

## The Atom and the Molecule

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Journal of the American Chemical Society

Volume 38, 1916, pages 762-786

Received January 26, 1916

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In a paper entitled "Valence and Tautomerism"<sup>1</sup> I took occasion

<sup>1</sup> This Journal, 35, 1448 (1913); see also the important article of Bray and Branch, *Ibid*, 35, 1440 (1913)

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to point out the great importance of substituting for the conventional classification of chemical substances, as inorganic or organic, the more general classification which distinguishes between polar and nonpolar substances. The two classifications roughly coincide, since most inorganic substances are distinctly polar, while the majority of organic substances belong to the nonpolar class; thus potassium chloride represents the extreme polar type and methane the nonpolar. Nevertheless, there are many inorganic substances which, under ordinary circumstances, are predominantly nonpolar, and many organic substances which, at least in a certain part of the molecule, are strongly polar.

This article was apparently unknown to Sir J.J. Thomson<sup>1</sup> when he wrote, in 1914, an extremely interesting paper on the "Forces between Atoms and Chemical Affinity" in which he reached conclusions in striking accord with my own and discussed in considerable detail the theories of

atomic and molecular structure which led him to those conclusions.

To enable us to appreciate the importance and usefulness of a distinction between the polar and nonpolar types of chemical molecules no hypotheses are necessary, but in a more minute examination of the nature of such a distinction some theory of atomic structure is indispensable. Such a theory I have employed for a number of years in the interpretation of chemical phenomena, but it has not hitherto been published. I shall present this theory briefly in the present paper, for, while it bears much resemblance to some current theories of the atom, it shows some radical points of departure from them. As an introduction it will be desirable to review the characteristics of polar and nonpolar compounds.

### □ Polar and Nonpolar Types □

The very striking differences in properties between extreme polar and the extreme nonpolar types are summarized in the following table quoted from my previous paper:

<u>Polar</u>	<u>NonPolar</u>
Mobile	Immobile
Reactive <sup>2</sup>	<u>Inert</u>
<u>Condensed structure</u>	<u>Frame Structure</u>
<u>Tautomerism</u>	<u>Isomerism</u>
<u>Electrophiles</u>	<u>Non-electrophiles</u>
<u>Ionized</u>	<u>Not ionized</u>
<u>Ionizing solvents</u>	<u>Nonionizing solvents</u>
<u>High dielectric constant</u>	<u>Low dielectric constant</u>
<u>Molecular complexes</u>	<u>No molecular complexes</u>
<u>Association</u>	<u>No association</u>
<u>Abnormal liquids</u>	<u>Normal liquids</u>

<sup>1</sup> Phil. Mag., 27, 757 (1914).

<sup>2</sup> In my former paper the words "inert" and "reactive" were inadvertently transposed and appear in the wrong columns.

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All of these properties with respect to which fundamental distinctions have been made between the two types, and which seem so unconnected, are in fact closely related, and the differences are all due to a single cause. Even before making any special hypothesis we may very safely assume that the essential difference between the polar and the nonpolar molecule is that, in the former, one or more electrons are held by sufficiently weak constraints so that they may become separated from their former positions in the atom, and in the extreme case pass altogether to another atom, this producing in the molecule a bipole or multipole of high electrical moment. Thus in an extremely polar molecule, such as that of sodium chloride, it is probable that at least in the great majority of molecules the chlorine atom has acquired a unit negative charge and therefore the sodium atom a unit positive charge, and that the process of ionization consists only in a further separation of these charged parts.

If then we consider the nonpolar molecule as one in which the electrons belonging to the individual atoms are held by such constraints that they do not move far from their normal positions, while in the polar molecule the electrons, being more mobile, so move as to separate the molecule into positive and negative parts, then all the distinguishing properties of the two types of compounds become necessary consequences of this assumption, as we may readily show.

Thus polar compounds with their mobile electrons fall readily into those combinations which represent the very few stable states, while the nonpolar molecules, in which the parts are held by firmer constraints, are inert and unreactive, and can therefore be built up into the numerous complicated structures of organic chemistry. Many organic compounds, especially those containing elements like oxygen and nitrogen, and those which are said to be unsaturated, show at least in some part of the molecule a decidedly polar character. In such cases we have the phenomena of tautomerism, where two or more forms of the molecule pass readily into one another and exist together in a condition of mobile equilibrium. Tautomerism is not characteristic of organic substances, but is, on the other hand, a predominant trait of most inorganic substances, which behave as if a great variety of forms were existing together in extremely mobile equilibrium.

When a molecule owing to the displacement of an electron, or electrons, becomes a bipole (or multipole) of high electrical moment, that is, when its charged parts are separated by an appreciable distance, its force of attraction for another molecular bipole will be felt over a considerable intervening distance, and two or more such bipoles will frequently be drawn together into a single aggregate in which the positive part of one molecule is brought as near as possible to the negative part of another. The molecules of a polar substance will therefore not

only exhibit an

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unusually high intermolecular attraction at a distance, but will frequently combine with one another and show the phenomenon known as association. It is indeed the substances which are distinctly polar, like ammonia, water, acids, and alcohols, which constitute, on account of association as well as of high intermolecular attraction, a class of liquids which are called abnormal with respect to numerous properties such as critical point, vapor pressure, heat of vaporization, viscosity, and surface tension.

Moreover a polar substance will combine with other substances to form those aggregates which are sometimes known as molecular compound or complexes, and it may so combine with substances which are not of themselves markedly polar, for in the presence of a polar substance all other substances become more polar.

This important effect of polar molecules in rendering others more polar, which I called attention in my previous paper, has been discussed in some detail by Thomson. A molecular bipole of small molecular moment, which would scarcely attract a similar molecule, will be very appreciably attracted by a polar molecule or bipole of high moment, and may form with it a double molecule. In this process the weaker bipole stretches and its moment increases. In general, if two molecules combine, or even approach one another, each weakens the constraints which hold together the charge of the other, and the electrical moment of each is increased.

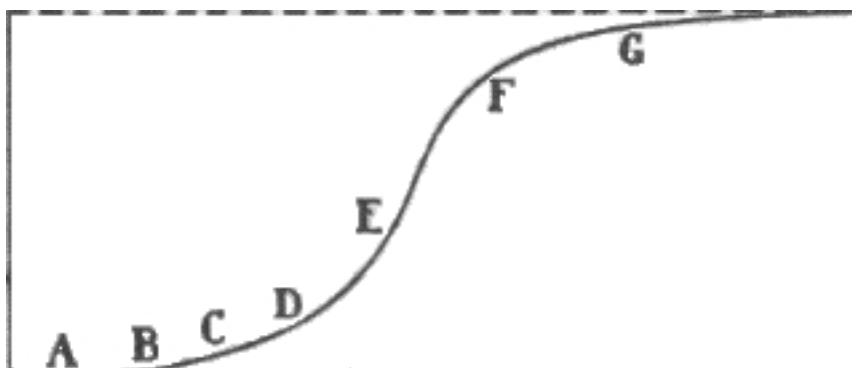
This increase in the polar character of a molecule when combined with, or in the neighborhood of, other polar molecules is to a remarkable degree cumulative, for when two molecules by their approach or combination become more polar they draw other molecules more strongly towards them, but this still further increases their polar character. This is strikingly illustrated in numerous phenomena. Thus two substances in the gaseous state may differ but little in polar character, but when they are condensed liquids the differences are frequently enormous. The polar character of a substance depends, therefore, not only upon the specific properties of the individual molecules, but also upon what we may call the strength of the polar environment.

Without attempting give any quantitative definition of our terms we may plot, in Fig. I, the degree of polarity of a substance as ordinate and the strength of the polar environment as abscissa. We then have for all substances a curve of the type shown in the figure where the dotted line represents the highest degree of polarity, namely complete ionization. Different pure substances in

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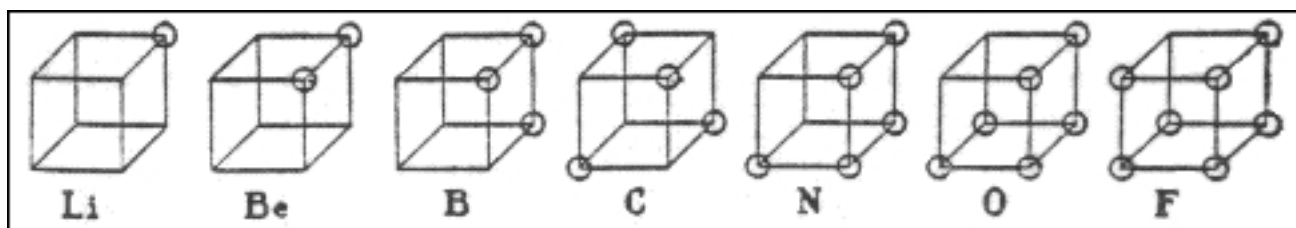
Scritto da Roberto Poeti

Domenica 20 Settembre 2009 22:43 - Ultimo aggiornamento Mercoledì 07 Ottobre 2009 20:40



### The Cubical Atom.

A number of years ago, to account for the striking fact which has become known as Abegg's law of valence and countervalence, and according to which the total difference between the maximum negative and positive valences or polar numbers of an element is frequently eight and is in no case more than eight, I designed what may be called the theory of the cubical atom. This theory, while it has become familiar to a number of my colleagues, has never been published, partly because it was in many respects incomplete. Although many of these elements of incompleteness remain, and although the theory lacks to-day much of the novelty which it originally possessed, it seems to me more probable intrinsically than some of the other theories of atomic structure which have been proposed, and I cannot discuss more fully the nature of the differences between polar and nonpolar compounds without a brief discussion of this theory.



The pictures of atomic structure which are reproduced in Fig. 2,<sup>1</sup> and in which the circles represent the electrons in the outer shell of the

<sup>1</sup>These figures are taken from a memorandum dated March 28, 1902, together the models are notes concerning different types of chemical compounds; the various possible arrangements of electrons in the outer atom and the possibility of intra-atomic isomerism; the relationship between symmetrical structure and atomic volume, and certain speculations as to the structure of the helium atom which we shall see were probably partly incorrect. The date of origin of this theory is mentioned not with the purpose of claiming any sort of priority with respect to those

portions which overlap existing theories, but because the fact that similar theories have been developed independently adds to the probability that all possess some characteristics of fundamental reality.

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neutral atom, were designed to explain a number of important laws of chemical behavior with the aid of the following postulates:

1. In every atom is an essential kernel which remains unaltered in ordinary chemical changes and which possesses an excess of positive charges corresponding in number to the ordinal number of the group in the periodic table to which the element belongs.
2. The atom is composed of the kernel and an outer atom or shell, which in the case of the neutral atom, contains negative electrons equal in number to the excess of positive charges of the kernel, but the number of electrons in the shell may vary during chemical change between 0 and 8.
3. The atom tends to hold an even number of electrons in the shell and especially to hold eight electrons which are normally arranged symmetrically at the eight corners of a cube.<sup>1</sup>
4. Two atomic shells are mutually interpenetrable.
5. Electrons may ordinarily pass with readiness from one position in the outer shell to another. Nevertheless they are held in position by more or less rigid constraints, and these positions and the magnitude of the constraints are determined by the nature of the atom and of such other atoms as are combined with it.
6. Electric forces between particles which are very close together do not obey the simple law of inverse squares which holds at greater distances.

Some further discussion of these postulates is necessary in order to make their meaning clear. The first postulate deals with the two parts of the atom which correspond roughly with the inner and outer rings of the Thomson atom. The kernel being that part of the atom which is unaltered by ordinary chemical change is of sufficient importance to merit a separate symbol. I propose that the common symbol of the element printed in a different type be used to represent the kernel. Thus **Li** will stand for the lithium kernel. It has a single positive charge and is equivalent to pure lithium ion  $\text{Li}^+$ . **Be** has two positive charges, **B** three, **C** four, **N** five, **O** six and

**F**  
seven.

We might expect the next element in the series, neon, to have an atomic kernel with eight positive charges and an outer shell consisting of eight electrons. In a certain sense this is doubtless the case. However, as has been stated in Postulate 3, a group of eight electrons in the shell is extremely stable, and this stability is the greater the smaller the difference in charge between the nucleus and this group of eight electrons. Thus in fluoride ion the kernel has a charge of +7, and the negative charge of the group of eight electrons only exceeds it by one unit. In fact in compounds of fluorine with all other elements, fluorine is assigned the polar number -1. In the case of oxygen, where the group of eight

<sup>1</sup> We shall see later the advisability of modifying this assumption of the cubic arrangement of the fundamental group of eight electrons.

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electrons has a charge exceeding that of the kernel by two units, the polar number is considered to be -2 in nearly every compound. Nitrogen is commonly assumed to have the polar number -3 in such compounds as ammonia and the nitrides. It may be convenient to assign occasionally to carbon the polar number -4, but it has never been found necessary to give boron a polar number -5, or beryllium -6, or lithium -7. But neon, with an inner positive charge of 8 and an outer group of eight electrons, is so extremely stable that it may, as a whole, be regarded as the kernel of neon and we may write **Ne** = Ne.<sup>1</sup>

The next element, sodium, begins a new outer shell<sup>2</sup> and **Na** =  $\text{Na}^+$ , **Mg** =  $\text{Mg}^{++}$ , and so on. In my original theory I considered the elements in the periodic table thus built up, as if block by block, forming concentric cubes. Thus potassium would be like sodium except that it would have one more cube in the kernel. This idea, as we shall see, will have to be modified, but nevertheless it gives a concrete picture to illustrate the theory.

We have then as kernels<sup>3</sup> with a single positive charge **H**, **Li**, **Na**, **K**, **Rb**, **Cs**; with two positive charges **Be**, **Mg**, **Ca**

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Domenica 20 Settembre 2009 22:43 - Ultimo aggiornamento Mercoledì 07 Ottobre 2009 20:40

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,  
**Sr**

,  
**Ba**  
; with three charges

**B**

,  
**Al**

,  
**Sc**  
; with four charges

**C**

,  
**Si**  
; with five charges

**N**

,  
**P**

,  
**As**

,  
**Sb**

,  
**Bi**  
; with six charges

**O**

,  
**S**

,  
**Se**

,  
**Te**  
and a group of radioactive isotopes; with seven charges

**F**

,  
**Cl**

,  
**Br**

,  
**I**  
; and with zero charge

**He**

,  
**Ne**

,  
**Ar**



,  
**Kr**

,  
**Xe**  
and

**Nt**

. These elements only will be discussed in the present paper. The remaining elements form a class in which the atomic kernel is probably neither uniquely determined nor invariable during chemical change. This is one of the elements of incompleteness in the theory. Nevertheless this classification is not arbitrary but forced upon us, and the elements which are included furnish so large a part of the material upon which the science of chemistry is based, that the study of their compounds offers in itself a problem of great importance.

Postulate 2 cannot be fully discussed except in connection with the fourth postulate, but assuming that we understand the meaning of the reduction or oxidation of an element (at least in the case of highly polar

<sup>1</sup> It must not be assumed, even in the case of the elements here chosen for discussion, that the distinction between kernel and shell is absolutely hard and fast. Thus in the ionization of neon by electric discharge electrons must be thrown off from the group which we consider as belonging to the kernel itself.

<sup>2</sup> The periodicity in the table of elements, due to successive additions of groups of eight electrons to the atomic kernel, is imitated closely by compounds. Thus ammonium ion has nine positive charges in the kernels and eight electrons in the shells, but these eight electrons forming a stable group make ammonium ion entirely analogous to the kernel of an alkali metal.

<sup>3</sup> I believe that it will be easily remembered that the sodium kernel has one positive charge, that of chlorine seven positive charges, etc.; but, it may occasionally be desirable for pedagogical purposes to attach to the symbol of the atomic kernel, a small numeral as an index, to show the number of charges.

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substances), reduction means an increase and oxidation a decrease in the number of electrons in the outer atom of the element. Thus for illustration, and with such reservations as will presently be shown necessary, we may state that chlorine has eight electrons in the outer shell in chlorides, six in hypochlorites, four in chlorites, two in chlorates and none in perchlorates.

Postulate 3 can best be illustrated by the use of formulae in which the electrons of the atomic shells are themselves considered as atoms of the element electricity<sup>1</sup> with the symbol **E**. Just as with ordinary symbols we use two types of formulae, one the gross formula representing hardly more than the chemical composition of the substance, the other a structural formula in which we attempt to represent the relative positions of the atoms, so, we may, with the new symbols,

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employ the two types of formulae. We shall later discuss the structural formula, but at this point we may consider the gross formula involving the atomic kernels and the electrons of the outer atoms. Lithium has one positive charge in the kernel, fluorine has seven such charges, so that the neutral molecule of lithium fluoride we may represent

**LiF**

8

. In lithium sulfate

**S**

and

**O**

each has six positive charges, and Li

2

**SO**

4

=

**Li**

2

**SO**

4

**E**

32

;  $\text{SO}_4^{--} =$

**SO**

4

**E**

32

. In every substance in which each element has either its highest or its lowest polar number, E will appear in multiples of 8. Thus NH

3

=

**NH**

3

**E**

8

, H

2

**O =**

**H**

2

**OE**

8

, KOH =

**KOHE**

8

,  $\text{NaNO}_3 =$

**NaNO**

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3

**E**

24

, AIO

3

H

3

=

**AIO**

3

**H**

3

**E**

24

, MgCl

2

=

**MgCl**

2

**E**

16

, K

2

CO

3

=

**K**

2

**CO**

3

**E**

24

. In compounds in which the elements have polar numbers intermediate between the highest and the lowest the number of electrons is not as a rule a multiple of 8, but is in almost all cases an even number. Thus SO

2

=

**SO**

2

**E**

18

, NaClO =

**NaClOE**

14

, C

2

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H

2

=

**C**

2

**H**

2

**E**

10

, C

6

H

6

O =

**C**

6

**H**

6

**OE**

36

.

The extraordinary generality of this rule is shown by the fact that among the tens of thousands of known compounds of the elements under consideration only a few exceptions are known. I may state here all of such compounds that are known to me as they form a very interesting class of substances. They all possess high reactivity and tend to go over into substances with an even number of electrons. First may be mentioned some of the elements themselves in the monatomic state, and as types we may take Na = **NaE** and I = **IE<sub>7</sub>**. In addition to these,<sup>2</sup> we have NO =

**NOE**

11

, NO

2

=

**NO<sub>2</sub>E**

17

, ClO

2

=

**ClO**

2

**E**

19

, (C

6

H

5

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)3C =

(C

6

H

5

)

3

CE

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as well as other tri-aryl methyls

3

and probably also the intensely colored

<sup>1</sup> Dr. Branch has kindly called my attention to a little book by Sir William Ramsay ("The Temple Primers; Modern Chemistry") in which he uses very similar formulae containing E.

<sup>2</sup> Possibly hypophosphoric acid is to be added to this list, but the evidence concerning its molecular weight does not seem conclusive.

<sup>3</sup> See the review by Gomberg, THIS JOURNAL, 36, 1144 (1914).

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compounds between alkali metals and di-aryl ketones,<sup>1</sup> and the colored substances which Wieland believes to contain bivalent and quadrivalent nitrogen.

2

It is to be particularly noted that such substances when placed in a polar environment almost invariably change into substances with an even number of electrons in the outer atoms. Thus NO<sub>2</sub> dissolved in water gives nitrous and nitric acids, and even in pure liquid nitrogen tetroxide we must assume, since it has electrical conductivity, that such ions as NO<sub>2</sub><sup>+</sup> = **NO<sub>2</sub>E<sub>16</sub>** and

NO

=

**NO**

2

**E**

13

[sic, the 13 should be 14] are present. Similarly, ClO

2

dissolves to form chlorous and chloric acids to a small extent, triphenyl methyl dissolves in liquid sulfur dioxide to form a conducting solution with ions presumably of the type (C

6

H

5

)

3

C<sup>+</sup> and (C

6

H

5

)

3

C<sup>-</sup>. Sodium in the metallic state, or when dissolved in such a solvent as liquid ammonia, dissociates according to the equation



. In general, therefore, we may state that a substance, in whose gross formula an odd number of electrons appears, holds one electron by weak constraints, and in a medium which weakens all electric constraints, namely in a polar medium, the odd electron may be given up completely. Of the cases mentioned, the odd electron appears to be most firmly bound in NO, and even in a polar environment the constraints are still sufficiently powerful to hold the electron. Nevertheless in the presence of any oxidizing agent such as oxygen, that is, in the presence of a substance which has a strong tendency to take up an electron, the interchange will occur at once.

Molecules of this class which contain an odd or unpaired electron will for the sake of brevity be called odd molecules. An odd molecule will contain at least one atom with an uneven number of electrons in the shell. This may be called an odd atom.

Postulate 4 raises a question of the very greatest importance. Ever since the first suggestion of Helmholtz, numerous efforts have been made to explain chemical combination by the assumption that in the formation of a compound some of the electrons of one atom pass completely into an other atom, and that the different charged parts of the molecule thus produced are held together by electrical forces. Such theories have, in my opinion, proved entirely inadequate except in the case of substances of the strongly polar type. This fact has been recognized by Thomson in his latest paper, in which he introduces an entirely different type of chemical combination in the case of the compounds which we have called nonpolar. However, according to the theory which I am now presenting, it is not necessary to consider the two extreme types of chemical combination, corresponding to the very polar and the very nonpolar compounds,

<sup>1</sup> Schlenk and Weickel, Ber., 44, 1182 (1911).

<sup>2</sup> Wieland, Ann., 381, 200 (1913); Ber., 47, 2111 (1914).

interpenetrability of the atomic shells which is made in Postulate 4. Thus an electron may form a part of the shell of two different atoms and cannot be said to belong to either one exclusively. Hence in general it is impossible to say that one element in a compound has, during chemical change, been oxidized or reduced and that another element has not suffered such a change; but it is only as we approach substances of the completely polar type that such distinctions become less and less ambiguous. Since this question is one to which we shall frequently revert it need not be discussed further at this point.

Postulate 5 is based upon the fact that we do not find what might be called intra-atomic isomers. If the electrons of the atomic shell could at one time occupy one set of positions and at another time another set and if there were no opportunity for ready transition from one of these sets of positions to another, we should have a large number of isomers differing from one another only in the situation of the electrons in the atomic shell. While there may possibly be a few cases where we might surmise the existence of just such isomers, in most cases it is evident that they do not exist, and we must assume, therefore, considerable freedom of change from one distribution of electrons in the shell to another.

Now there are only two ways in which one body can be held by another. It may, owing to a force of attraction, be drawn toward the second body until this force is gradually offset by a more rapidly increasing force of repulsion. In this case it comes to rest at a point where the net attraction or repulsion is zero, and is therefore in a condition of constraint with respect to any motion along the line joining the two centers; for if the distance between the two bodies is diminished they repel one another, while if the distance is increased they are attracted toward one another. An example of this type is a body attracted toward the earth but resting upon an elastic substance where the attractive force of gravity is offset by the repulsive force which we happen to call elastic; but it would be a mistake to consider the forces of elasticity to be different in character from other known forces. Indeed it is evident that just as we have the law of universal attraction between particles at great distances, so at small distances we have the equally universal law of repulsion.

The other way in which one body may hold another is that in which the planets are held by the sun, and this is the way that in some current theories of atomic structure the electrons are supposed to be held by the atom. Such an assumption seems inadequate to explain even the simplest chemical properties of the atom, and I imagine it has been introduced only for the sake of maintaining the laws of electromagnetics which are known to be valid at large distances. The fact is, however, that in the more prominent of these theories even this questionable advantage

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disappears, for the common laws of electricity are not preserved. The most interesting and suggestive of these theories is the one proposed by Bohr<sup>1</sup> and based upon Planck's quantum theory. Planck in his elementary oscillator which maintains its motion at the absolute zero, and Bohr in his electron moving in a fixed orbit, have invented systems containing electrons of which the motion produces no effect upon external charges. Now this is not only inconsistent with the accepted laws of electromagnetics but, I may add, is logically objectionable, for that state of

motion which produces no physical effect whatsoever may better be called a state of rest. Indeed it seems hardly likely that much progress can be made in the solution of the difficult problems relating to chemical combination by assigning in advance definite laws of force between the positive and negative constituents of an atom, and then on the basis of these laws building up mechanical models of the atom. We must first of all, from a study of chemical phenomena, learn the structure and the arrangement of the atoms, and if we find it necessary to alter the law of force acting between charged particles at small distances, even to the extent of changing the sign of that force, it will not be the first time in the history of science that an increase in the range of observational material has required a modification of generalizations based upon a smaller field of observation. Indeed in the present case, entirely aside from any chemical reasons, a study of the mathematical theory of the electron leads, I believe, irresistably to the conclusion that Coulomb's law of inverse squares must fail at small distances. In this connection I wish to call attention to an extremely interesting paper by Mr. A. L. Parson<sup>2</sup> which has only just been published, but which I had an opportunity of looking over with the author over a year ago. The fundamental assumption of Parson's theory is. that the electron is not merely an electric charge but is also a small magnet, or, in his terminology, a magneton. Assuming therefore the existence of magnetic as well as electric forces between the different parts of the atom, Parson

<sup>1</sup> I believe that there is one part of Bohr's theory for which the assumption of the orbital electron is not necessary, since it may be translated directly into the terms of the present theory. He explains the spectral series of hydrogen by assuming that an electron can move freely in any one of a series of orbits in which the velocities differ by steps, these steps being simply expressed in terms of ultimate units (in his theory Planck's  $h$  is such a unit), and that radiation occurs when the electron passes from one orbital velocity to the next. It seems to me far simpler to assume that an electron may be held in the atom in stable equilibrium in a series of different positions, each of which having definite constraints, corresponds to a definite frequency of the electron the intervals between the constraints in successive positions being simply expressible in terms of ultimate rational units (see Lewis and Adams, *Phys. Rev.*, 3, 92 (1914)).

<sup>2</sup> A "Magnetion Theory of the Structure of the Atom," Smithsonian Publication 2371, Washington, 1915.

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was led entirely independently to the conclusion which I have stated above, namely that the most stable condition for the atomic shell is, the one in which eight electrons are held at the corners of a cube. Not only in this but in a number of other important points the theory which I am presenting will be seen to coincide with that of Parson's paper. The results of the magnetic experiments with which he proposes to test the magneton theory will be of great interest. Meanwhile we may attempt to find, apart from any a priori consideration, just what atomic



structure best explains known chemical facts.

There is one part of Parson's theory which agrees with my own former theory but which I now believe to be incorrect. The idea that argon is a system of concentric cubes (in Parson's theory cubes side by side), and that neon is a similar system with one less cube, led naturally to the assumption that helium is similarly constituted. But recent evidence from radioactive phenomena, and from Moseley's study of the X-ray spectrum, makes it seem almost certain that helium has a total not of eight but of either two or four electrons.<sup>1</sup> Assuming that helium is the only element between hydrogen and lithium and that it has two electrons, then it is evident from the inert character of helium, and from the resemblance of this element to the other inert gases, that here the pair of electrons plays the same role as the group of eight in the heavier atoms, and that in the row of the periodic table comprising hydrogen and helium we have in place of the rule of eight the rule of two. Therefore hydrogen not only has one electron in its outer shell, which may pass into the shell of another atom just as the electron of lithium or sodium may, but it is capable of taking up one electron to form the stable pair, just as fluorine or chlorine takes up one electron to form the stable group of eight. Hydrogen therefore must be regarded as the first member of the halogens as well as of the lithium group. According to this view lithium hydride is a salt<sup>2</sup> although perhaps less polar than lithium fluoride or chloride. Therefore in what follows we shall regard the acquisition of one additional electron by hydrogen as entirely analogous to the acquisition of enough electrons to form the group of eight in the case of other atoms.

## **Molecular Structure.**

I shall now attempt to show how, by a single type of chemical com-

<sup>1</sup> Two, if hydrogen and helium are the only elements of lower atomic weight than lithium; four, if we assume with Rydberg that there are two rows in the periodic table, one containing hydrogen and proto-helium and one containing eka-hydrogen and helium. The above discussion will be the same on either of these assumptions, and although Rydberg's assumption has a very high degree of plausibility I have adopted for simplicity the more familiar one.

<sup>2</sup> In order to test this view experiments have been begun by Professor O. F. Stafford. These experiments have not progressed far but they at least indicate that fused lithium hydride is a good electrolyte.

ination, we may explain the widely varying phenomena of chemical change. With the original assumption of Helmholtz, which has been used by some authors under the name of the electron theory of valence, and according to which a given electron either does or does not pass

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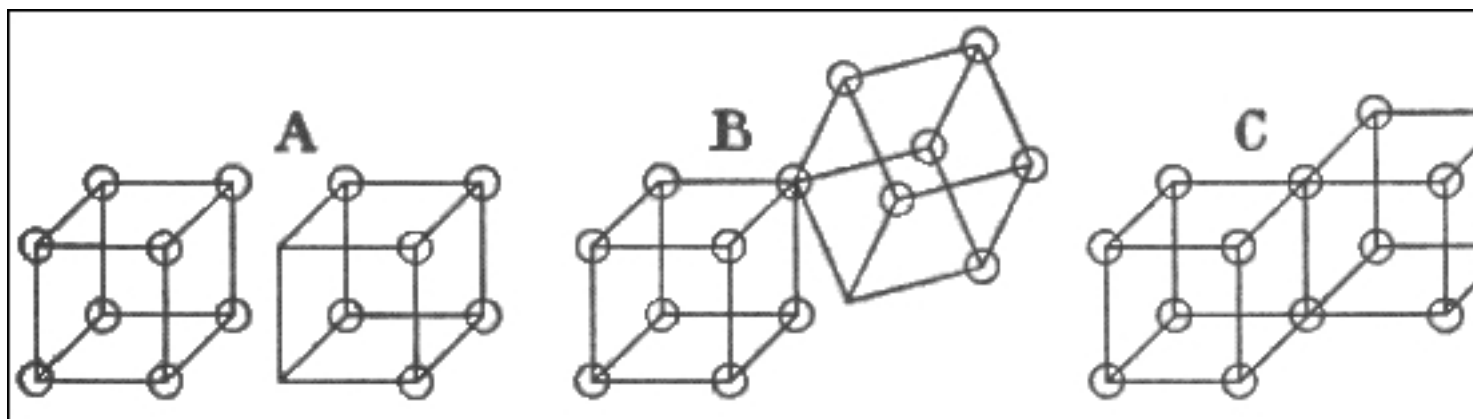
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completely from one atom to another, it is possible to give a very satisfactory explanation of compounds which are of distinctly polar type, but the method becomes less and less satisfactory as we approach the nonpolar type. Great as the difference is between the typical polar and nonpolar substances, we may show how a single molecule may, according to its environment, pass from the extreme polar to the extreme nonpolar form, not per saltum, but by imperceptible gradations, as soon as we admit that an electron may be the common property of two atomic shells.

Let us consider first the very polar compounds. Here we find elements with but few electrons in their shells tending to give up these electrons altogether to form positive ions, and elements which already possess a number of electrons tending to increase this number to form the group of eight. Thus  $\text{Na}^+$  and  $\text{Ca}^{++}$  are kernels without a shell, while chloride ion, sulfide ion, nitride ion (as in fused nitrides) may each be represented by an atom having in the shell eight electrons at the corners of a cube.

As an introduction to the study of substances of slightly polar type we may consider the halogens. In Fig. 3 I have attempted to show the



different forms of the iodine molecule  $\text{I}_2$ . A represents the molecule as completely ionized, as it undoubtedly is to a measurable extent in liquid iodine <sup>1</sup>.

Without ionization we may still have one of the electrons of one atom fitting into the outer shell of the second atom, thus completing its group of eight as in B. But at the same time an electron of the second atom may fit into the shell of the first, thus satisfying both groups of eight and giving the form C which is the predominant and characteristic structure of the halogens. Now notwithstanding the symmetry of the form C, if the two atoms are for any reason tending to separate the two common electrons may cling more firmly sometimes to one of the atoms, sometimes to the other, thus producing some dissymmetry in the molecule as a whole, and one atom will have a slight excess of positive charge, the other of negative. This separation of the charges and the conse-

<sup>1</sup> See Lewis and Wheeler, Loc. cit.

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quent increase in the polar character of the molecule will increase as the atoms become separated to a greater distance until complete ionization results.<sup>1</sup> Thus between the perfectly symmetrical and nonpolar molecule C and the completely polar and ionized molecule represented by A there will be an infinity of positions representing a greater or lesser degree of polarity. Now in a substance like liquid iodine it must not be assumed that all of the molecules are in the same state, but rather that some are highly polar, some almost nonpolar, and others represent all gradations between the two. When we find that iodine in different environments shows different degrees of polarity, it means merely that in one medium there is a larger percentage of the more polar forms. So bromine, although represented by an entirely similar formula, is less polar than iodine. In other words, in the average molecule the separation of the charge is less than in the case of iodine. Chlorine and fluorine are less polar than either and can be regarded as composed almost completely of molecules of the form C.

I wish to emphasize once more the meaning that must be ascribed to the term tautomerism. In the simplest case where we deal with a single tautomeric change we speak of the two tautomers and sometimes write definite formulae to express the two. But we must not assume that all of the molecules of the substance possess either one structure or the other, but rather that these forms represent the two limiting types, and that the individual molecules range all the way from one limit to the other. In certain cases where the majority of molecules lie very near to one limit or to the other, it is very convenient and desirable to attempt to express the percentage of the molecules belonging to the one or to the other tautomeric form; but in a case where the majority of molecules lie in the intermediate range and relatively few in the immediate neighborhood of the two limiting forms, such a calculation loses most of its significance. With the halogens it is a matter of chance as to which of the atoms acquires a positive and which a negative charge, but in the case of a binary compound composed of different elements the atoms of one element will be positive in most, though not necessarily all, of the molecules. Thus in Br<sub>2</sub> the bromine atom is as often positive as negative, but in BrCl it will be usually positive and in IBr usually negative, although in all these substances which are not very polar the separation of charges in the molecule will be slight, whereas in the metallic halides the separation is nearly complete and the halogen atoms acquire almost complete possession of the electrons. In order to express this idea of chemical union in symbols I would sug-

<sup>1</sup> When the separation occurs in a nonpolar environment the atoms may separate in such a way that each retains one of the two common electrons, as in the thermal dissociation of iodine gas.

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gest the use of a colon, or two dots arranged in some other manner, to represent the two electrons which act as the connecting links between the two atoms. Thus we may write  $\text{Cl}_2$  as  $\text{Cl} : \text{Cl}$ . If in certain cases we wish to show that one atom in the molecule is on the average negatively charged we may bring the colon nearer to the negative element. Thus we may write  $\text{Na} : \text{I}$ , and  $\text{I} : \text{Cl}$ . Different spacings to represent different degrees of polarity can of course be more freely employed at a blackboard than in type.

It will be noted that, since in the hydrogen-helium row we have the rule of two in the place of the rule of eight, the insertion of one electron into the shell of the hydrogen atom is entirely analogous to the completion of the cube in the case of the halogens. Thus we may consider ordinary hydrogen as a hydride of positive hydrogen in the same sense that chlorine may be regarded as a chloride of positive chlorine. But  $\text{H}$ , is far less polar even than  $\text{Cl}_2$ . The three main types of hydrogen compounds may be represented therefore by  $\text{H} : \text{Cl}$ ,  $\text{H} : \text{H}$ , and  $\text{Na} : \text{H}$ . We may go further and give a complete formula for each compound by using the symbol of the kernel instead of the ordinary atomic symbol and by adjoining to each symbol a number of dots corresponding to the number of electrons in the atomic shell. Thus we may write  $\text{H} : \text{H}$ ,  $\text{H} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}} : \text{H}$ ,  $\text{H} :$

but we shall see that in many cases such a formula represents only one of the numerous extreme tautomeric forms. For the sake of simplicity we may also use occasionally formulae which show only those electrons concerned in the union of two atoms, as in the preceding paragraphs.

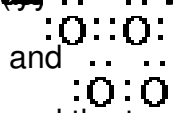
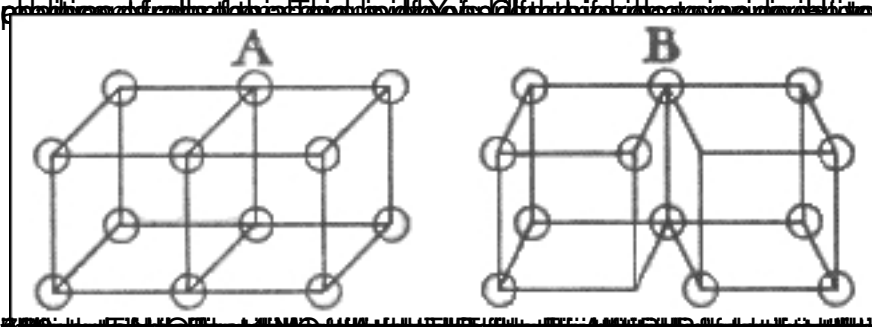
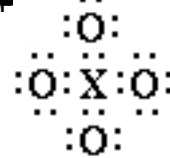
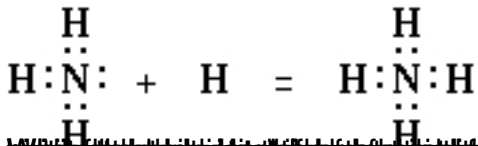
It is evident that the type of union which we have so far pictured, although it involves two electrons held in common by two atoms, nevertheless corresponds to the single bond as it is commonly used in graphical formulae. In order to illustrate this point further we may discuss a problem which has proved extremely embarrassing to a number of theories of valence. I refer to the structure of ammonia and of ammonium ion. Ammonium ion may of course, on account of the extremely polar character of ammonia and hydrogen ion, be regarded as a loose complex due to the electrical attraction of the two polar molecules. However, as we consider the effect of substituting hydrogen by organic groups we pass gradually into a field where we may be perfectly certain that four groups are attached directly to the nitrogen atom, and these groups are held with sufficient firmness so that numerous stereochemical isomers have been obtained. The solution of this problem in terms of the theory here presented is extremely simple and satisfactory, and it will be sufficient to write an equation in terms of the new symbols in order to make the explanation obvious. Thus for  $\text{NH}_3 + \text{H}^+ = \text{NH}_4^+$  we write

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and the two forms of ethylene<sup>1</sup> as

