THE ELECTRON THEORY OF VALENCE

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The scientist has of late been repeatedly warned by the philosophers that he should be careful about pushing the limits of his domain too far, lest he find himself in the forbidden territory of metaphysics. Those of us who are interested in the nature of matter may be startled to find that in our speculations concerning the atom we have raised questions of a philosophical nature, which we shall probably not be able to answer, without going outside what is considered by many to be the proper field of science. This is perhaps only a dignified way of saying that they can not be answered at all.

Bridgman (1) points out that the atom is a "construct;" that is, a mechanism designed to explain the behavior of matter. The atom seems destined forever to escape direct observation; the evidence for its existence is wholly inferential. The most important atomic property that is directly measured is electric charge; as it is defined the measurements indicate that it exists in discrete units. The ratio of e/m is of course a result of measurement; but the mass appears to vary with speed because the charge is assumed to be constant. The proton and electron have come to seem very real to us but actually they are "constructs," which represent a long extrapolation beyond the atom, which itself cannot be seen. The most difficult problem of the physicist is to account for the structure of the atom itself. The only experimental law, which he has for guidance, is Coulomb's law of the force varying as the inverse square of the distance between charges. This law is wholly insufficient to account for the structure of the atom or even the stability of the electron and proton. Why the electron does not explode spontaneously, or fall into the proton with catastrophic results at the first approach is not explained. Eddington (2) and others have speculated on the possibility of this happening. Any attempt to explain the fundamental behavior of electrical charges must involve the assumption of a modification of the Coulomb law of force; such a hypothesis has been elaborated mathematically by Birkhoff (3). The Bohr atom, as was pointed out by G. N. Lewis (4), in addition to assuming the proton and electron of the Rutherford atom, assumes lapses at certain times and places of the laws of electrostatics and electrodynamics. That the proton and the electron are condensed into infinitesimal volumes is itself an assumption. The Schroedinger wave equation has been interpreted to indicate a diffuse electron but it seems more satisfactory to interpret it as a sort of smoothed out or continuous function which indicates the discontinuous probability of location in time and space of the corpuscles of matter and radiation. Since the atom is a "construct" or hypothetical mechanism invented to explain the behavior of matter, it should be designed in the simplest possible way that will serve the purpose. The Bohr atom was designed to explain radiation only and was never a satisfactory model for the chemist. It seems more than a coincidence that Born, the leader of the revolution in thought known as the new quantum theory, is a man who has a large familiarity with the facts of chemistry. The statement that the orbit exists only when it can be observed sounds like a paraphase of the statement made by G. N. Lewis when he said more than ten years ago that an electron should not be said to be in motion when it had none of the properties of motion. Heisenberg's (5) Principle of Indetermination in which he denies the possibility of locating an electron at a given instant is somewhat reminiscent of Ostwald's denial of the existence of the atom itself. Ostwald led the physical chemists on what appears now to have been an inglorious retreat. The refusal to make pictures, however much it may seem to be justified on philosophical grounds, or those of common sense, appears to be a sterile procedure from the standpoint of advancing knowledge. The invention of models, no matter how crude and artificial they may be, seems justified by the experiments that are inevitably suggested. The results of these experiments seldom confirm the hypothesis, or worse still they may not even answer the question in an unambiguous manner, but they almost always give us new and interesting information.

The chemist and especially the organic chemist has accumulated the largest amount of consistent data without a rational underlying theory that a science has ever known. The physicist has constructed the most intricate theory of atomic structure, largely from the data of spectroscopy, that the history of science records. Until recently the theory of the physicist and facts of the chemist have seemed a long way apart. Within the last few years the two have been drawing together very rapidly and in this process the physicist seems to have yielded more ground than the chemist. The facts of chemistry seem more obvious and more direct in inference than the data of spectroscopy. The physicist appears to have learned more from the chemist than the chemist has learned from the physicist. The physicist now tells the chemist that his ways of looking at things are really quite right because the new theories of the atom justify that interpretation, but of course the chemist has known all the time that his theories had at least the justification of correspondence with a great number and variety of experimental facts.

The model of the atom currently accepted by the physicist is a Rutherford nucleus about which the electrons are arranged in groups or shells, of substantially the same energies, which correspond to the periods 2, 8, 8, 18, etc., of the Thomsen arrangement of the periodic table. The outermost group never contains more than eight electrons. With the underlying group the chemist is never directly concerned for no fact seems more certain than that the valence electrons are in the outermost group. These shells are commonly designated, started from the nucleus outward by the letters K, L, M, etc. To the physicist they represent merely a classification of the electrons into levels of approximately the same energy and are commonly designated by the principal quantum numbers 1, 2, 3, etc. According to the Main Smith-Stoner scheme of electron arrangement the completed outer group of eight electrons in an inert gas may be divided into three sublevels which are filled by 2, 2 and 4 electrons respectively.

This arrangement agrees with the spectroscopic evidence; the agreement with the chemical evidence will be discussed later.

With such structure postulated for the atom and Coulomb's law one can do much toward explaining the formation of molecules in a qualitative way. G. N. Lewis (4) has stressed the complete failure of the electrochemical theory of Berzelius in accounting for the formation of any considerable number of compounds. It must be remembered, however, that the electrochemical theory was invented at a time when the atom was supposed to be made up of matter and electrical charge was supposed to be acquired more or less incidentally, as a dust particle might adhere to a larger object. When it is recognized that the atom is made up primarily of electrical charges, then the theory must of course be greatly modified and if so modified, the theory is by no means so inadequate as has been stated. The mutual attractions between the nucleus of one atom and the electrons of another are quite sufficient to account for the energy of formation of molecules, provided a suitable arrangement of the electrons around the nucleus is assumed. Thus an excuse is to be made for the failure of the physicist to calculate the energy formation of sodium chloride from the ionizing potential of sodium and the electron affinity of chlorine. These quantities are measured for the respective atoms in the gaseous state, but sodium chloride in the gaseous state is not a polar compound in the sense that the electron is completely transferred from the bond between the sodium and the chlorine atoms. It must be noted to the credit of the physicist that he is now able to calculate heats of dissociation of diatomic molecules[1] and that the Schroedinger wave equation has been used to calculate the energy of formation of the hydrogen molecule. The outstanding difficulty then in a theory of valence is not to account for the forces which bind the atoms into molecules. The electrochemical theory can do that. It is rather to account for the existence of some compounds, the nonexistence of others and particularly, the discrete unitary

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[1] Mr. E. C. Walters working with the author at the University of Illinois has obtained results confirming the prediction of the physicist that sodium vapor contains diatomic molecules.

nature of valence, which can be expressed by a series of small whole numbers for the chemical elements and consequently, leads to the law of multiple proportions. These characteristics of valence are accounted for by the brilliant theories of G. N. Lewis (4) in a remarkably satisfactory manner, at least from the chemist's point of view. Lewis has formulated his theory in part as a set of numerical rules, concerning the disposition of the valence electrons in the atom and molecule. These rules must appear, however, in a sense, arbitrary, until they are related to the structure of the atom as the physicist pictures it. We shall state these rules in turn and consider the theoretical basis for each.

THE RULE OF TWO

Lewis was led to his conclusion that the electrons tend to arrange themselves in pairs by the extraordinary significance which even numbers appear to have for the arrangement of the electrons both within and without the nucleus. The following are some of the generalizations.

1. Even number of electrons in the nucleus (usually).
2. β-decompositions of radioactive elements occur in pairs.
3. Very few "odd" molecules.
4. Ionizing potential of odd-numbered elements usually lower than adjacent even-numbered elements.
5. All odd-numbered elements are paramagnetic.

The most important of these generalizations for the chemist is undoubtedly the third one; namely the scarcity of molecules containing an odd number of electrons. From this Lewis was led to the theory that the nonpolar valence bond is a pair of electrons occupying a position intermediate between the two atoms. This theory does not follow from the generalizations above by direct inference any more than the atomic theory can be inferred from the laws of chemical combinations but it appears to be the only explanation of these facts that any one can offer. Since according to Coulomb's law two electrons should exert a repulsion for each other, the pairing of electrons seems at first glance to be a bizarre idea indeed. In order to account for the peculiar behavior Lewis assumed the existence of a magnetic attraction between the electrons. One of the most striking of the experimental generalizations is (5) the fact that all atoms of elements of odd atomic number are paramagnetic while the atoms of most even numbered elements are not. Lewis has attributed a good deal of importance to the generalization that the ionizing potentials of the odd numbered elements are usually higher than the adjacent even numbered elements. Figure 1 is a curve showing the ionizing potentials of the first three periods of the elements according to Millikan and Bowen.[2] It must not be assumed however that magnetism is a simple, readily comprehended explanation of the pairing of electrons. Magnetism in the atom is intimately connected with the peculiar phenomenon of space quanti-

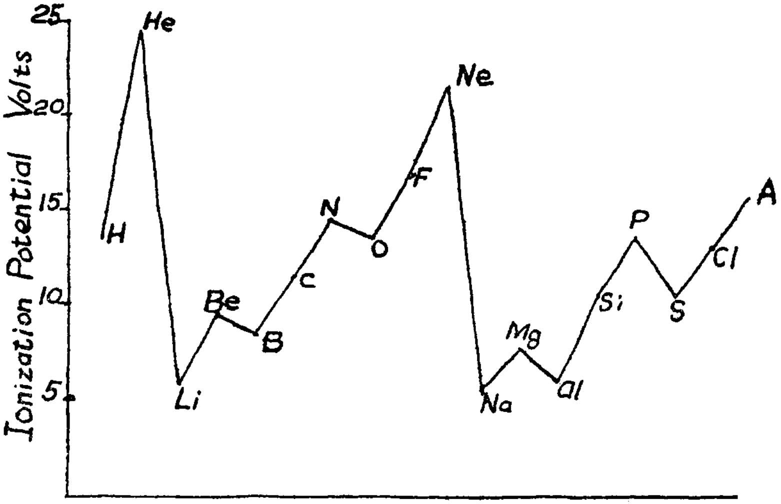

FIG. 1

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[2] Millikan and Bowen, Proc. Nat. Acad. Sci. **13,** 531 (1927). It will be noted that nitrogen and oxygen are reversed in the curve; likewise, phosphorus and sulfur. Nitrogen contains an odd number of electrons in the nucleus, while oxygen is anomalous in its magnetic properties. Unfortunately, the explanation is not applicable to phosphorus and sulfur.

zation. Instead of a random orientation with respect to the field simple paramagnetic atoms are oriented in parallel and antiparallel positions to the field. The parallel position is of course plausible enough but the antiparallel position seems more mysterious. A little reflection will show, however, that if the mass susceptibility is to remain constant that this partition between parallel and antiparallel must approach equality as the field is decreased to zero. This orientation gives rise to the peculiar results of the Stern-Gerlach experiment in which a beam of atoms passing through an inhomogeneous magnetic field is split into two components. Results have been obtained in this laboratory[3] (6) recently on atomic hydrogen, sodium and potassium, which show the typical behavior of paramagnetic atoms. A further difficulty in explaining this experiment is in accounting for the energy necessary to produce the orientation since the atom requires only 10^{-4} seconds to traverse the field. This energy is more easily accounted for if instead of the atom being oriented as a whole the electron itself possessed a magnetic moment and is oriented independently of the atom.

The magneton or magnetic electron has been invented repeatedly to account for atomic phenomena although it has not yet been discovered, i.e., its existence demonstrated by direct experiment. Parson (7) was one of the early writers to suggest the significance of the magneton in chemical valence. Recently Uhlenbeck and Goudsmit (8) have suggested that the electron spins on its own axis with a velocity sufficient to give it a magnetic moment $\left(\frac{eh}{4\,\pi\, mc}\right)$ equal to the Bohr magneton. The Bohr magneton is of course the unit magnetic moment which would be associated with an electron moving in an orbit with one quantum of angular momentum.

The spinning electron appears to have been an extraordinarily happy suggestion to both the physicist and the chemist. It furnishes a basis for Pauli's Exclusion Principle (9). The electron was formerly presumed to have three degrees of freedom and was

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[3] Laboratory of Physical Chemistry, University of Illinois.

assigned three quantum numbers, n, the "principle" quantum number locates the electron in its shell or group; 1 gives the number of quanta of angular momenta associated with the motion of the electron and m_l gives the component of angular momentum in the direction of an external magnetic field. Pauli assumes another degree of freedom connected with the spacial orientation of the spin axis and assigns a fourth quantum number $m_s = \pm \frac{1}{2}$, designating parallel and antiparallel orientations. Pauli's Principle states that no two electrons in an atom can have identical values for all four quantum numbers. Stated in another way this means that there will be a pair of electrons corresponding to identical values of the first three quantum numbers in the atom, but these two electrons will differ in that their spin axes are oriented in opposite directions to each other. In other words they will neutralize each other magnetically. Hence every atom with an odd number of electrons must contain at least one free magneton. Taken in connection with the possible values of the quantum numbers for the different shells,—Pauli's Exclusion Principle limits the total number of electrons possible in the atom and gives the arrangement of 2, 8, 8, 18, etc., together with the Main Smith-Stoner scheme of sublevels. It is an extraordinarily simple and comprehensive rule and in that sense may be said to be logically satisfying, in so far as any principle connected with the quantum theory can be logically satisfying.

It will be recognized by the chemist however that Pauli's rule is only a short hand way of saying what Lewis has assumed for many years as the basis of his magnetochemical theory (10) of valence. If the electrons are paired in the atom magnetically, it is easy to see how two unpaired electrons in different atoms may be coupled magnetically and form the nonpolar bond. The exclusion principle is therefore extended to molecules and Pauli and Somerfeld have even proposed to extend it to the conducting electrons in a whole crystal lattice of a metal. The chemist has been inclined to attribute this energy of formation of the electron pair to the magnetism of the electrons. The physicist says that this is not true; that the magnetic energy is so small as to be quite negligible. London (11) in a recent paper has shown that the energy associated with a pair of electrons, magnetically coupled between two atoms is due to a "resonance" effect discovered by Heisenberg (12). It results from what may be pictured as an oscillatory interchange of the electrons between the two atoms so that the electron appears to be a part of both atoms. This evidently corresponds to what the chemist means when he says a pair of electrons is shared between two atoms. This "exchange energy" is negative and binds the two atoms together if the electrons have their spin axes opposed so as to neutralize each other magnetically, but if they do not neutralize each other magnetically it leads to a repulsion between the two atoms. The energy of the molecule thus depends upon the magnetic pairing of the electrons and in dealing with anything so elusive as energy in a quantized system, it appears to the layman somewhat rhetorical to say that the energy depends upon the magnetism but is not magnetic in origin. At any rate the success of the paired electron theory in assigning valence structure to the hundreds of thousands of compounds in chemistry is so well known to chemists as to need no further recital here.

THE RULE OF EIGHT

The rule of eight appears to be almost as universal in its validity and as important in its consequences as the rule of two. Strictly speaking it should be stated as follows: every atom in a chemical compound tends to take on a configuration of its valence electrons, similar to that of the nearest inert gas. This is two for helium and eight for neon, argon, etc. The change from two to eight takes place somewhere in the middle of the second period of elements and it is possible that carbon and nitrogen sometimes form stable groups of six electrons. There are probably not many more exceptions to the rule of eight than to the rule of two. On the other hand the physical basis for the rule of eight seems to be more obscure than for Pauli's Exclusion Principle. However mysterious the Pauli Exclusion Principle may seem, it has the obvious physical basis of the pairing of magnetons. From the rule that the auxiliary quantum number 1 may not be greater than the principle quantum number decreased by one ($1 \leqq$

$n-1$), Pauli's Exclusion Principle limits the possible number of electrons for helium to two and the possible number for neon to eight. For argon and the other inert gases however no such limitation appears to exist, and we might expect that more than eight electrons would be found in the outermost group. The assignment of a definite number of energy levels and sublevels which are designated by the various combinations of quantum numbers must seem to the chemist a very arbitrary procedure although it is possible to predict these, presumably, by calculations from the Schroedinger wave theory. This has only been done for the simplest molecule, hydrogen, since the mathematical difficulties are very great for the more complicated atoms. The great importance for the rule of eight to the chemist is that it determines the possible chemical compounds. The vast majority of the predicted compounds have been made in the laboratory.

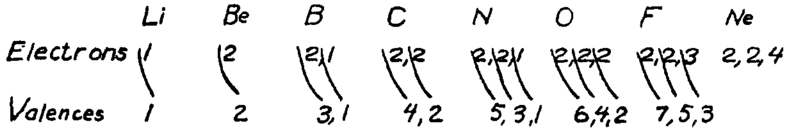

FIG. 2

The first attempt of the physicists to calculate possible valences for the various elements was made in connection with the Main Smith-Stoner scheme of sublevels aready referred to. According to this scheme in passing from an alkali metal at the beginning of a period of eight to the inert gas at the end of the period, electrons are added successively in the subgroups, of two, two and four. The idea proposed was that the lowest valence of an element would involve all of the electrons in the last subgroup; the next higher valence would include the electrons of the second subgroup and the highest valence would include all of the valence electrons. Reference to figure 2 will make this clear. Main Smith (13) claimed that this scheme agreed with the chemical evidence and Grimm and Sommerfeld (14) published a paper in which they apparently found a correlation. The agreement, however, is far from satisfactory. In the first place the fact that oxygen and fluorine show but one valence is entirely unaccounted for. Furthermore chlorine has a valence of one, nitrogen perhaps never has a valence of one, and boron does not have a valence of one. All three cases disagree with the scheme. On the other hand the rule of two will account in a very satisfactory manner for the behavior of these elements with the exception of the absence of a valence of one for boron. The rule of eight explains nicely the practical nonoccurrence of a valence of one for nitrogen.

Recently London (11) has discussed the valence of these elements in a very interesting paper. He is evidently thinking in terms of the old valence theory, in which an element has one valence toward oxygen and another toward hydrogen, which will prejudice the chemists against his ideas somewhat, since these old valence theories have proved inadequate. Also London talks in terms of heteropolar and homopolar valences, which we shall point out later is not a happy terminology. London makes one assumption which will evidently lead to radically different results from the Lewis theory, namely that, when a pair of electrons is shared between two atoms, one electron must be contributed from each atom. This leads him to the conclusion apparently that the chlorine in perchlorate ion shares seven pairs of electrons with the oxygen, thus doing away with the rule of eight. It is not clear why chlorine should not show a valence of seven towards other elements such as hydrogen if it does so for oxygen. The chemist is inclined to regard the combination of oxygen and chlorine in perchlorate ion as analogous to the combination of hydrogen and nitrogen in the ammonium ion and will be loathe to abandon the rule of eight for this compound. The most interesting part of London's paper is perhaps his attempt to show why nitrogen, oxygen and fluorine do not have as many different valences as phosphorus, sulfur and chlorine. He does this by showing that the Pauli Exclusion Principle taken together with the possible quantum numbers for nitrogen, oxygen and fluorine limits the number of unpaired electrons in these atoms to three for nitrogen, two for oxygen and one for fluorine. This is undoubtedly correct but if we accept his principle that a pair of electrons, belonging to one atom originally, cannot act as a valence bond then oxygen cannot form a complex analogous to the ammonium ion, whereas the H_3O^+ ion certainly exists in solution. The chemist would prefer to assume that any pair of electrons can act as a bond and explain the nonexistence of higher valences for nitrogen, oxygen and fluorine as being due to energy considerations. The chemist does not require a quantum prohibition to explain the non existence of nitrogen pentachloride knowing as he does the properties of nitrogen trichloride. He would rather have an explanation for the instability of nitrogen trichloride. London's explanation of nitric acid as a polar hydroxide is somewhat far fetched. His explanation of the absence of univalent nitrogen is not obvious but he relates it to the fact that the spectroscopic ground term for nitrogen indicates three unpaired electrons. It is evident that London's reasoning would wipe out all differences in degree of stability between chemical compounds and substitute the hard and fast discontinuities of the quantum theory. There is much justification for this view from what we know about the atom and it may be that the rule of eight is a sort of chemical correspondence principle which seems to work because our methods of measuring chemical properties are essentially qualitative. The fact that the rule of eight works well is not absolute proof of its correctness; the old valence theories could be formulated in rules which had a wide applicability. On the other hand a rule which works for the hundreds of thousands of compounds with so few exceptions as the rule of eight is not to be discarded lightly and the chemist who has observed the variation of properties through a series of similar molecules will be loathe to discard the idea of differences of degree in stability. For the present at least the chemist will be inclined to continue to use the the rule of eight for what it is worth.

THE RULE OF FOUR

The rule of eight leads to the rule of four, that the maximum number of atoms which may be attached to a central bond by nonpolar bonds is four. This is obviously a limiting rule only.

Under the old valence rules the emphasis is upon the number of atoms linked to the central atom. In the new theory an atom is "saturated" when it has eight electrons regardless of the number of atoms to which it is linked. This is one of the most radical differences between the old and the new theories and greatly increases the number of stable molecules possible. This rule makes possible such things as bivalent carbon and univalent oxygen which were absurd under the old theory. This gives us tetrahedral symmetry and the beautiful stereochemistry of Van't Hoff which has been one of the triumphs of organic chemistry. Recently x-ray studies of pentaerythrite have indicated that the carbon atom is at the apex of a pyramid with the four carbinol groups forming the base. Weissenberg (15) and Henri have made much of this, claiming that the stereochemistry is all wrong and even Willstätter seems to have been impressed with the theory. The burden of proof is upon the new theory and the x-ray evidence in the case of pentaerythrite is disputed. The fact that methyl chloride and chloroform have electrical moments, while carbon tetrachloride does not, would seem to be almost convincing evidence for the tetrahedral structure of the carbon tetrachloride molecule.

POLARITY

While it is important to account for the structure of the known chemical compounds by a theory of valence, it is of even greater practical importance to predict the chemical properties and reactivity of molecules once their structure has been assigned. In the old valence theories a bond was a rigid unyielding link, the same whenever it was found. Now that we picture the bond as a pair of electrons held between atoms of different nuclear charges, we begin to see how the properties of the bond must vary from one molecule to another. One of the most important of the factors which determine the character of a bond is the degree of polarity. We may remark parenthetically that the use of the terms homopolar and heteropolar does not seem to make for clearness in discussing the structure of molecules. We have polar compounds such as sodium chloride in the crystal state where the sodium is a positive ion and the chlorine is a negative ion and no molecules appear to exist. All other molecules appear to be made up of atoms joined together by nonpolar bonds, that is, pairs of electrons.[4] The terms positive and negative have been used in so many ways in connection with the properties of molecules that they are likewise ambiguous. The words may be used in two connections. In the first place, we may wish to designate the charge on an ion as the chlorine in sodium chloride. We can avoid ambiguity here by saying that the chlorine is negatively charged. The terms positive and negative may also be used to characterize the field surrounding the atom. At a distance the field of a neutral atom is zero, but the chemical properties depend upon the field in the immediate neighborhood of an atom. With positive and negative charges grouped together in an atom but separated from each other by finite distances we obtain complex fields which vary as the inverse cube or higher powers of the distance from the atom.[5] The field in the neighborhood of all atoms except the inert gases is positive, that is, the atom will attract electrons. The higher the effective nuclear charge[6] the more positive the atom. Thus sodium would be designated as weakly positive and chlorine as strongly positive. This is contrary to the current usage in inorganic chemistry where chlorine is usually termed negative or electronegative, but the current usage arose before the discovery of the electron and there seems to be no good reason for adhering to an illogical terminology.

The term electroaffinity was used many years ago to characterize this important property of an atom, i.e., its field at small distances, and there seems to be no better term available for the purpose.

The ionizing potential of an atom appears to be a rough measure of its electroaffinity. Elements whose ionizing potentials are

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[4] Thus sodium chloride in the vapor state is apparently a molecule with the sodium ion joined to the chlorine by a pair of electrons. London quotes Franck as having advanced the idea that the hydrogen halides are nonpolar in the pure state, but this is scarcely a new idea to the chemist.

[5] Thus it can be shown from Coulomb's law that the field due to a dipole varies as the inverse cube of the distance.

[6] The effective nuclear charge is equal to the atomic number diminished by the screening effect or repulsive action of all the other electrons of the atom.

above ten volts are distinctly non-metallic in character while those whose ionizing potentials are much below are characteristic metals. Hydrogen is thus clearly classified with the halogens rather than with the alkali metals. The electroaffinity of the atoms is the most fundamental factor in determining the chemical properties of compounds, especially in inorganic chemistry. Many of the more characteristic properties of molecules depend upon the combination of two atoms with considerable difference in electroaffinity. If the difference is great enough we may get a "completely polar" substance like sodium chloride where the molecule is split into ions and the analogy to a dipole has disappeared. On the other hand, in a large number of molecules such as water and hydrogen chloride there is only a slight degree of polarity which may be confirmed by the calculation of the electrical moment from the temperature coefficient of the dielectric constant. Too much significance must not be given to the electrical moment in the gaseous state. It is not possible for instance to predict from it the dielectric constant in the liquid state. We can see how this comes about by considering the water molecule. If the water molecule had a symmetrical structure (atoms in a straight line) its electrical moment would be zero. Most of the important properties due to polarity appear only in the liquid state or in solution. Where we may expect a slight degree of "internal" polarity to be greatly augmented by the influence of adjacent molecules.

Atoms or groups of atoms of high electroaffinity are conspicuously oxidizing and acid forming in their behavior. Atoms of low electroaffinity are base-forming and reducing. The relation oxidation and neutralization is shown by the following type reactions.

(a) $Na + \frac{1}{2} Cl_2 \rightarrow Na^+ + Cl^-$
(b) $NH_3 + HCl \rightarrow NH_4^+ + Cl^-$
(c) $HNO_3 + Sn \rightarrow SnO_2 + NO_2 + H_2O$

(a) is a typical oxidation reaction; an electron is transferred from the sodium to the chlorine.

(b) is a typical neutralization; a hydrogen ion is transferred from the chlorine to the ammonia. But the hydrogen ion is the proton or positive electron and the transfer of positive electricity in one direction is the same as the transfer of negative electricity in the opposite direction. (a) and (b) are therefore completely analogous. (c) appears somewhat different in that a neutral oxygen atom is transferred but if we remember that the oxygen atom is "deficient" in electrons it becomes analogous to the other two reactions; from the standpoint of the transfer of electricity. By deficient in electrons we do not mean that the oxygen is not electrically neutral but rather that it carries but six electrons while it seeks a complete group of eight. When oxygen and nitrogen combine with each other or with carbon there is usually a deficiency in electrons, i.e., there are not enough electrons to give each atom a complete group of eight without sharing more than one pair of electrons between two atoms. Such a group usually behaves as if "unsaturated" and strongly positive. The only elements which can replace oxygen in a reaction of type (c) are those which form double bonds. Nitrogen and sulfur are known to act in this way but carbon apparently does not.

POLARITY IN ORGANIC REACTIONS

When we attempt to predict the relative positivity of two atoms joined by pairs of electrons we must recognize a peculiar effect. The displacement of the electrons from the less positive to the more positive atom or group may more or less completely compensate the difference in positivity. At first thought we might expect the positivity to be exactly compensated, but the quantum theory would lead us to expect the actual displacement would be such as to produce either over or under compensation and the facts of organic chemistry appear to confirm this. In order to decide the relative positivity of neighboring atoms then we shall have to scrutinize each individual case.

It may be remarked here parenthetically that the designation of positive and negative atoms in an organic chain by plus and minus symbols appears to be undesirable since it suggests the positively and negatively charged ions of inorganic chemistry.

We certainly have no degree of polarity in ordinary organic compounds which approaches that of sodium chloride.[7]

Since we cannot detect slight polarities by physical means we are forced to rely on chemical reactions. The most reliable reagent for polarity appears to be the Grignard reagent. The large number of compounds with which the Grignard reagent reacts and the speed of the reaction are characteristics which are suggestive of ionic reactions. Indeed it has been suggested (16) that the compound RMgX is a typically polar compound in both the Mg-R and the Mg-X linkages. It is well known that ether solutions of the Grignard show considerable electrical conductivity (17). In the hope of demonstrating by physical means the extent of the polarity of the bond between a metal and an organic radical, numerous experiments in the electrolysis of compounds in which this bond is present, have been made by Dr. J. M. Peterson working with the author in the Laboratory of Physical Chemistry at the University of Illinois.

Repeated attempts were made to isolate the products of electrolysis from ether solutions of magnesium ethyl iodide and magnesium phenyl iodide. At the cathode magnesium is precipitated as might be expected but the liberation of iodine at the anode masked completely any effects due to the organic radical, although Gaddum (18) has apparently been more successful in similar experiments.

In order to avoid the effects due to the highly ionized halogen, zinc diethyl was substituted for the magnesium compounds in these experiments. Any inference which can be drawn as to the polarity of zinc diethyl must apply in some measure to the Mg-R linkage since the two metals are undoubtedly very similar in their behavior. Hein (19) has shown that sodium ethyl dissolved in zinc diethyl is a conductor but that pure zinc diethyl is not. This latter conclusion was confirmed by us. Zinc diethyl when carefully prepared and purified by distillation in a dry inert atmosphere does not show an appreciable conductivity. If, however, a small amount of pure dry ether is distilled into the cell

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[7] For a discussion of the properties of highly polar compounds see Latimer and Rodebush, J. Am. Chem. Soc. **42**, 1419 (1920).

containing the zinc ethyl a specific conductivity between 10^{-5} and 10^{-4} is at once obtained and using 110 volts appreciable quantities of zinc may be deposited on the cathode. The hydrocarbons which must be formed at the anode are of course dissolved in the solution and not easily detected in small amounts. Since the ether has no conductivity the ions which carry the current must come from the zinc diethyl and must be $(ZnC_2H_5)^+$ and $C_2H_5^-$ (possibly Zn^{++}).

Undoubtedly sodium ethyl if it could be brought into a liquid condition would show the ionization and conductivity of a typical polar fused salt. Magnesium and zinc however, belong to a group of metals of which the two lower members cadmium and mercury show slight ionization in combination with halogen. Magnesium and zinc show a decided tendency to coördinate auxiliary valence groups as does cobalt in the cobalt amines. Ionization in the salts of these metals appears to take place readily only when the anion is replaced by a molecule of the solvent. The bond between the zinc and ethyl radical is essentially a nonpolar linkage and it is only when the oxygen of the ether is present to offer its electrons as a substitute, that the zinc ion lets go of the ethyl group. Since the dielectric constant of the solution is low the separation of the ions is not favored and the conductivity will be low unless ions are present in great numbers. A much greater ionization could be expected if we could introduce a solvent like ammonia or water without disturbing reactions.

The same conclusions must apply to the alkyl or aryl magnesium halides. The Mg-X bond must possess a considerable degree of polarity. The negatively charged ion R: where R is a saturated aliphatic hydrocarbon radical is the most basic of any group that we know, using the term basic in the sense of readiness to share electrons. Magnesium has a considerable affinity for electrons and the bond Mg-R is to be regarded as distinctly of the non-polar type. If this bond were strong no dissociation could occur. But the effective nuclear charge of the magnesium atom is only 2^+ and the bond does not possess the rigidity of a carbon to carbon bond. Dissociation may take place especially if the magnesium atom transfers its attraction to the electrons of the oxygen of the ether molecule. The fact that the Grignard reagent combines with two molecules of ether is evidence that this tendency exists. The amount of the dissociation is a statistical property of the relative readiness with which the organic radical ion and the oxygen of the ether share electrons with the magnesium atom. Since oxygen is less basic than nitrogen, and much less basic than carbon, we should expect the dissociation to be slight. However, the dissociation need not be large in order for a reaction of an ionic character to proceed rapidly. For instance aluminum chloride reacts rapidly with water although neither substance is highly ionized. From the foregoing it might be predicted that the Grignard reagent would be more reactive in ether than in a more inert solvent such as benzene, for the benzene molecule would not attach itself so readily to the magnesium ion. This prediction appears to be borne out by the facts.

The simplest reaction that the Grignard reagent undergoes is the addition of acid hydrogen to the basic hydrocarbon, a reaction that is exactly analogous to neutralization except that the product formed is a hydrocarbon instead of water Most other reactions can be classified as the addition of the negatively charged hydrocarbon radical to the positive atom of an unsaturated pair, a reaction that is analogous to the hydrolysis of aluminum chloride.

Typical examples of such pairs are $C=O$, $C=N$, $N=O$. Here in each case the Grignard radical adds to the first atom of the pair. The part played by the magnesium and halogen are of no significance since they are essentially ions. It will be noted that in each case the second atom of the group has the higher nuclear charge and should be the more positive but the electron displacement has more than compensated for the difference. Thus the carbon atom in $C=O$ is the more positive atom. It is very striking that while we began by using the term positive to mean exactly the opposite of its common use in inorganic chemistry we end by finding our usage to coincide exactly with the long established usage of organic chemistry.

There appear to be no important exceptions to the above rule of behavior of the Grignard reagent and it constitutes a convincing proof of an appreciable degree of polarity in organic linkages. On the other hand the Grignard reagent does not add to the $C=C$ bond and the reason here seems to be that this bond is symmetrical and the deficiency of electrons being divided equally between the two atoms is not great enough in either to pull in the R: group and bring about a reaction.

The case of the ethylenic linkage becomes particularly clear when we consider a conjugated system such as butadiene where 1, 4 addition usually takes place.[8] The reason for this can be readily seen. If we regard the 3, 4 linkage simply as a group deficient in electrons then its effect on the 1, 2 group is to displace the electrons toward the second carbon atom leaving the first carbon atom positive. In a similar way the 1, 2 linkage causes the fourth carbon to become positive by displacement of electrons toward the third. Atoms carrying electrons will then tend to add to the two end carbons. As soon as the addition takes place the excess electrons in the 1–2 and 3–4 bonds will shift to the 2–3 position. Thus the Grignard reagent may be made to react with the ethylenic linkage in some conjugated systems.

The theory of alternating polarities of the atoms in a carbon chain does not appear to be substantiated by the experimental evidence. Instead of assuming that the carbons in the benzene ring have alternately six and eight electrons, it seems much more reasonable to assume a conjugation of ethylenic linkages. That binary groups do not add 1, 4 as in the case of butadiene may be explained by assuming that for the addition of the binary group the 1, 4 atoms must come in juxtaposition and this would be prevented by the rigidity of the six membered ring.

REACTIVITY IN ORGANIC COMPOUNDS

The difficulty of explaining reactivity in organic compounds is illustrated by the following typical case. A halogen attached to the carbon of a double bond is very inert; while a halogen at-

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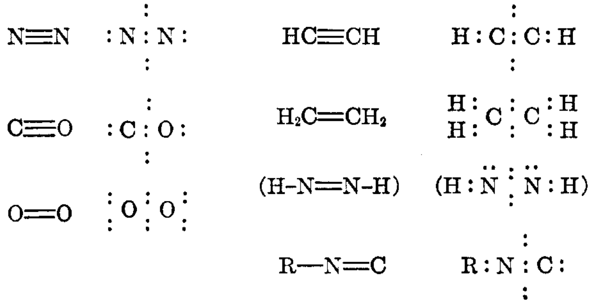
[8] Lowry (16) writes butadiene in the following manner $CH_2^+ = CH^- - CH^+ = CH_2^-$. If we were to use plus and minus signs, we should prefer $CH_2^+ = CH^- CH^- = CH_2^+$.

tached to a carbon adjacent to the double bond shows a high reactivity. The first case is plausible. The halogen can only be removed as a negative ion and the carbon holds on to the electrons. The second case seems at first thought contradictory.

There seems to be no justification for any theory of alternating polarity of the carbon atoms. What we are forced to assume is that under strain from the action of opposing groups (here the halogen and the double bond) oscillations in the electron systems are set up. In the case of the halogen attached to a double bond, these oscillations are not of sufficient amplitude to rupture the bonds. In the allyl chloride on the other hand with a greater inertia the frequency of oscillation corresponds to that of the molecular bombardment and the amplitude of oscillation becomes great enough for the halogen to break loose.

MULTIPLE BONDS

There appears to be a great deal of confusion in the minds of many as to whether a double bond is twice as strong as a single bond or whether Bayer's strain theory holds a multiple bond should behave as if unstable. The question appears to be solved by considering the two classes of multiple bonds.



$N\equiv N \qquad :N\overset{:}{\underset{:}{:}}N:$

$C\equiv O \qquad :C\overset{:}{\underset{:}{:}}O:$

$O=O \qquad \vdots O \vdots O \vdots$

$HC\equiv CH \qquad H:C\overset{:}{\underset{:}{:}}C:H$

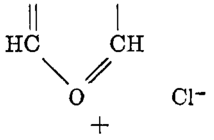
$H_2C=CH_2 \qquad \begin{matrix}H:\\H:\end{matrix}C\,\vdots\,C\begin{matrix}:H\\:H\end{matrix}$

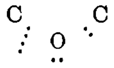
$(H\text{-}N=N\text{-}H) \qquad (H:\ddot{N}\,\vdots\,\ddot{N}:H)$

$R-N=C \qquad R:N\overset{:}{\underset{:}{:}}C:$

The first group are characteristically inert and stable while the second group behave as if unsaturated. Evidently two small atoms may combine to form a stable molecule but if a third and fourth atom are attached a strain is produced. The fact that the carbide ion $C\equiv C^{--}$ in sodium and calcium carbide is stable while the less polar silver and copper acetylides are explosive agrees with the above generalization. The structure for carbon monoxide resembles that of the nitrogen molecule; the two atoms are connected by three pairs of electrons. This structure accounts for the saturated behavior of the gas. It might be supposed that the molecule would be unbalanced electrically. The molecule does show a small electrical moment but due to overcompensation which has been mentioned previously the electrons are probably shifted toward the oxygen and the carbon is probably the more positive atom. The cyanide (isocyanide) ion should have a structure similar to carbon monoxide.

While not the most important, one of the most interesting applications of the electron theory of valence is in explaining the structure of compounds like the carbon monoxide and isocyanide above which were quite impossible on the old valence theories. The flexibility of the electron theory leads to peculiar valences such as univalent oxygen in the amine oxide and bivalent hydrogen.[7] One of the interesting structures commonly accepted by the organic chemist is trivalent oxygen as found in the pyrillium ions.





This structure is not absolutely confirmed by the experimental evidence but it is a possible one. It would be a serious contradiction to London's theory as to the valence of oxygen. The organic chemists apparently have not realized that this oxygen is in a radically different state from oxygen in any other compounds except perhaps carbon monoxide.

The possibility of carbon forming a stable shell of six electrons has been mentioned. The structure

$$\mathrm{RO}:\overset{..}{\mathrm{C}}:\mathrm{OR}$$

is a possible one for the compound ($C(OR)_2$) which Scheibler (20) claims to have prepared.

It will be seen from the foregoing that the electron theory of valence is capable of being brought into correspondence with an enormous number of experimental facts. The same may of course be said for the quantum theory of the atom. On the other hand it seems impossible at present to get rid of arbitrary postulates in either theory. These postulates must of course eventually become the same for both theories. It is evident at last that physicist and chemist are observing the same atom and the chemist may be confident that his observations will be given more consideration in theories of atomic structure in the future than they have been given in the past.

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