose water, giving



$$O{=}N{\begin{smallmatrix}OH\\NH\end{smallmatrix}}$$

first and then $O{=}N{\equiv}N$. Such a structure takes account of the probability that one nitrogen atom remains positive and the other negative throughout the series while the formula usually given implies that at least one valence of one nitrogen atom changes from negative to positive. The formula here proposed also seems more in accord with the ease with which nitrous oxide gives up its oxygen.

I can not take the time to consider the very interesting discussions of Falk and Nelson, of Fry and of Jones nor the valuable additions to our experimental knowledge made by the last two. As was remarked at the beginning, every important advance must combine experimental evidence with new explanations of natural phenomena.

G. N. Lewis has proposed the hypothesis that carbon compounds are not held together by polar valences because they do not readily ionize. It seems possible that this is true in some cases but it is difficult to believe that there is any very essential difference between the reaction of methyl iodide with silver nitrate and that of potassium iodide with the same reagent.

Werner distinguishes between primary valences which hold simple compounds together and also cause the binding of carbon atoms, and secondary valences, which are effective in the formation of complex, molecular compounds. Strong reasons have been given for thinking that the ammonium compounds are genuine valence compounds and not molecular compounds, as Werner supposes them to be. If we assume rotating electrons, as we are almost compelled to do, molecules may well be held together by magnetic attractions and it seems possible that such attractions give rise to the secondary valences of Werner. He and his students have done magnificent work in the study of complex inorganic compounds, and some apparent contradictions between his ideas and those of organic chemists will doubtless be cleared up in the future.

To repeat, the most important recent advance in the theory of valence has been the interpretation of the theory in connection with the electron theory and a beginning toward the study of positive and negative atoms in organic compounds.

It is not very safe to prophesy, but I am impressed with the need of a more definite knowledge of the structure of atoms as a basis for a better understanding of valence. So much progress has been made in this direction during the past twenty years that further advance seems probable. Several different lines of study may be suggested, the coordination of which might lead to further knowledge.

The spectra of the elements must be intimately connected with the structure of the atoms. Professor Morley once suggested that the problem is something like that of a man who should endeavor to determine the mechanism of a grand piano with only sound waves to guide him. Yet the matter seems by no means hopeless and a beginning has already been made. It is noticeable that spectral lines are only given out by ionized gases and are possibly connected with the motion of valence electrons.

Certain forms of structure, especially those forms in which there are what Baeyer so aptly called *fliesende doppelte Bindunge,* absorb light of certain wave-lengths and give us colored compounds. This means that it is possible to calculate exactly the rate at which certain atoms, or parts of atoms, or of molecules vibrate.

The atomic numbers determined by X-ray spectra must be due to some more rapid and very fundamental sort of vibration which changes as the nucleus of the atom increases in weight from one element to another of the periodic system.

By means of X-rays it has been possible to determine the actual arrangement of atoms in crystals. The conclusion has been drawn from some of this work that the results do not agree with our customary conceptions of valence. I am inclined to think that the achievements of organic chemistry are not to be discarded so easily.

The Walden inversion has been interpreted by Fischer and Werner in terms of general attraction between atoms as opposed to localized attraction. The subject deserves careful study.

The evidence from radioactive disintegrations that helium atoms and electrons form essential parts of some atoms and very probably of all, is certainly important. The speculations of W. D. Harkins in this connection may be mentioned. The enormous quantity of energy liberated by the disintegration of an atom is certainly significant.

Three suggestions as to the functions of electrons in holding atoms together may be mentioned. One is that one or two electrons rotate about a line joining the centers of two positive nuclei, at a point midway between them. In ionization these electrons must remain with the negative ion. A second suggestion is that the magnetic effect produced by rotating electrons may cause an attraction between atoms. This is the magneton theory of Parsons and something of the same sort was suggested by Sir William Ramsay in the last paper which he published. It would also account for the non-polar combinations of G. N. Lewis. A third suggestion is that an electron may rotate about positive nuclei situated in two atoms. The velocity of electrons must be so much greater than ordinary motions of atoms that the atoms might be kept together in this way.

Whatever conclusions may finally be reached with regard to the structure of atoms it seems very certain that the structure will be found to be dynamic rather than static. It is hard to conceive of a quiescent electron.

William Albert Noyes

SOME RECENT CONTRIBUTIONS TO THE PHYSICS OF THE AIR. II

BAROMETRIC FLUCTUATIONS

Another meteorological phenomenon that has been the subject of numerous investigations, is the pressure of the atmosphere. This pressure undergoes many changes, and the causes of some of them, such as its variations between summer and winter, and between ocean and continent, have long been known. But the causes of certain others, notably the great changes that accompany cyclones and anticyclones, have not yet been fully determined. Neither of these classes of changes, that is, those whose causes have long been known, and those whose causes still remain partially obscure, will be discussed here, though each is important and full of interest. But there are two other classes, namely, barometric ripples, and the pressure wave of semidiurnal period, that, because of their obvious interest to physicists, will be briefly considered.

Barometric "Ripples."—Small pressure changes having amplitudes usually of 0.1 mm. to 0.3 mm. and periods of 5 minutes to 10 minutes, and continuing for hours or even days together, are very common during cold weather. They are not greatly different in magnitude from the well known wind effects on the barometer, but obviously of different origin since their amplitude has no relation to the local wind velocity.

Their explanation appears to lie in the fact that whenever layers of air that differ in density at their interface flow over each other, long billows, analogous to water waves, and generated in the same way, are produced. If, now, the under layer is colder than the upper, as it is during the radiation or surface inversions of winter, and rather shallow, 100

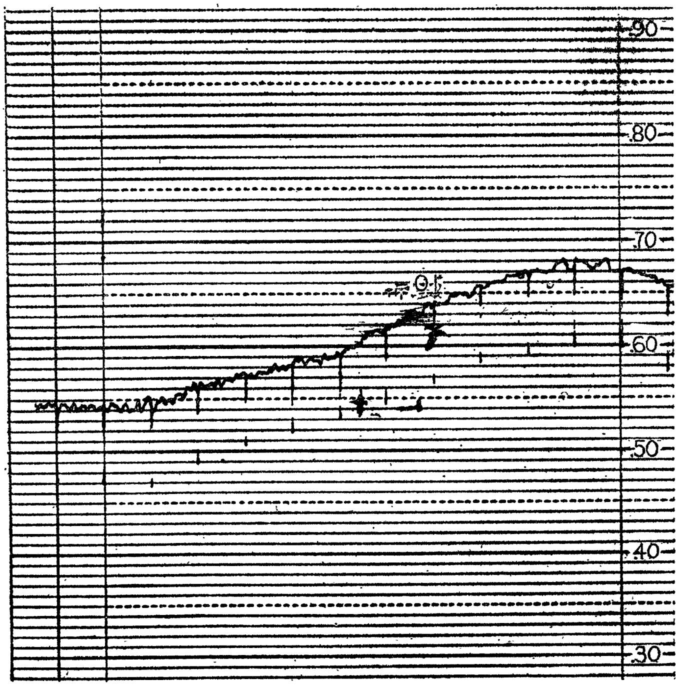


Fig. 4. Barometric Ripples.