ELECTRONIC THEORIES

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Unless we are willing to take the view of Bishop Berkeley that we know nothing which occurs outside of our own bodies and that our senses and the testimony of others are untrustworthy, we must consider that it is the function of science to acquire the best knowledge possible about everything with which our intellectual lives are concerned. In this category I include feeling and will of the old philosophy and not merely physics and biology. Hypotheses and theories are not merely temporary tools for the direction of our experimental work, but are the necessary method by which we gain a better insight into the character of a real, intelligible, and dependable universe, which is logically interrelated in all its parts.

In discussing electronic theories, therefore, I wish to pick out, so far as I can, the origin of those ideas which still guide us in the development of the subject. As with all other branches of science, the first ideas were based on simple observations and were crude and partly erroneous. The grave danger, today, is that a scientist who is working in some narrow part of this field, such as the beautiful and accurate conclusions from wave quantum mechanics, x-ray analysis, thermodynamics, or statistical mechanics, is liable to disregard results obtained in the older fields of valence, structure of organic compounds, optical activity, and molecular volumes. Each of these must be carefully checked by the others before we can hope for a true picture of the whole field.

I cannot refrain from stopping for a moment to remark the same danger in economics and in international relations. Manufacturers and bankers who think that they can base their operations solely on the motive of profit and disregard the motive of service, and statesmen who think they can consider exclusively the interests of their own nation and disregard the interests of other nations, are likely to be brought up with a jolt, as manufacturers have been in our six years of depression, not yet over, and as the world was in the Great War.

Some of the ideas on which our electronic theories rest go back more than

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two hundred and fifty years, and some hypotheses which seemed at that time wholly incompatible have been reconciled in the twentieth century. Such a result is not infrequent in physics and chemistry.

In what follows an attempt is made to state the origin of the ideas which seem most important and to tie them together into a logical, comprehensive system, pointing out where earlier ideas have been imperfect or confusing.

LIGHT

1680–1700. Near the close of the seventeenth century Newton proposed his "corpuscular" (atomic) theory of light, and Huyghens proposed the undulatory theory. It was not until the twentieth century that it was demonstrated that each theory is partly right.

1818. Fresnel showed that a beam of monochromatic light, separated into two parts which are brought together after travelling paths of different lengths, give alternate light and dark bands. He concluded that light is an undulatory motion in a hypothetical medium called the ether.

1814. Fraunhofer discovered and mapped many of the dark lines of the solar spectrum without understanding their significance.

1860. Bunsen and Kirchoff showed that the light emitted by sodium in a Bunsen flame or by iron in an electric spark has the same frequency (wave length) as the light absorbed by these elements in the gaseous state. This gave a satisfactory explanation of the Fraunhofer lines and has revealed the composition of the sun and stars and demonstrated the unity of the universe.

More than half a century later, Planck, Bohr, and others developed the theory that light consists of photons having characteristic frequencies, and that a photon of the right frequency may impart its energy to an electron in the shell of an atom and cause it to rise to an orbit further from the nucleus; also that the electron will, later, fall back to its original orbit, emitting a photon of the same frequency as that of the photon taken up or two or more photons of a smaller frequency.

The long waves of Hertz used in wireless telegraphy, the x-rays of Röntgen, the α-, β-, and γ-rays of Becquerel, the Curies, and Rutherford, and the "cosmic" rays of Kohlhörster, Millikan, and Compton need only to be mentioned here.

In an important sense photons may be thought of as the connecting link between matter and energy.

ELECTRICITY

1729. Gray showed that metals (elements whose valence electrons are loosely held, allowing them to pass easily from one atom to another through a wire) conduct electricity, while glass, sulfur, and resins do not.

1735. Dufay distinguished between vitreous electricity, obtained by rubbing glass, and resinous electricity, obtained by rubbing amber and other resinous substances, and found that bodies charged with electricity of the same kind repel each other, but that if charged with different kinds they attract each other. This is the most fundamental postulate in all electronic theories, but the question of how bodies not in contact can attract or repel each other has not been solved.

1747. Franklin, in a letter to Peter Collison in England, suggested his "one fluid" theory, calling bodies which contain an excess of the "fluid" positive and those with a deficiency negative. He was dealing with electrons in his experiments and his theory was fully justified, but through a mistake in interpreting his experiments he called bodies charged with resinous electricity (containing an excess of electrons) negative.

In 1786 Galvani discovered current electricity, and about 1800 Volta invented the first primary batteries.

1790. Lavoisier came to think of oxygen as the central element of chemistry and defined acids as the oxides of non-metals, bases as oxides of metals, and salts as compounds of acids and bases.

Davy, making use of a battery devised by Volta, prepared metallic potassium; in 1807 he proposed (9) an electrochemical theory in which oxygen was positive toward non-metals and negative toward metals. Berzelius (4) developed this into the old electrochemical theory, which dominated chemistry for thirty to fifty years. In salts the base was positive and the acid negative; $\overset{+}{\overset{+}{\mathrm{Ca}}\overset{-}{\mathrm{O}}}\cdot\overset{-}{\overset{-}{\mathrm{S}}\overset{+}{\mathrm{O}_3}}$. After this theory fell into disrepute for the last half of the nineteenth century, new electrochemical theories retaining some of the ideas of the older theory were proposed by Arrhenius, Abegg, Lewis, and Kossel.

1831. Faraday demonstrated the interconvertibility of electrical and mechanical energy and formed very clear ideas about electrical fields and magnetic lines of force. Maxwell (43) in his *Electricity and Magnetism*, published in 1873, translated Faraday's ideas into accurate mathematical language and laid the basis for the methods used by electrical engineers ever since. His object was "to construct a theory of electricity in which action at a distance should have no place." He succeeded by means of the theory of an ether. Weber and Kohlrausch had previously demonstrated the remarkable fact that the ratio of the electromagnetic and electrostatic units of electricity is the velocity of light. This fact and the studies of Maxwell gave the electromagnetic theory of light; from that time on it has been necessary to consider light and electricity as two phases of the same subject. To these we must now add atomic phenomena, so that mechanical energy, light, electricity, and chemical atoms are inseparably connected with each other.

ATOMS

1807. Dalton first gave to the theory that material substances are composed of minute, individual particles, a form which connected it with their quantitative composition and made it practically useful. The theory was known to the ancients as a philosophical speculation, but no one had been able to connect it accurately with experimental observations.

Dalton's crude and partly erroneous system, which for many years left many chemists in doubt whether true atomic weights could ever be determined, was developed by steps so well known that they need only to be mentioned—Avogadro's law, the law of Dulong and Petit, the isomorphism of Mitscherlich, and the Periodic System of Newlands, Mendeléef, and Lothar Meyer. The visit of Cannizzaro to Karlsruhe in 1858, where he made such a convincing presentation of the law of Avogadro that the adherence of German chemists was secured, must be recognized as one of the factors in the rapid advances which followed.

The democratic methods of research developed in Liebig's laboratory, the "type" theory of Gerhardt and Laurent, and Frankland's theory of valance had already laid the foundation for a rapid development of organic chemistry. Cannizzaro's visit came the same year that Couper and Kekulé proposed, independently, the theory of chains of carbon atoms, and for the thirty years that followed hundreds of students flocked to Germany to study chemistry. Pasteur had already discovered the optical dissymmetry of tartaric acid and had prepared the way for the thought of Le Bel and van't Hoff that the four groups attached to a carbon atom are more or less held in a somewhat rigid, irregular dissymmetry about it. This led, further, to the thought of Wislicenus that doubly united carbon atoms and rings give a *cis* and *trans* isomerism. The return of foreign chemists from Germany to their homes, where they established new centers of research, and the publication in German journals of articles from other countries, and especially from America, gave an era of international coöperation in science never before equalled.

Unfortunately, since the World War, an era of supernationalism, so dangerous for international relations and so disastrous for the world's economic progress, finds its counterpart in science. Each nation thinks that it must develop its own scientific literature as independently as possible; Holland, Germany, and France follow Kossel's theory of intramolecular ions, while American and English chemists follow G. N. Lewis' idea of shared electrons, and many of them are doubtful about intramolecular ions.

Kossel and Lewis proposed their theories quite independently in 1916, but the theories rest on a common background and some of their details are identical. Soon after, the two men were on opposite sides in the great conflict. When we remember the confused and conflicting systems of atomic weights during the first half of the nineteenth century and how these were reconciled in a single system which has not been questioned for seventy-five years, we may feel sure that our electronic theories will be fused into a consistent, comprehensive whole. May we not take that as an omen that Eden and Hitler, who were in trenches opposite each other across the battle line, may help to build that permanent peace which we all so earnestly desire? All sensible men now see that war in the twentieth century is a senseless and useless anachronism and, in spite of the reactionary tendencies of Japan and Italy, I have the faith to believe that the statesmen of the world will consolidate a peace in which all nations must be considered as equals. The unification of electronic theories is the work of hundreds of individuals. The new world order growing before our eyes is the work of thousands, and we as scientific men must see our obligation to "do our part" in this great coöperative and democratic undertaking.

1834. Faraday (13) discovered the fact that if the same electric current is passed through a series of solutions of electrolytes, the quantities of the elements liberated at the electrodes in each solution are proportional to the atomic weights of the elements. It should be remembered that at that time physicists and chemists were not very confident that the accepted atomic weights were really proportional to the weights of the actual atoms. Faraday drew no theoretical conclusions.

Helmholtz (22) drew, for the first time, the logical conclusion that there are two equal and opposite atoms of electricity. Such an idea was quite foreign to the thought of the chemists and physicists of that time. The negative electron was not discovered until 1897 and the positron in 1933.

1878. Crookes (8) had discovered the cathode rays, which are a stream of electrons, shortly before, and had demonstrated that they have mass and an electrical charge.

J. J. Thomson (92) and Kaufmann (25) discovered the electron in 1897.

Michelson and Morley (45; see also 46), in 1886–87, demonstrated that the velocity of light is independent of the direction in which the earth is moving. This is inconsistent with the theory of an all-pervading ether as the medium for the transmission of light, and was one of the reasons which led Einstein to propose his theory of relativity (10).

1901. Planck (74) proposed the theory that radiant energy is emitted, transmitted, and taken up only in definite units which he called quanta. This theory was later developed by Planck, Einstein (12), and others.

Planck's quanta may now be defined as atoms of radiant energy and are identical with photons and with Newton's corpuscles of light. They are of an infinite variety, each having a definite frequency, ν, found by dividing the velocity of light, 3×10^{10} cm. per second, by the wave length of the photon, and a definite energy, $h\nu$, in which h is Planck's constant, 6.5×10^{-27} erg seconds.

Einstein (11) in 1905 also made the statement, "The mass of a body is a measure of its energy content. If this energy changes by L, the mass changes by $L/9 \times 10^{20}$, the energy being measured in ergs and the mass in grams." The denominator of the fraction, 9×10^{20}, is the square of the velocity of light.

This ratio between mass and energy may also be stated by saying that one gram is equal to one erg multiplied by the square of the velocity of light.

These theories, together with the discovery of radium by the Curies, the disintegration of atoms by Rutherford, the transmutations of atoms by many chemists and physicists, of isotopes by McCoy, Boltwood, Thomson, and Aston, of the interferences of protons and electrons similar to the interferences of waves of light, the demonstration by Rutherford (77) that an atom consists of a small nucleus with a multiple positive charge, surrounded by electrons, and the discovery of the positron by Anderson (3) have given in the twentieth century quite new concepts about the universe in which we live. The only ultimate entities about which we can speak with some assurance are protons or neutrons, electrons, positrons, and photons. This recalls how Ostwald at St. Louis in 1904, after his genial remarks about a lecture by van't Hoff on atoms, picked up a piece of chalk and wrote under "Radioactivity," "explodirt," and under the whole, "Energie."

G. N. Lewis (40), when he was teaching a class in elementary chemistry in 1902, seems to have made the first attempt to connect electrons with chemical phenomena by means of his first crude sketches of the "cubical" atom. He thought his attempt too speculative, however, and it was not until fourteen years later that he published his theory.

J. J. Thomson (93) in 1904 gave the first published electronic theory of chemical combination. He supposed that an atom consists of a uniform sphere of positive electrification and that electrons within such a sphere arrange themselves according to their attraction toward the center and their repulsion from each other. This proposal was accompanied by a careful mathematical analysis. The incident illustrates the uselessness of mathematics when the postulates employed are wrong.

The fundamental idea of the static attraction between atoms when an electron is transferred from one atom to another is still valid, however, for isolated atomic ions, but the use of the hypothesis to explain homoöpolar unions, by Falk and Nelson, Fry, Noyes, and others, delayed the acceptance of the theory of G. N. Lewis.

1904. Abegg (1) proposed his system of "principal" and "contra" valences, e.g., for chlorine, one principal (negative) valence toward hydrogen and seven contra (positive) valences toward oxygen. This has some resemblance to the old electrochemistry and evidently had a great influence on Kossel and Lewis in the development of the theories which they proposed in 1916. At the close of his paper Abegg proposed an electronic interpretation.

1911. Rutherford (77), by a study of the scattering of alpha particles shot through a thin film of gold, demonstrated that the positive nucleus is small and is surrounded by electrons. This has been accepted as the basis for all subsequent theories of the electronic structure of atoms.

1913. Bohr (5) proposed his theory of atoms as consisting of positive nuclei surrounded by rotating electrons arranged in groups at successive energy levels. In the heavier atoms these groups contain, when complete, 2, 8, 18, and 32 electrons. Each noble gas contains in its outer group 8 electrons, and the next atom in the Periodic System begins a new group with a single electron. By combining this with the quantum theory of Planck and Einstein, which is now interpreted by means of photons, Bohr was able to give an explanation for the Rydberg, Balmer, Lyman, and other series of spectral lines.

In some of its details Bohr's theory has not been entirely satisfactory and it has been replaced by, or, speaking more accurately, it has been developed into the wave quantum mechanics. It still remains the only satisfactory mechanical picture that we have for the relation between the electrons and nuclei of atoms and molecules. It is of especial value because it emphasizes the fact, which no one questions, that each electron retains its identity and does not merge with other electrons in any ordinary chemical process.

1915. Parson (71) published a paper entitled, "A Magneton Theory of the Structure of the Atom." Owing to the medium of publication, which was occasioned by the difficulty of securing the publication of a long theoretical paper, Parson's paper has not received the attention which it deserves. Lewis refers to it several times in his book on valence and acknowledges his indebtedness to Parson for some of the ideas which he used.

1916. Kossel (30) proposed an electronic theory of the structure of atoms and molecules based on Abegg's principal and contra valences and Bohr's theory of atomic structures. This was proposed in Germany at the same time that Lewis' theory was proposed in America. The two theories were developed independently but have a common background, causing them to have a number of identical ideas. Indeed, many chemists seem to think that there is little difference between the two theories.

The most significant principles in Kossel's theory are as follows:

1. All elements after helium have an inner group of electrons, called by Lewis the *kernel*, which has the structure of the next preceding noble gas.

2. The electrons which take part in ordinary chemical reactions are situated outside the kernel. It is now recognized that in the longer periods there are two energy levels outside of the kernel for some of the atoms and that in some atoms electrons may be transferred from one of these levels to the other, e.g., for iron.

3. Electrons may be transferred from one atom to another, the atom losing an electron becoming positive and the one receiving it becoming negative.

4. Elements just above a noble gas lose electrons easily; those just below gain them easily.

5. Elements of the first two periods may lose all their valence electrons. Chlorine may become heptapositive and sulfur hexapositive. This is a very important difference from Lewis' theory and a most objectionable feature.

6. Atoms are held in combination as intramolecular ions. Carbon is negative in methane and positive in carbon tetrachloride.

7. No definite location for the valences of atoms is attempted. The theory furnishes no explanation for optical dissymmetry or *cis-trans* isomerism. Some of the later developments of Lewis' theory do this.

8. In papers published in 1919 and 1920, Kossel (31) discusses homoöpolar compounds at some length and presents some ideas which approach those of Lewis closely.

Georg Hahn (19) has recently made an attempt to account for homoöpolar unions on the basis of Lewis' theory but has shown little understanding of the way in which the theory has been developed in America and in England.

1916. G. N. Lewis (39) published in the same year as Kossel an electronic theory of the structure of atoms and molecules, which he had been considering for fourteen years and had often discussed with his colleagues at the University of California. This theory now receives almost as general acceptance in America and England as the theories of structural organic chemistry. Lewis acknowledges his indebtedness to organic chemistry and to his discussions with Parson while formulating the theory. It has been developed and modified by hundreds of chemists, physicists, and astronomers (65, 67). Not all of these have given proper consideration to the work of others and not all have remembered facts and ideas which have come down from preëlectronic times.

The brilliant presentation of Lewis' theory by Langmuir (34) contributed very much to its rapid acceptance in America. Langmuir suggested the term "covalence," which has become very useful. He also discussed the relation between isosterism and isomorphism and electronic structures.

The following ideas in Lewis' theory and in its development by others seem most important:

1. Electrons, both in atoms and in molecules, usually occur in pairs. Odd electrons are magnetic (14, 33, 73, 90, 91). Because of their "spins" (18) in opposite directions (54), pairs of electrons are non-magnetic.

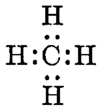
2. Helium has a pair of electrons. This pair is repeated in all atoms except hydrogen, and the x-ray spectra of these electrons (K series, Moseley (47)) furnishes the best basis for determining the position of an element in the Periodic System and for identifying a new element.

3. All other atoms have a "kernel" with a structure the same as that of the next preceding noble gas, or, for atoms having two energy levels for electrons outside of that structure, a secondary, intermediate kernel.

4. Atoms have a tendency to assume the electronic structure of a noble gas or of the intermediate kernel. They may do this in two ways.

5. *Atomic, ionic valences.* By losing the valence electrons exterior to either of the kernels defined in paragraph 3, or by taking up electrons and assuming the structure of the kernel of the atoms of the next period. Ions of these types are identical with the ions of Kossel's theory, e.g., Na^+ and $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Br}}:^-$.

6. *Covalences.* By sharing pairs of electrons, e.g.



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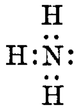


$$\begin{array}{c} H \\ H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}: \\ H \end{array}$$

It is here that Lewis's theory differs radically from that of Kossel, who in his first paper thought the carbon of methane negative. There has been a closer approach to Lewis in the later papers quoted and especially in some of the later expositions of his theory. With the exception of a very few compounds of nitrogen, the elements between boron and scandium all have a valence shell of four, five, or six pairs of electrons. Some chemists have assumed "singlet" bonds formed by single electrons, but well-established bonds of this type are rare. Compounds with four pairs of electrons in the valence shell are by far the most common. Some pairs are unshared, as in ammonia, nitric acid, and many other compounds.

In his first paper Lewis thought of the pair of electrons as in a static position between the two atoms. In his book (pp. 56, 57) he inclined to ascribe orbital motions to the electrons. In the paper last quoted (39) he accepted a tetrahedral arrangement for the orbits of the four pairs of electrons. A similar conclusion has been reached by Pauling (72) and by Slater (84) on the basis of quantum mechanics.

7. *Inclusive orbits.* In 1917 the author (50; see also 15) suggested that two atoms might be held together by an electron which included two positive nuclei in its orbit. The suggestion was erroneous in several particulars and has had no effect in the development of our theory. In 1923, N. R. Campbell (6), Sidgwick (79), and C. A. Knorr (27) made a similar suggestion for pairs of electrons. The close relation between these suggestions and quantum mechanics is evident. Dynamic relations between electrons and nuclei are certainly much more acceptable than static ones.

8. *Relation of the electron pair to the atoms held together.* The original idea of Lewis that the pair are situated between the atoms has led some chemists to speak of them as closer to one of them than to the other. In a certain sense this is true. The nitrogen atom of nitrogen trichloride will usually retain the covalent electrons when a chlorine atom separates from it, while the phosphorus atom of phosphorus trichloride will allow a chlorine atom to carry away the pair of electrons, because nitrogen has only two electrons in its kernel while phosphorus has ten (55). Stieglitz expresses this relation by a plus and a minus sign between the two atoms, placing the plus sign next the atom which remains positive.

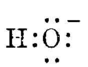
While it is clear that in the sense just stated the electron pair is not equally shared by the two atoms, it should always be remembered that, so far as atoms at a distance are concerned, the pair balances a unit positive charge in each of the atoms. In current literature authors frequently speak of positive charges as shifting from one atom to another. This is impossible, because the positive charges of every system are fixed and indivisible and are located in the nuclei of the respective atoms of the system. Any apparent shift of a positive charge must be due to a shift of the electrons in accordance with the rule given in paragraph 9 for complex and intramolecular ions.

The "polar environment" of which Lewis (37), Ingold (23), Kharasch (26), and many others speak, whether intramolecular, as in induced polarity, or extramolecular, as in the solvent, may have a large effect on ionization (e.g., chloroacetic acid) or on the course of reactions.

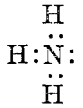
External, unshared electrons may also give a dipole moment to molecules and a negative effect in relation to nearby atoms, but that a single covalence can give rise to electromers does not seem consistent with the idea of inclusive orbits. See, however, Stieglitz (86), who holds a different view.

9. *Complex ions. Intramolecular ions.* In every electrically neutral molecule which is not a complex ion and which does not contain an intramolecular ion, the sum of the covalences and unshared electrons is equal to the kernel charge for each atom. Conversely, any atom in a compound for which the sum of the covalences and unshared electrons is greater or

less than its kernel charge is either an intramolecular ion or the significant part of an intramolecular or intermolecular ion; e.g.,



$$\mathrm{H}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}:^{-}$$



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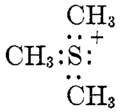
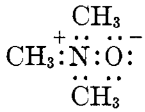
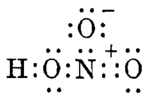


$$\mathrm{CH_3}:\underset{\underset{\mathrm{CH_3}}{\cdot\cdot}}{\overset{\overset{\mathrm{CH_3}}{\cdot\cdot}}{\mathrm{S}}}:^{+}$$



$$\mathrm{CH_3}\overset{+}{:}\underset{\underset{\mathrm{CH_3}}{\cdot\cdot}}{\overset{\overset{\mathrm{CH_3}}{\cdot\cdot}}{\mathrm{N}}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}:^{-}$$



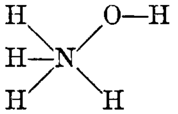
$$\mathrm{H}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}:\overset{\overset{:\overset{\cdot\cdot}{\mathrm{O}}:^{-}}{\cdot\cdot}}{\mathrm{N}}\overset{+}{::}\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}$$

In trimethylammonium oxide, the oxygen atom with a single covalence is a negative ion and the trimethylammonium group is a positive ion. The latter is demonstrated by the fact that if the oxide is treated with hydrobromic acid a hydrogen atom is added to the oxygen ion making that electrically neutral, and the positive trimethylhydroxyammonium ion formed has a high conductivity characteristic of quaternary ammonium ions (52). The fact that one of the oxygen atoms of nitric acid is semi-ionic is demonstrated by the parachor of the nitric esters and nitro compounds. These two cases demonstrate that a nitrogen atom with four covalences is always positive, irrespective of the atoms with which it is united. It also confirms the principle implied in the rule that while the covalence pair is not equally shared when the atoms are different, the inequality of sharing is not so great as to cause one of the atoms to become an ion with respect to the other.

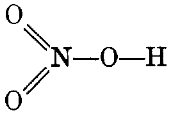
Some of my friends have objected to the term "ion" as applied to atoms and groups which do not move in reference to their companions. The word is constantly used for similar relations in the expositions of Kossel's theory and I know of no satisfactory substitute. The word "ion" has three important meanings designated by the single word: (1) An atom or group with a positive or negative charge. (2) Such an atom or group which is balanced by another atom or group having a charge of the opposite sign in the neighborhood. (3) An atom or group which moves independently through a solution under the influence of a potential gradient. The ions under discussion have the first two characteristics, but not the third. The sodium and chlorine atoms of crystallized sodium chloride do not have the third characteristic, but I think no one would hesitate to call them ions. We do not hesitate to call the atomic weight of chlorine 35.458, although we know that no single atom of chlorine has this atomic weight.

The rules given at the beginning of this section were published eight years ago (56), and no one has been able to cite a reasonable electronic structure for a compound which does not agree with the rule. The rules make it clear that the character of a complex ion or an intramolecular ion is just as definitely fixed by the relation between the kernel charge and the valence shell of some atom in the group as an atomic ion is characterized by the relation between its kernel charge and the next noble gas above or below it in the Periodic System. The rules are especially useful for the light they throw on the nature of Werner's coördinated compounds. They also emphasize the fact that positive charges are indivisible and change only by whole numbers. They shift from one atom to another by shifts of electrons in the valence shells of covalent compounds.

Thirty years ago the structural formulas in common use for ammonium hydroxide and nitric acid were,

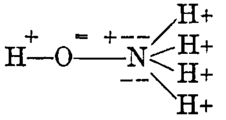


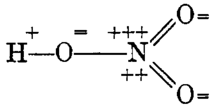
and



The nitrogen was quinquevalent in both formulas, and it was not altogether clear why one compound should be a very weak base and the other a very strong acid.

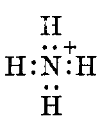
In 1912 an attempt (49) was made to explain this phenomenon on the basis of Thomson's theory that atoms are held in combination by static attraction due to the transfer of an electron from one atom to the other:



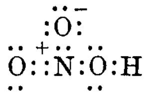


It seemed evident that the negative nitrogen of the ammonium hydroxide would hold the hydroxide ion less firmly than the positive nitrogen of the nitric acid.

The electronic formulas now used give a much better explanation:



$$\overset{-\,\cdot\cdot}{:\mathrm{O}}\underset{\cdot\cdot}{}:\mathrm{H}$$



The nitrogen is quinquevalent in both formulas, and each nitrogen atom has four covalences and one ionic valence, but with the difference that the ionic valence of the nitric acid is of the semi-ionic type (see below). In addition to this the ionization potentials of the ammonium group and of water must be nearly equal, with the result that because of the equilibrium,

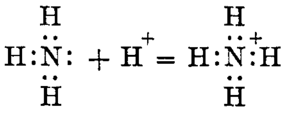
$$\mathrm{NH}_4^+ + \overset{-\,\cdot\cdot}{:}\underset{\cdot\cdot}{\mathrm{O}}:\mathrm{H} \rightleftarrows \mathrm{NH}_3 + \mathrm{H}_2\mathrm{O}$$

there can be very few of both ammonium and hydroxide ions present in the same solution. No similar relation exists for the nitric acid.

Ammonium hydroxide, so far as it exists in the solution, is probably a base of about the same strength as potassium hydroxide. A solution of ammonia in water is a weak base because very few molecules of ammonium hydroxide are present.

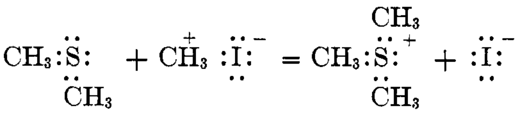
It is worth while to remark that the ammonium ion has almost the same electronic structure as the potassium ion and the two ions closely resemble each other, as methane and argon resemble each other (15, 50).

10. *"Donor" and "acceptor."* In discussing coördination, Sidgwick (83) calls an atom which furnishes both of the electrons to form a covalence a "donor" and the atom which receives the electrons an "acceptor." These terms have a much wider application than Sidgwick seems to have recognized and are very useful. Three simple illustrations are the following: The addition of a hydrogen ion to ammonia



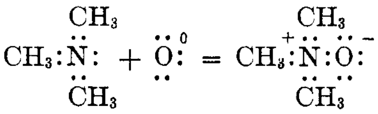
$$\begin{array}{ccccc} & \mathrm{H} & & & \mathrm{H} \\ \mathrm{H}: & \overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{N}}}: & +\ \mathrm{H}^{+} = & \mathrm{H}: & \overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{N}}}{:}\mathrm{H}^{+} \\ & \mathrm{H} & & & \mathrm{H} \end{array}$$

The addition of a positive methyl ion to dimethyl sulfide,



$$\begin{array}{ccccccc} & & & & \mathrm{CH_3} & & \\ \mathrm{CH_3}: & \overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{S}}}: & +\ \mathrm{CH_3}^{+}\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{I}}}:^{-} & = & \mathrm{CH_3}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{S}}}:^{+} & + & :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{I}}}:^{-} \\ & \mathrm{CH_3} & & & \mathrm{CH_3} & & \end{array}$$

The addition of an oxygen atom from ozone to trimethylamine,

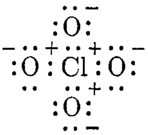


$$\begin{array}{ccccc} & \mathrm{CH_3} & & & \mathrm{CH_3} \\ \mathrm{CH_3}: & \overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{N}}}: & +\ \overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}:^{0} & = & \mathrm{CH_3}:\overset{+\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{N}}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}:^{-} \\ & \mathrm{CH_3} & & & \mathrm{CH_3} \end{array}$$

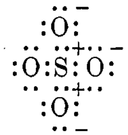
Sidgwick recognized that a donor which exchanges a pair of unshared electrons for a covalence becomes more positive and the acceptor becomes more negative. The discussion of the nature of covalences and the illustrations prepare us for the following useful rules: In forming a covalence the donor increases its positive charge by one unit; the acceptor decreases its positive charge by one unit (64).

11. *Semi-ionic bonds.* Lowry (42) seems to have been the first to recognize clearly that double bonds may be of two types,—double covalences and half covalence and half ionic valence. Lowry called the latter mixed double bonds. Sugden (88) called them semipolar bonds. The term semi-ionic seems to be more suitable, because some compounds which are not semi-ionic show polarity because of unshared electrons.

In discussing the electronic structure of the perchlorate, sulfate, and orthophosphate ions, Lewis (38) says, "We may now write formulae in which an atom of oxygen is tied by only one pair of electrons to another atom and yet have every element in the compound completely saturated." Such a statement seems to imply that the oxygen atom which had been considered bivalent becomes univalent in these compounds. The semi-ionic formulas show at once that the oxygen is still bivalent in these ions and also show why the perchlorate ion is unibasic and the sulfate ion bibasic.



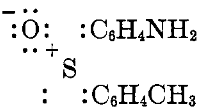
$$\begin{array}{c} \cdot\cdot\,- \\ :\mathrm{O}: \\ -\cdot\cdot+\cdot\cdot+\cdot\cdot- \\ :\mathrm{O}:\mathrm{Cl}:\mathrm{O}: \\ \cdot\cdot\quad\cdot\cdot+\cdot\cdot \\ :\mathrm{O}: \\ \cdot\cdot\,- \end{array}$$



$$\begin{array}{c} \cdot\cdot\,- \\ :\mathrm{O}: \\ \cdot\cdot\;\cdot\cdot+\cdot\cdot- \\ :\mathrm{O}:\mathrm{S}:\mathrm{O}: \\ \cdot\cdot\;\cdot\cdot+\cdot\cdot \\ :\mathrm{O}: \\ \cdot\cdot\,- \end{array}$$

Chlorine has a kernel charge of seven. Four of these are balanced by the covalences with the four oxygen atoms, and the other three by three negative ionic valences of oxygen atoms, leaving one negative valence for the perchlorate ion. Sulfur has a kernel charge of six. Four of these are balanced by the four covalences of the oxygen atoms and two by the negative ionic valences of oxygen atoms, leaving two negative valences for the sulfate ion.

12. *Double and triple covalences.* Kopp (29), by determining the molecular volumes of compounds at their boiling points, discovered that an oxygen atom fills a greater volume when it is "in a radical" (i.e., when it has a double covalence) than it fills when it is "outside the radical" (i.e., has two single covalences). Sugden (87) has developed a function called the parachor, which depends on the properties of compounds at their critical temperatures. This has shown, more accurately, the same differences between single and double covalences that had been found by Kopp, and has shown that the parachor is still further increased by a triple covalence. The parachor of an oxygen atom with a semi-ionic union indicates a single covalence (89). This has been particularly interesting and valuable for the sulfinic compound (21),

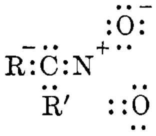


$$\begin{array}{lll} \overset{-\,\cdot\cdot}{:\mathrm{O}:} & & :C_6H_4NH_2 \\ \cdot\cdot+ & \mathrm{S} & \\ : & & :C_6H_4CH_3 \end{array}$$

If there were a double covalence between the oxygen and sulfur, the compound would be optically inactive. The parachor has demonstrated a semi-ionic union with a single covalence. This also confirms the evidence from active sulfonium compounds

$$\begin{array}{r@{}l} & R'' \\ R': & S: \\ & R \end{array}$$

and from the active sodium salts of aliphatic nitro compounds studied by Kuhn (32) and Shriner (78),

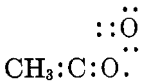


$$\begin{array}{l@{\quad}l} & :\overset{\cdot\cdot}{O}:^{-} \\ R:\overset{-\,\cdot\cdot}{C}:\overset{+\,\cdot\cdot}{N} & \\ \overset{\cdot\cdot}{R'} & ::\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}} \end{array}$$

that a pair of unshared electrons may furnish the fourth element in tetrahedral dissymmetry.

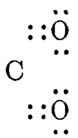
The greater volume occupied by atoms held together by a double covalence, in spite of the fact that other methods have shown that the centers of the atoms are closer together than when they are held by a single covalence, seems to indicate that the tendency to a tetrahedral arrangement causes the pair of electrons to extend out on both sides of the line between the atoms. This is consistent with the *cis-trans* isomerism characteristic of such compounds and recalls Baeyer's Strain Theory. He thought the double union the limiting case of rings.

13. *Free radicals; odd electrons.* Kolbe (28) discovered that the electrolysis of potassium acetate gives ethane and carbon dioxide. The removal of an electron from the acetate ion gives the ephemeral compound,



$$\begin{array}{r@{}l} & ::\overset{\cdot\cdot}{O} \\ CH_3:C: & \overset{\cdot\cdot}{O}{}^{\cdot} \end{array}$$

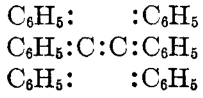
with an odd electron on the oxygen atom. The oxygen captures an electron from the covalence between the methyl and the carbon, and carbon dioxide is formed by rearrangement.



$$\begin{array}{l@{}l} & ::\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}} \\ C & \\ & ::\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}} \end{array}$$

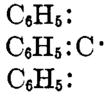
The methyl with an odd electron unites with another to form ethane, $H_3C:CH_3$. A very reactive free methyl radical was postulated to explain the course of the reaction long before an electronic interpretation was possible.

Gomberg (17) in 1900 discovered hexaphenylethane,



$$\begin{array}{r@{}c@{}l} C_6H_5: & & :C_6H_5 \\ C_6H_5: & C:C & :C_6H_5 \\ C_6H_5: & & :C_6H_5 \end{array}$$

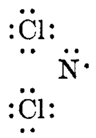
which he called at first triphenylmethyl,



$$\begin{array}{l} C_6H_5: \\ C_6H_5:C\cdot \\ C_6H_5: \end{array}$$

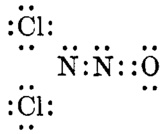
because hexaphenylethane dissociates readily to this "free radical," which reacts with iodine to give triphenylmethyl iodide and with oxygen to give triphenylmethyl peroxide. Later, other workers isolated other similar free radicals which were sufficiently stable to exist as independent molecules. These were the first free radicals of this type to be isolated as independent molecules. More recently, Paneth (70) and Rice (75, 76) have demonstrated the existence of ethyl and methyl as free radicals for a very brief but measurable time.

At −80°C., nitric oxide, $\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}::\overset{\cdot\cdot}{N}\cdot$, which has a free electron, takes a chlorine atom with a free electron, $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}\cdot$, from nitrogen trichloride forming nitrosyl chloride, $\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}::\overset{\cdot\cdot}{N}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:$, and leaving nitrogen dichloride.



$$\begin{array}{ll} :\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: & \\ & \overset{\cdot\cdot}{N}\cdot \\ :\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: & \end{array}$$

The latter unites with a second molecule of nitric oxide to form dichlorodinitrogen oxide



$$\begin{array}{ll} :\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: & \\ & \overset{\cdot\cdot}{N}:\overset{\cdot\cdot}{N}::\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}} \\ :\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: & \end{array}$$

This immediately decomposes at −80°C. into free chlorine and nitrous oxide, $:N:::\overset{+}{N}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:^{-}$ (53).

At −150°C. the dichloro compound is more stable and nitric oxide takes a second atom of chlorine from it, giving a second molecule of nitrosyl chloride (59).

14. *Ionic reactions.* (a) Electrolytes. The electronic structure of electrolytes is so clearly recognized and their reactions have been so carefully studied that they need not be mentioned, further than to recall the unique character of the hydrogen ion discussed by Latimer and Rode-

bush (36). Because the hydrogen ion has no exterior electron it can approach the outer electrons of any negative ion, or, indeed of any other atom, more easily than any other positive ion can do this. For this reason acetic acid has a very low ionization constant, while that of sodium acetate is high. Probably a number of other chemical phenomena have the same reason.

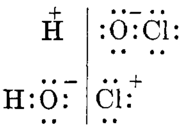
(b) Non-electrolytes. Van't Hoff (95) first demonstrated an ionic character for a reaction of a non-electrolyte by determining the stoichiometric relation between the amount of phosphorus oxidized and the amount of ozone formed when oxygen is in contact with moist phosphorus.

Jakowkin (24) demonstrated accurately, by means of partition experiments, that chlorine and water react in the dark to form hypochlorous and hydrochloric acids. An equilibrium between the four substances is very quickly reached, and the reaction is quantitatively reversible. The course of the experiment has all the usual characteristics of an ionic reaction, but Jakowkin did not suggest this explanation.

Two years later Stieglitz (85) interpreted Jakowkin's results by the ionic equation,

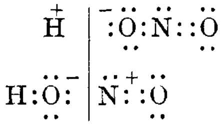
$$HO^- + Cl^+ + HOCl + H^+ + Cl^- \rightarrow Cl_2 + H_2O$$

Twenty-two years later Noyes (51) suggested that this older, positive-negative theory is consistent with Lewis's theory if we assume that the two electrons of a covalence may remain together when the atoms separate in a chemical reaction. This suggestion has received strong support by the discovery that the electrons of a covalence have spins in opposite directions. According to this suggestion the atoms of a molecule of chlorine separate into $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}{}^{+}$ and $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:^{-}$. Further support is given by the independent demonstration by Goldschmidt (16) and by Noyes and Wilson (69) that chlorine monoxide is present in the gaseous phase above the aqueous solution of hypochlorous acid. This is most simply explained by the relation,



$$\begin{array}{r|l} \overset{+}{H} & :\overset{\cdot\cdot -}{\underset{\cdot\cdot}{O}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}: \\ H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:^{-} & \overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:^{+} \end{array}$$

A similar relation for nitrous acid,

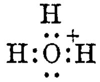


$$\begin{array}{r|l} \overset{+}{H} & {}^{-}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:\overset{\cdot\cdot}{N}::\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} \\ H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:^{-} & \overset{\cdot\cdot}{N}\overset{+}{:}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} \end{array}$$

makes it possible to prepare alkyl nitrites quantitatively in a dilute aqueous solution (61).

In the same year that Stieglitz interpreted Jakowkin's reaction, Noyes and Lyon (66) and Lapworth (35) interpreted other reactions in a similar manner.

Ionic reactions furnish the simplest interpretation of a great variety of reactions. It is probable that many of these reactions occur through the immediate contact of the reacting compounds (48) or through the intervention of intermediate compounds. In cases where positive radicals with atoms having only six electrons are involved, these are, undoubtedly, ephemeral (60), as was demonstrated for positive chlorine by Noyes and Wilson in their study of hypochlorous acid (69). While this may be true and should be remembered in discussing reactions of this type, it seems impossible to deny that atoms and groups having the electronic structures given in this paper are actually transferred from one molecule to another and it is very convenient to use such formulas. It is altogether probable that hydrogen ions exist in aqueous solutions almost exclusively as positive oxonium ions,



$$\begin{array}{c} \mathrm{H} \\ \mathrm{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}\overset{+}{:}\mathrm{H} \end{array}$$

positive because the oxygen has three covalences. In writing reactions involving hydrogen ions no one thinks it necessary to represent them by this formula.

Organic chemists constantly use formulas for radicals which have never been isolated and which have odd electrons in the few cases where their independent existence has been demonstrated. It is a little difficult to see why so many chemists hesitate to use electronic formulas which have an even better basis than these formulas for radicals and which throw a clear light on the course of many reactions.

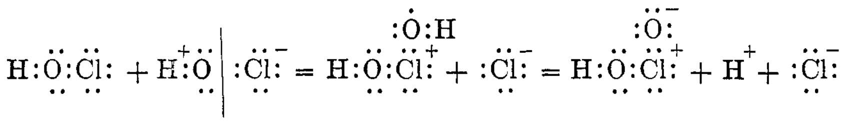
The following additional illustrations of ionic reactions of covalent compounds may be of service.

(1) The oxidation of a tertiary amine to the quaternary hydroxyammonium ion by hydrogen peroxide.

$$\mathrm{R_3N:} + \mathrm{H}\overset{+}{:}\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}\,\Big|\,\overset{-}{:}\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}:\mathrm{H} = \mathrm{R_3N}\overset{+}{:}\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}:\mathrm{H} + \overset{-}{:}\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}:\mathrm{H}$$

The separation of hydrogen peroxide into positive and negative hydroxyl (58) is similar to the separation of the chlorine molecule into positive and negative chlorine.

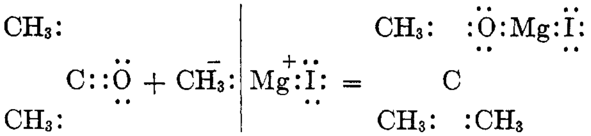
(2) The oxidation of hypochlorous acid to chloric acid by the positive hydroxyl from another molecule of hypochlorous acid (57);



$$H:\underset{\cdot\cdot}{\ddot{O}}:\underset{\cdot\cdot}{\ddot{Cl}}: + \overset{+}{H}:\underset{\cdot\cdot}{\ddot{O}}\;\Big|\;:\underset{\cdot\cdot}{\ddot{Cl}}:^{-} = H:\underset{\cdot\cdot}{\ddot{O}}:\overset{:\dot{O}:H}{\underset{\cdot\cdot}{\ddot{Cl}}:^{+}} + :\underset{\cdot\cdot}{\ddot{Cl}}:^{-} = H:\underset{\cdot\cdot}{\ddot{O}}:\overset{:\ddot{O}:^{-}}{\underset{\cdot\cdot}{\ddot{Cl}}:^{+}} + \overset{+}{H} + :\underset{\cdot\cdot}{\ddot{Cl}}:^{-}$$

This first step gives chlorous acid. A repetition gives chloric acid.

(3) The reaction of a Grignard reagent with an aldehyde or a ketone;



$$\begin{array}{lll} CH_3: & & CH_3:\ \ :\underset{\cdot\cdot}{\ddot{O}}:Mg:\underset{\cdot\cdot}{\ddot{I}}: \\ & C::\underset{\cdot\cdot}{\ddot{O}} + \overset{-}{CH_3}:\Big|\,\overset{+}{Mg}:\underset{\cdot\cdot}{\ddot{I}}: \ = & \qquad C \\ CH_3: & & CH_3:\ \ :CH_3 \end{array}$$

The magnesium, as a metal, allows the methyl to separate in the negative form carrying the pair of electrons. The positive radical, $\overset{+}{Mg}:\underset{\cdot\cdot}{\ddot{I}}:$, then attaches itself to a pair of unshared electrons of the oxygen atom, causing that to become, momentarily, positive. This positive oxygen will then take a pair of covalence electrons from its double union with the carbon atom. This leaves the carbon atom positive, ready to combine with the negative methyl.

Water is a covalent compound but chemists find no difficulty in assuming the presence of hydrogen ions in alkaline solutions where the number of hydrogen ions must be excessively small. The assumption that hydrogen ions may separate from a carbon atom which is adjacent to another carbon atom which carries an oxygen atom, especially when the oxygen is in the semi-ionic condition characteristic of a sodium salt, enables us to account very simply for thousands of condensation reactions, e.g., for the Perkin, Kolbe, and Reimer-Tiemann reactions.

15. *Positive, neutral, and negative radicals.* From the discussions which have preceded this we may expect atoms and radicals to separate in three forms:

(1) Positive: H^+ from water, acids, many compounds of carbon, ammonia, ammonium and their derivatives; $H:\overset{H}{\underset{H}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}}}{}^{+}$ from methyl iodide; $N::\ddot{O}^{+}$ from nitrous acid; $:\underset{\cdot\cdot}{\ddot{Cl}}{}^{+}$ from molecular chlorine, from hypochlorous acid, and from nitrogen trichloride.

(2) Electrically neutral: $H^{\cdot}$ in the Langmuir blowpipe, in the magnetic hydrogen atoms of Phipps and Taylor, and probably in the reactions of

molecular hydrogen in the presence of a catalyst; $:\overset{..}{\underset{..}{Cl}}\cdot$ in the thermal dissociation of chlorine (Victor Meyer) and probably in photochemical reactions and in the reaction of nitrogen trichloride with nitric oxide; $H:\overset{\overset{H}{..}}{\underset{..}{C}}\cdot$ from the electrolysis of sodium acetate and in thermal dissociations (Paneth, Rice).

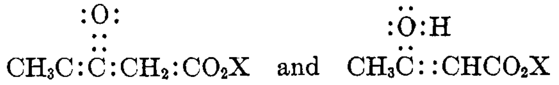
(3) Negative: $H\overset{-}{:}$ from the electrolysis of lithium hydride and in the mass spectra of Thomson; chloride ion, $:\overset{..\,-}{\underset{..}{Cl}}:$ in the negative ion of hydrochloric acid; $Cl_2\overset{..\,-}{N}:$ in the addition reactions of nitrogen trichloride (7); and $CH_3\overset{-}{:}$ in the reactions of the Grignard reagent.

It is difficult to express these relations satisfactorily without the use of dots to represent single and paired electrons, as was first proposed by Lewis.

16. *Optical activity.* The tetrahedral dissymmetry of optically active compounds seems to be confirmed by the quantum mechanics studies of Pauling (72), which have been referred to. The optically active sulfonium compounds and the optically active sodium salts of aliphatic nitro compounds are of especial interest, because a pair of unshared electrons on a sulfur or on a carbon atom furnishes one of the four dissymmetric groups (21, 32, 78). See p. 14.

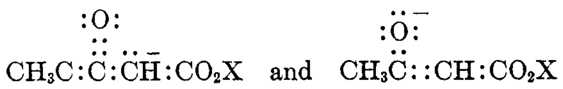
The static attraction between two ions in the same molecule which may hold the molecule in a stable cyclic configuration (68) when the ring contains six atoms does not do so when the ring would have seven atoms. The authors of the paper did not recognize, then, that the closure of the ring is due to an ionic valence and not to a covalence.

17. *Tautomerism.* It is now generally recognized that tautomerism is due to the existence of two isomers which have hydrogen atoms in different positions and with one or more double covalences which shift from one position to another. Occasionally there are labile methyl, phenyl, or other groups. For acetoacetic ester the two forms are:



$$CH_3C:\overset{\overset{:O:}{..}}{C}:CH_2:CO_2X \quad\text{and}\quad CH_3\overset{\overset{:\overset{..}{O}:H}{..}}{C}::CHCO_2X$$

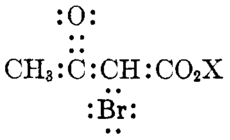
The shift of the hydrogen atom implies that it assumes the ionic form by leaving either the carbon or the oxygen. There are, therefore, two different ions:



$$CH_3C:\overset{\overset{:O:}{..}}{C}:\overset{..\,-}{CH}:CO_2X \quad\text{and}\quad CH_3\overset{\overset{:\overset{..\,-}{O}:}{..}}{C}::CH:CO_2X$$

In the first the pair of unshared electrons which give the negative character are on the carbon; in the second they are on the oxygen. When we recall that hydrogen attached to an oxygen atom ionizes easily in the presence of sodium and hydroxide ions, while hydrogen attached to carbon ionizes far less easily and usually leaves an ephemeral negative carbon atom having a pair of unshared electrons, it is evident that acids will favor the formation of the first form in an unionized condition and that alkalies will favor the formation of the second form (enol), in which the semi-ionic oxygen is balanced by metallic ions. These statements appear to the writer to be much more easily understood than the somewhat cumbersome terminology used by English authors.

Kurt Meyer (44) has shown that on treatment of the keto and enol forms of acetoacetic ester with bromine under suitable conditions the ketone is not affected but the enol is converted to the bromoacetoacetic ester,



$$CH_3{:}\overset{\overset{\displaystyle :O:}{\cdot\cdot}}{\overset{\cdot\cdot}{C}}{:}\underset{:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Br}}:}{CH}{:}CO_2X$$

Evidently the negative bromine atom from the bromine molecule unites with the labile hydrogen of the enol group, and one of the covalences between the two carbon atoms shifts to receive the positive bromine atom, while the pair to which the enol hydrogen was attached shifts to form a double covalence between the carbon and oxygen. The bromine atom combined with a carbon atom situated between two other carbon atoms, each of which is united to oxygen, may leave its covalence electrons with the carbon and separate in the positive form, $:\underset{\cdot\cdot}{Br}:$. In this form the bromine will take the hydrogen and a pair of electrons from two molecules of hydriodic acid, liberating free iodine. One atom of the hydrogen replaces the positive bromine and regenerates the original acetoacetic ester in the keto form. The other hydrogen atom remains as an ion to balance the bromine, which has become negative by accepting the pair of electrons taken from the iodine when two iodide ions become free iodine.

The induced polarity of the carbon atom between two carbonyl groups is similar to the induced polarity of the oxygen of acetic acid produced by a chlorine atom in the α-position, increasing the ionization constant of the acid.

Hydrocyanic acid exists in two tautomeric forms, $H{:}C{:}{:}{:}N{:}$ and $\overset{-}{:C}{:}{:}{:}\overset{+}{N}{:}H$ (94). Removal of hydrogen from either form leaves the same negative ion, $\overset{-}{:C}{:}{:}{:}N{:}$. Because of the mobility of the hydrogen ion the two forms are in equilibrium, with the first form in very large excess.

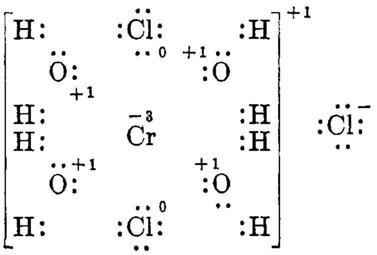
As often happens in similar cases, replacement of the hydrogen by phenyl or other groups gives two different compounds, phenyl cyanide, $C_6H_5{:}C{:}{:}{:}N{:}$, which is easily hydrolyzed to benzoic acid and ammonia, and phenyl isocyanide, $C_6H_5{:}\overset{+}{N}{:}{:}{:}\overset{-}{C}{:}$, which may be oxidized to phenyl isocyanate and hydrolyzed to aniline and a carbonate. The electronic structure of the isomers has been quite conclusively determined by means of the parachors, dipole moments, and other properties (20).

18. *Coördination.* Many years ago Werner discovered that atoms and molecules may be combined with a central metallic atom in different ways. For example, there are three hydrates of chromic chloride,

$$[Cr(OH_2)_6]^{+3}Cl_3 \qquad [Cr(OH_2)_5Cl]^{+2}Cl_2 \qquad [Cr(OH_2)_4Cl_2]^{+1}Cl$$

In the first all the chlorine ionizes and may be precipitated by silver nitrate; in the second two-thirds, and in the third only one-third can be precipitated. Werner called the chlorine and water within the brackets "coördinated."

Sidgwick (80) threw a flood of light on the nature of these compounds when he suggested that the coördinated atoms and groups are held to the central atom by covalences. According to this, the electronic structure of the third compound is



Sidgwick introduced the terms "donor" and "acceptor" in connection with the covalences of coördinate compounds and called such a covalence a "coördinate link." He recognized that the central atom, which is the acceptor, increases its negative charge, but not so clearly that the chloride ions and water increase their positive charges exactly as ammonia increases its positive charge when it is donor to a hydrogen ion (see p. 13). He seems to overlook the fact that each covalence must balance two positive unit charges situated in the nuclei of two *different* atoms. While the negative charges of the two covalent electrons may not be equally distributed, good reasons have been given earlier in this paper for thinking that they are approximately so distributed, and this gives us a very simple method for estimating the distribution of the charges within the complex. The chromium kernel has a positive charge of three units. The chlorine atoms enter the complex as negative ions, not as neutral atoms, as Sidgwick has supposed.

As donors, these two negative ions become electrically neutral and the chromium atom, as an acceptor, acquires two negative charges from the two chlorine atoms. The four molecules of water enter the complex as neutral molecules, and as donor each acquires a positive charge, as ammonia acquires a positive charge when it unites with a hydrogen ion. The chromium as acceptor of the four molecules of water acquires four negative charges, a total of six in all. Three of the six are balanced by the three positive charges of the chromium kernel, three are balanced by three of the positive oxonium groups, leaving one positive charge for the complex as a whole. This positive charge is balanced by the external chloride ion (62). No matter how the charges may be distributed between the chromium kernel, the water molecules, and the chlorine atoms within the complex, this net result must be true for the complex as a whole. The net result is, of course, the same as that of Sidgwick (82).

There is a fourth chromic chloride hydrate, because the form with two coördinated chlorine atoms has a *cis-trans* isomerism. A fifth form with all three chlorine atoms coördinated is theoretically possible. These forms do not affect the principles which determine the positive or negative character of the atoms and groups within the complex and the ionic charge of the complex when there are exterior ions.

Sidgwick defines a coördinate link as one in which one of the atoms furnishes the two electrons for a covalence. This overlooks the fact that a covalence is the same, when once formed, when one of the atoms furnishes the pair as when each atom furnishes one of the pair. Water is the same when it is formed by the union of a hydroxide ion with a hydrogen ion as when it is formed by burning hydrogen in oxygen. When a hydrogen ion combines with ammonia to form an ammonium ion, it becomes identical with the three hydrogen atoms coming from the ammonia. It was at this point that Werner's discussion of ammonium salts was not satisfactory.

A definition of coördination should not emphasize the manner in which the covalences are formed. The two characteristics of most importance are: (1) A coördinated atom has, usually, a larger number of covalences than the number of positive units in its kernel charge. Silicon is coördinated in the fluosilicate ion, SiF_6^{--}, in which the silicon atom has six covalences. (2) When the pair of electrons for a covalence is furnished by one of the atoms or by a neutral molecule the donor increases its positive charge and the acceptor its negative charge. The negative charge of the fluosilicate ion is due to the fact that a silicon atom which has four positive units in its kernel charge has six covalences.

In a paper published two years ago (63) I used the coördinate formula $H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:\overset{-}{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:$ for bimolecular hydrofluoric acid. Sidgwick had previously used the same formula (81). The chemical evidence points strongly to such a conclusion, especially the well-known fact that H_2F_2 is a bibasic acid forming well-defined salts of the type KHF_2, the very low ionization constant, and the association in the gaseous state at ordinary temperatures. Abegg (2) states that the acid is ionized only to the extent of 15 per cent in a normal solution and that five-sixths of the ionization is to H^+ and F_2H^-. These facts indicate that the ion F_2H^- is a well-defined complex having properties similar to those of coördinate compounds and more stable than many of these. These chemical facts are most simply explained by assuming that the group is a covalent one, the hydrogen having two covalences and the two fluorine atoms being electrically neutral as they are in silicon tetrafluoride and in the fluosilicate ion. Silicon tetrafluoride has, almost certainly, a tetrahedral covalence shell of electrons, while the analogy from compounds studied by Werner indicates an enlarged octahedral covalence shell for SiF_6^{--}. It does not seem unreasonable to think that hydrogen might have an enlarged covalent shell with four electrons. However, both Mulliken and Pauling think this impossible or, at least, extremely improbable and Sidgwick is of the same opinion (83a). Pauling and Sidgwick think there may be a "resonance" between

$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:H\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:\quad\text{and}\quad :\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:\ H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:$$

Important advances have been made in the study of electronic structures during the past decade by de Broglie, Pauli, Heisenberg, Born and Jordan, Dirac, Goudsmit and Uhlenbeck, Schrödinger, Davisson and Germer, Mulliken and Pauling. I am not competent to discuss these advances in detail and could not hope to add to the very illuminating paper by Lewis (41).

I wish to express appreciation of my indebtedness to Professors Sidgwick, Lowry, W. Albert Noyes, Mulliken, Pauling, and Stieglitz, who have read this paper and offered many valuable suggestions. It will be understood, of course, that we are not entirely agreed about some points, but it is hoped that this attempt will help to clarify our ideas and contribute toward a unification of electronic theories.

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