was nearly twice that produced in the chloride by the same amount of dilution, whereas the thermal change in the trichloroacetate, caused by a dilution only half as great, was considerably larger than that brought about in the sulfate.

The values for the heats of neutralization of hydroxylamine are approximately the same as Thomsen's, our figures ranging from 0.3% to 2.6% higher. In the case of tetramethylammonium hydroxide, however, the values obtained are about 7.5% lower than Thomsen's. No data on the heats of neutralization of the two bases with trichloroacetic acid have been found in the literature for comparison.

The results recorded in this paper are believed to possess an unusually high degree of precision, and yet, such results are to be expected from the exact method of calorimetry employed.

Summary.

1. The heats of neutralization of hydroxylamine and tetramethylammonium hydroxide when neutralized by hydrochloric, sulfuric, and trichloroacetic acids, in aqueous solutions, have been measured adiabatically.

2. The results obtained for hydroxylamine are from 0.3% to 2.6% higher and for tetramethylammonium hydroxide about 7.5% lower than Thomsen's values for the same bases (Table VII).

3. The heats of neutralization of hydroxylamine and tetramethylammonium hydroxide with trichloroacetic acid have been measured for the first time, as far as we are aware.

In conclusion the writer wishes to express his obligation to Professor J. H. Mathews for helpful suggestions as well as for aid in obtaining the apparatus used.

MADISON, WIS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE.]

A CRITICISM OF THE ELECTRON CONCEPTION OF VALENCE.

BY ROGER F. BRUNEL.

Received January 18, 1915.

Physical investigations of recent years have convinced most chemists that atoms of all elements contain, if they are not made up of, negative electrons, held in position by a positive charge. The attractive force between atoms is thus electrical in origin. This view is shared by the author.

In 1909, Nelson, Beans, and Falk[1] published an article developing the idea that "every chemical bond formed between two atoms involves the transfer of a corpuscle from one atom to the other,"[2] a conception for which

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[1] *School Mines Quart.*, 30, 179 (1909).

[2] THIS JOURNAL, 35, 1810 (1913).

J. J. Thomson[1] was originally responsible, although he has now abandoned it. The resulting electrostatic charges are apparently considered responsible for the interatomic attraction. This conception is now commonly referred to in THIS JOURNAL as the "Electron Conception of Valence," and has been extensively developed by Nelson, Beans, and Falk, Fry, L. W. Jones and others.[2] According to this hypothesis chemical bonds are to be represented as $Cl \longrightarrow Cl$, $C \longrightarrow C$, $H \longrightarrow Cl$, or $\overset{+}{Cl}$——$\overset{-}{Cl}$, etc. This hypothesis is by no means generally accepted, as is the fundamental conception of the electrical constitution of the atom, and is by no means a necessary corollary of that.

Objections to this conception from the physical point of view, all of which appear to the author to be valid, have recently been brought forward by Bates.[3] Bray and Branch,[4] Lewis,[5] and Arsem,[6] have recently proposed other hypotheses dealing with the same question, and Thomson[7] now offers quite a different explanation of the manner of chemical union. Some of these views will be referred to further below. The object of this paper is to call attention to certain weaknesses in the arguments put forward in support of this conception and certain difficulties that arise in applying it to chemical phenomena.

The development and application of this conception have involved the formulation of several supplementary hypotheses, and we must turn to the earlier papers on the subject for direct arguments, based on simple phenomena, for the fundamental assumption on which it is based. I would first call attention to certain of these arguments, advanced by Nelson, Beans, and Falk.[8]

(*a*) These authors note that according to their hypothesis ethane must have the unsymmetrical structure $H_3\overset{+}{C}$——$\overset{-}{C}H_3$. To meet the objections likely to be called forth from the organic chemist by such an assumption, it is stated that one substance, triphenylmethyl, shows evidence of such a polar structure in that it forms a conducting solution in sulfur dioxide, where these authors assume that the ions $(C_6H_5)_3\overset{+}{C}$ and $(C_6H_5)_3\overset{-}{C}$ are present.

In the first place this assumes one of the points at issue, for the ad-

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[1] *Phil. Mag.*, [6] **7**, 237.

[2] References to numerous papers on this subject will be found in THIS JOURNAL, **35**, 1813 (1913); and **36**, 1035 (1914).

[3] THIS JOURNAL, **36**, 789 (1914).

[4] *Ibid.*, **35**, 1440 (1913).

[5] *Ibid.*, **35**, 1448.

[6] *Ibid.*, **36**, 1655.

[7] *Phil. Mag.*, [6] **27**, 757 (1914).

[8] *School Mines Quart.*, **30**, 179 (1909). Practically the same arguments are to be found in THIS JOURNAL, **32**, 1637 (1910).

vocates of the theory have first to offer proof that the ability of a substance to split into charged ions in solution is evidence that the dissociating parts are already charged in the molecule before dissociation occurs.

But, furthermore, there is little evidence that the ionization of triphenylmethyl is of the sort indicated, the present tendency being, in the case of nonaqueous solvents at least, to assume the ionization of some complex formed with the solvent. Gomberg[1] assumed that triphenylmethyl ions are present in sulfur dioxide solution, but with no direct evidence except that he noted the similarity between this case and the formation of conducting solutions of bromine in various solvents, especially in sulfur dioxide. Such an argument loses its force in view of the recent investigations of Bruner and Galecki,[2] and Bruner and Bekier,[3] who obtained evidence that in solutions of bromine, and iodine, ICl and ICl_3, in nitrobenzene and sulfur dioxide no halogen kations are present.

Schlenck[4] has also shown that although triphenylmethyl sodium forms a conducting solution in ether, it cannot be due to dissociation in the sense $\overset{-}{(C_6H_5)_3C} + \overset{+}{Na}$, but rather to the ionization of some more complex molecules formed in the solution.

The ionization in these cases is thus of a more complex sort than at first appears, and at the present stage of our knowledge of such phenomena can hardly furnish proof that in sulfur dioxide solution of triphenylmethyl we have the ions assumed by Nelson, Beans, and Falk. In general, we can certainly say that in organic compounds there is not the slightest evidence of such polarity as is demanded by this theory on the part of the carbon atoms.

(*b*) The next use made of the directed valences is in explaining the well-known fact that the melting points of the homologous series of $\omega\omega'$ saturated dibasic acids fall on a zigzag curve, those of alternate members of the series being lower than those of the preceding and following members. An explanation is proposed which is based on the presence of similar groups at the ends of the carbon chain. This results in alternate symmetrical and unsymmetrical valence structures for the members of the series, which might be responsible for alternate high and low melting points. These authors suggest that the same may be found to hold true for the series of monobasic acids, for which, they remark, the electronic formulas cannot yet be written. The last remark is not particularly convincing, since it would appear that we know as much about the monobasic acids as about their more complex dibasic relatives. The fact that the melting points

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[1] *Ber.*, 37, 2050 (1904).

[2] *Z. Physik. Chem.*, 84, 513 (1913).

[3] *Ibid.*, 84, 570.

[4] *Ber.*, 47, 1678 (1914).

of the monobasic acids do fall on a zigzag curve[1] exactly similar to that for the dibasic acids appears to invalidate the argument for the "electron conception valence" based on the latter, since the explanation proposed for the dibasic acids rests fundamentally on the presence of similar groups at both ends of the carbon chain and would demand a smooth curve for the monobasic acids.

Furthermore, if we examine other homologous series we find, in as far as data are available in the latest edition of the Richter Lexikon, similar zigzag melting point curves for the ethyl esters of monobasic acids, for the amides of dibasic acids, and for the ωω′-glycols; a smooth curve for the monohydric alcohols; a curve with a minimum point for the *n*-aldoximes and for the dialkylsulfones; and an altogether irregular curve for the amides of monobasic acids. Even allowing for errors in melting points of less easily accessible compounds, it is not evident that there is justification for choosing one homologous series from this group and basing on it an argument for the valence hypothesis. Thus the proposed explanation of the zigzag curve of the dibasic acids is misleading.

(*c*) Double bonds between carbon atoms are next taken up. Of the three possible formulas, $\rightleftarrows$, $\rightrightarrows$, and $\leftleftarrows$, $\rightleftarrows$ is chosen as the stable arrangement from the fact that the stable hydrocarbon, propene, gives, on treatment with hydriodic acid, a mixture of primary and secondary propyl iodides. Since the iodine (negatively charged) goes partly to each carbon atom it is assumed that there must be positive ends of bonds on both carbon atoms, indicating the formula $CH_3CH \rightleftarrows CH_2$. Since this reaction is offered as evidence for assuming a symmetrical distribution of the positive and negative charges between the two unsaturated carbon atoms, it is somewhat surprising on examining the quantitative data to discover that over 99.5% of the product of the reaction is the secondary propyl iodide. The authors tell us that this is due to the influence of the methyl group. The addition of ClBr and ClI to propene is somewhat better, the ratio of the two possible addition products being 7 : 5 and 4 : 1, respectively. These reactions furnish the entire basis for determining how the double bond is to be written in all stable compounds with the ethylene linkage. It is not evident to the author how the above facts furnish any reason for assuming any connection whatever between the direction of the valences and the course followed by such addition reactions.

Furthermore, the addition of halogen acids to alkenes is a still more perplexing matter than is here implied. The author has investigated extensively the addition of hydrobromic acid to isobutene, and has ob-

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[1] Levene and Jacobs, *J. Biol. Chem.*, 18, 463 (1914) have recently published data for the m. ps. of the acids C_{11}-C_{16} which assign to the acid C_{15} a higher value than that of C_{14}. The melting point curve for the series therefore loses its zigzag character at this point, but retains it elsewhere.

tained by this process products containing all the way from 0% to 55% of isobutyl bromide, the remainder being tertiary bromide, depending upon experimental conditions. A reaction which may be subject to such wide variation can be of little value as evidence for any valence hypothesis.

(*d*) The theory is applied to double bond isomerism of the maleic-fumaric type. The most obvious objection to this application, namely, that three isomers are in general predicted by the theory whereas in nearly all cases only two are known, is forestalled by the statement of the authors that the prediction of unknown facts by a theory is a far less serious fault than the failure to account for known ones, and the convenient assumption that all the predicted but unknown isomers are very unstable if not incapable of isolation. There must surely be limits beyond which this attitude becomes unsafe. But to the theory even with these elastic reservations, there are objections.

The case of the cinnamic acids, referred to by Nelson, Beans and Falk as one where the expected number of isomers exist; has now become rather an argument against their hypothesis, since the existence of four isomers has been established, the theory calling for three, while the recent work of Stobbe and Schönburg[1] has shown them not to be due to polymorphism, but, apparently, to chemical isomerism.

There is also further objection to the use of the theory for this type of isomerism. In the preceding argument, (*c*), the formula for propene is deduced from its behavior on addition of hydriodic acid, the assumption being made that the iodine tends to unite with such carbon atoms as carry the positive ends of valences, that is, positive charges. The isomeric unsaturated acids (maleic-fumaric type) are now assumed to differ in the directions of their valences, $\rightleftarrows$, and $\rightrightarrows$. If the argument applied to propene is of any significance, then the isomeric unsaturated acids must give different addition products with halogen acids. Unfortunately it is with the halogens that such so-called geometrical isomers give isomeric addition products (stereoisomeric products), whereas it is well known that with halogen acids the addition products are the same from both members of such a pair.[2] It is impossible to see the slightest ground for the use of these polar valences in connection with this type of isomerism.

(*e*) The existence of unexplained isomeric nitrotoluenes and other compounds described by Ostromisslensky[3] is accounted for by isomerism of the above type in the benzene ring. In view of our slight knowledge as to the nature of such isomerism the case can hardly be discussed profitably. The Kekulé theory would explain it as satisfactorily.

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[1] *Ann.*, **402**, 187 (1913).

[2] Michael and Freer, *J. prakt. Chem.*, N. F., 40, 95, and Michael, *Ibid.*, **40**, 171 (1889).

[3] *Z. physik. Chem.*, **57**, 341 (1907).

(*f*) When it comes to application of the conception to the behavior of compounds with the acetylene union, it will first be necessary to explain some of the inconsistencies noted under (*d*) and formulate a somewhat exact system of hypotheses before the discussion can be profitable.[1]

The paper from which the above illustrations are taken takes up numerous other organic problems—the diazo compounds, tautomerism, etc., but little more is shown than that the formulas of the compounds could be written in this new nomenclature, the problems being complex ones and the theory elastic.

The further the electron conception of valence is developed the more qualifying factors we have to admit. In a later paper,[2] Falk presents a classification of the unsaturated acids, in the attempt to show that when the bonds of the unsaturated linkage are directed in certain ways the affinity constants of the acids fall within certain limits.

The value of the classification in itself or as evidence for the valence theory, however, becomes small when we note that outside of a rather restricted number of compounds the values of the affinity constants depart widely from those predicted. This is attributed to "constitutive influences." But if this new theory of chemical combination contributes nothing to the elucidation of this large unknown factor of organic chemistry, it becomes still more difficult to find proof for it in its application to the more complex problems.

Most applications of the electron theory of valence have been in connection with some of the most perplexing questions of organic chemistry. We are, however, not justified in applying a hypothesis merely because it provides a convenient method of formulating or even of correlating a limited number of phenomena, if it is inconsistent as soon as we step outside narrow limits, or if it is not fundamentally suited to explain the manner of chemical combination. The author has little sympathy with the statement of Falk[3] that its "convenient symbolism alone...would justify its use in practical work." This conception of valence involves necessarily certain assumptions regarding the nature of union between atoms and the mechanism of chemical reactions, and there are certain questions to which I would call attention.

The statement is made by W. A. Noyes[4] that "all reactions involving decomposition of molecules are preceded by an ionization of the parts of

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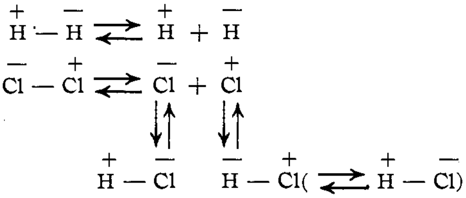
[1] Only a slight examination of the somewhat confusing relations between the isomeric unsaturated acids and the corresponding saturated compounds is needed to show how superficial are the arguments put forward by Falk for the application of the electron conception of valence to the various types of unsaturated compounds.

[2] THIS JOURNAL, **33**, 1140 (1911).

[3] *Ibid.*, **35**, 1811 (1913).

[4] *Ibid.*, **23**, 460 (1901). An interesting discussion of this question is to be found in the article by Berthoud, *J. chim. phys.*, **10**, 578 (1912).

the molecule," and this view is evidently adopted by other advocates of this conception. Thermal dissociation of such molecules as hydrogen, hydrogen chloride, phosphorus pentachloride, etc., is thus assumed to yield primarily charged atoms or radicals. Let us examine the reaction between hydrogen and chlorine, as formulated by Fry.[1] The bracketed reaction appears to be implied and is added by the author. The decomposition of hydrogen chloride would, of course, involve the reversal of these steps.



$$\overset{+}{H}-\overset{-}{H} \rightleftarrows \overset{+}{H} + \overset{-}{H}$$

$$\overset{-}{Cl}-\overset{+}{Cl} \rightleftarrows \overset{-}{Cl} + \overset{+}{Cl}$$

$$\overset{+}{H}-\overset{-}{Cl} \qquad \overset{-}{H}-\overset{+}{Cl}(\rightleftarrows \overset{+}{H}-\overset{-}{Cl})$$

The electromer $\overset{-}{H}$——$\overset{+}{Cl}$ must be present in traces only, since otherwise there is no reason why it should not ionize in solution, and why, for example, chlorine should not appear at the cathode in electrolysis. This electromer is thus very unstable.

Let us consider the following question: Why does HCl exist in preference to the system $H_2 + Cl_2$? Instead of saying that H and Cl atoms have a greater affinity for each other than for other atoms of their own sort, the electron conception of valence would enable us to be more specific and state that H and Cl have a great tendency, respectively, to lose and gain an electron. Here we are apparently nearly touching upon Abegg's "electroaffinity," although he assumed atoms to become charged only when ionization occurred.

One of the fundamental problems of chemistry is surely the determination or exact specification of the relative tendencies of various sorts of atoms to combine with each other, but it is not certain that we are greatly assisted by restating the problem as that of determining the relative tendencies of atoms to gain and lose electrons from each other. The somewhat puzzling stability of the hydrogen and chlorine molecules is not explained merely by writing signs above the atoms. Nor can we so easily escape the conflicts that arise in trying to assign relatively positive and negative characters to different elements. For example, if chlorine and hydrogen combine with each other for the reason suggested above, we must also expect that chlorine would combine with any element somewhat more or less negative than itself more energetically than with itself, but the properties of oxides of chlorine or of Br-Cl do not bear out this expectation.

If we look further into this question of the relative tendencies of differ-

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[1] This Journal, 23, 263 (1914).

ent atoms to gain and lose electrons, we have not to go far to find inconsistencies among the electronic formulas. For example, we find, according to Jones[1] that the compound $(CH_3^+)_3\equiv N\substack{-+\,Cl\\+-\,OH}$ changes to $(CH_3^+)_3\equiv N\substack{+-\,Cl\\+-\,OH}$, the chlorine taking two electrons from the nitrogen. The compound $(Cl_3^-)\begin{smallmatrix}+\\+\\+\end{smallmatrix}P\substack{+-\,Cl\\+-\,Cl}$ exists in equilibrium with $(Cl_3^-)\begin{smallmatrix}+\\+\\+\end{smallmatrix}P\substack{-+\,Cl\\+-\,Cl}$. The compound $(CH_3^+)_3\equiv N\substack{-+\,Br\\+-\,Br}$, however, is assumed not to change to $(CH_3^-)\equiv N\substack{+-\,Br\\+-\,Br}$. We must conclude, then, that bromine has less tendency than chlorine to take an electron from nitrogen, that it is less negative.[2] Similarly the compound $(CH_3^+)_3\equiv N\substack{-+\,OH\\+-\,OCH_3}$ is quite stable. OH has thus also *less* tendency than chlorine to take an electron from nitrogen, that is, like bromine, it is *less* "negative" than chlorine. This conclusion is, however, contradicted by the assumption made throughout this paper by Jones and in other articles dealing with this subject, that the stable form of hypochlorous acid is $HO\overset{-\quad+}{\text{——}}Cl$, the OH having taking an electron from the chlorine. It is here assumed to be *more* "negative" than chlorine. I shall mention this compound again below.

A hypothesis which deals with the nature of the attractive force between atoms contains inevitably expressed or implied assumptions regarding chemical affinity. If our above assumptions in connection with the hydrogen chloride equilibrium are incorrect, *then there is plainly great need of some explicit statement as to what principles do control the gain and loss of electrons, and how this property is related to chemical affinity.* With the whole theory in its present vague state, a multitude of contradictory hypotheses can easily be hidden by the complex and elastic nomenclature.

Since the algebraic sum of the positive and negative charges in any chemical compound or system must, according to our fundamental conception, be zero, it naturally follows that we shall never be at a loss to properly arrange the charges so that any ions may interact, provided we assume the proper exchanges of electrons. The reaction, sodium plus chlorine, would be somewhat different from that examined above.[3]

$$\begin{array}{ccccc} \overset{+}{Cl}-\overset{-}{Cl} & \rightleftarrows & \overset{+}{Cl}+\overset{-}{Cl} & & \overset{-}{Cl}+\overset{-}{Cl} \\ & & & \longrightarrow & \\ 2Na & \rightleftarrows & Na+Na & & \overset{+}{Na}+\overset{+}{Na} \end{array}$$

Evidently we must assume that one chlorine takes an electron from each of the two sodium atoms; or we may assume that we have

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[1] This Journal, 36, 1268 (1914).

[2] There is opportunity for confusion of terms here. By a "negative" atom is meant one tending to become negatively charged, the customary usage. This will of course be one tending to gain an electron, *i. e.*, one which before it gains the electron is presumably as a whole, or at some point, strongly positive.

[3] Other simple reactions are formulated by Fry, This Journal, 36, 267 (1914).

$$2\mathrm{Na} \rightleftarrows \overset{+}{\mathrm{Na}} + \overset{-}{\mathrm{Na}}.$$

In this reaction and that between hydrogen and chlorine two assumptions are involved which must constantly be employed in applying the electron conception of valence. First, we assume a great mobility on the part of the electrons—such, in fact, that the nonexistence of the hypothetical less stable electromers is not surprising. Secondly, we assume the existence, always, in equilibrium, of all the possible electromers.

Once, however, these assumptions are admitted, all plausibility disappears from those arguments commonly employed by the advocates of the theory, in which the charge on some atom in a compound is deduced from the charge judged to be present on it after the compound has been subjected to a reaction of some sort. For example, hypochlorous acid, supposed to be $\overset{-}{\mathrm{HO}}\text{—}\overset{+}{\mathrm{Cl}}$ is a substance commonly used for reference. If a compound, say RCl, reacts thus:

$$\mathrm{R—Cl + H—OH = R—H + Cl—OH}$$

it is concluded that the chlorine, positive in $\overset{+}{\mathrm{Cl}}\text{–}\overset{-}{\mathrm{OH}}$, must also be positive in RCl, thus $\overset{-}{\mathrm{R}}\text{–}\overset{+}{\mathrm{Cl}}$.[1]

In the first place we must inquire further into the reasons for supposing hypochlorous acid to be necessarily $\overset{+}{\mathrm{Cl}}\text{–}\overset{-}{\mathrm{OH}}$. Oxygen is not necessarily negative any more than is chlorine. In fact, from its position in the periodic system, which according to Falk[2] must furnish the basis for distribution of the charges in the simpler compounds, we should expect it to be less inclined to carry the negative charge than chlorine. Here, where it has already gained one electron from the hydrogen, its tendency to take another should be rather decreased than increased. Why, then, is not the stable form of hypochlorous acid $\overset{-}{\mathrm{Cl}}\text{–}\overset{+}{\mathrm{OH}}$ rather than $\overset{+}{\mathrm{Cl}}\text{–}\overset{-}{\mathrm{OH}}$? There hardly appears to be justification for the certainty with which fry states[3] that "to admit the existence of hypochlorous acid is to admit the existence of positive chlorine." We must ask again what principle is supposed to controll this gain and loss of electrons.

But, assuming the formula $\overset{+}{\mathrm{Cl}}\text{–}\overset{-}{\mathrm{OH}}$ to be correct, we must note that the substances reacting in the above equation are really to be represented as

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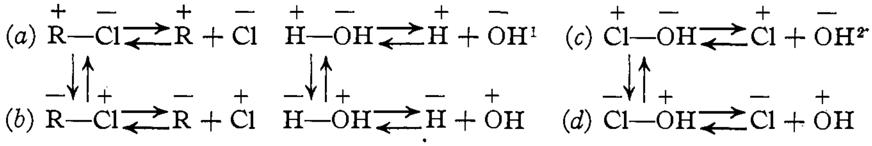
[1] This type of argument is commonly employed, for example in two articles by Fry, This Journal, **36**, 248 and 262 (1914); Nelson, Beans and Falk, *Ibid.*, **35**, 1816 (1913) designate such hydrolytic reactions as one of the chief means for determining the charges present on atoms.

[2] This Journal, **32**, 1637 (1910).

[3] *Ibid.*, **36**, 267 (1914).



$$\begin{array}{llll}
(a)\ \overset{+}{\mathrm{R}}\text{—}\overset{-}{\mathrm{Cl}} \rightleftarrows \overset{+}{\mathrm{R}} + \overset{-}{\mathrm{Cl}} & \overset{+}{\mathrm{H}}\text{—}\overset{-}{\mathrm{OH}} \rightleftarrows \overset{+}{\mathrm{H}} + \overset{-}{\mathrm{OH}}\text{[1]} & (c)\ \overset{+}{\mathrm{Cl}}\text{—}\overset{-}{\mathrm{OH}} \rightleftarrows \overset{+}{\mathrm{Cl}} + \overset{-}{\mathrm{OH}}\text{[2]} \\
\quad \downarrow\uparrow & \quad \downarrow\uparrow & \quad \downarrow\uparrow \\
(b)\ \overset{-}{\mathrm{R}}\text{—}\overset{+}{\mathrm{Cl}} \rightleftarrows \overset{-}{\mathrm{R}} + \overset{+}{\mathrm{Cl}} & \overset{-}{\mathrm{H}}\text{—}\overset{+}{\mathrm{OH}} \rightleftarrows \overset{-}{\mathrm{H}} + \overset{+}{\mathrm{OH}} & (d)\ \overset{-}{\mathrm{Cl}}\text{—}\overset{+}{\mathrm{OH}} \rightleftarrows \overset{-}{\mathrm{Cl}} + \overset{+}{\mathrm{OH}}
\end{array}$$

With this scheme as a basis there will be no difficulty in explaining the formation of compound (*d*) from compound (*b*), or of (*c*) from (*a*). Assuming the formula of HOCl to be known it is clear that we cannot draw conclusions as to the formula of our compound RCl. Further conclusions as to which of the ions present are reacting with each other will appear to depend upon assumptions, based on analogy, as to the relative affinity of various radicals for each other, just such as most organic chemists employ, expressed in some terms or other.

In view of these supplementary hypotheses which the electron conception of valence has come to demand, which permits us to distribute the electrons largely in accordance with the exigencies of the particular equation in hand it appears to the author to have developed into merely a new system of nomenclature, desirable, if correct, but as far without direct support. This complex array of hypothetical electromeric substances does not appear to be an acquisition to the science which is desirable in itself.

Of the other applications of the theory to more complex problems the author would mention only that of Fry[3] to the question of substitution in the benzene ring. The rule governing the position of substituents which Fry puts forward with the utmost confidence[4] is so simple as to arouse distrust at once. It would appear sufficient to say that in view of the extensive investigations carried on in this field in recent years by Hollemann, Flürscheim, Obermiller and others, if any such simple rule could cover the facts it would have been discovered long ago empirically, even if not expressed in the same terms. Hollemann[5] has, however, recently called attention to a number of cases of substitution reactions where it is quite impossible to apply Fry's rule.

Bray and Branch,[6] and Lewis[7] have recently advocated the view that there are both "polar" and "nonpolar" bonds. Certain difficulties appear to lie in this hypothesis, one of them being that mentioned by Nelson and Falk[8] of determining which bonds are polar and which not. Additional

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[1] Jones, THIS JOURNAL, 36, 1277.

[2] *Ibid.*, 1282.

[3] THIS JOURNAL, 36, 248 (1914).

[4] *Ibid.*, p. 252.

[5] *Ibid.*, 36, 2495.

[6] *Ibid.*, 35, 1440 (1913).

[7] *Ibid.*, 35, 1448.

[8] *Ibid.*, 36, 209 (1914).

hypotheses will also be needed in explaining such a reaction as a double decomposition between a polar and a nonpolar compound.

Lewis[1] gives a list of the characteristics of compounds with polar and nonpolar bonds, from which it is clear that no sharp dividing line exists. It does not appear altogether clear just how we are to conceive of bonds representing a gradation between the polar and nonpolar condition, particularly as regards their behavior in chemical transformations.

The chief reason prompting Lewis to favor polar bonds appears to be the desire to represent certain compounds as having a very indefinite and mobile molecular structure. What value this conception may have in itself can hardly be clear until it is developed further, but the author questions whether, if adopted, it involves necessarily the assumption of polar bonds.

The recently expressed view of J. J. Thomson[2] also employs the conception that the exchange of an electron occurs between certain atoms in certain molecules, this phenomenon being designated as intramolecular ionization; but it is to be noted that in such cases it is not a step necessary to the union of the atoms but a phenomenon, so to speak, superimposed on that. Furthermore it is evidently considered to be the exceptional rather than the usual occurrence in the case of atomic unions. The union of atoms through electrical forces is satisfactorily accounted for without it.

Thomson's reason for assuming such intramolecular ionization lies in the attempt to account for the high dielectric constants of certain substances and the fact that these dielectric constants depart from the value predicted by the rule of Maxwell expressing a relation between dielectric constant and square of the refractive index. The high dielectric constants of the substances are accounted for by the high electric moments of the molecules, and these in turn are attributed to transfers of electrons within the molecule.

It does not appear certain, however, that the large electrical moments of some molecules could not be accounted for in some other way. We are here on rather speculative ground from the physical point of view; and in a field where many assumptions would be possible, in view of the complex system of electrical charges which the molecule, according to Thomson's conception, will represent, we can hardly look for conclusive evidence for the phenomenon of "intramolecular ionization." Thomson's basis for the classification of "polar" and "nonpolar" compounds is also such that, as with that of Lewis, a sharp dividing line between the two will not appear.

Nelson and Falk[3] raise other objections to the conception of both

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[1] *Loc. cit.*, p. 1450.

[2] *Phil. Mag.*, [6] **27**, 757 (1914).

[3] THIS JOURNAL, 36, 210 (1914).

polar and nonpolar bonds, and since one of these would be as well an objection to a theory involving no polar bonds I shall refer to it here. They note that this view would represent the gradual oxidation of methane to carbon dioxide as a series of steps without any change in the charges on the carbon atom, and they remark that such a supposition is untenable. This statement is somewhat too categorical in view of the fact that it is only the assumptions involved in the theory they are defending that render it untenable. If we choose to assume no charges on the carbon, the picture of the oxidation process is moderately satisfactory. It is the definition of oxidation put forward by the advocates of the electron theory, based on the behavior electrolytes in aqueous solution, which necessitates the assumption of the charges on the carbon.

There appears to be little justification for any very dogmatic statements regarding the oxidation of methane. The oxidation of Fe'' to Fe''' in aqueous solution is, for example, a process in which we suppose a change in the electric charge on the ions is concerned. But as far as the molecular forms of the reacting substances are concerned, we can only say that $FeCl_2$ is gradually replaced by $FeCl_3$. It is quite an unproved assumption that the charges are still present on the iron in the undissociated molecules, except in as far as the advocates of this theory have proved it; it is then also an assumption that the change of $FeCl_2$ to $FeCl_3$ could not be brought about except by a process involving ionization and changes in which electric charges are concerned. It is thus also an assumption that anything ionic is involved in the replacement of the hydrogen of methane by oxygen. There appears to be in the paper of Falk and Nelson an underlying desire to consider all reactions ionic because some are. But it appears doubtful whether most, or even very many chemists are prepared to adopt this position. The tendency among organic chemists appears to be rather in the opposite direction, since the view long advocated by Michael that the first step in chemical reactions is the formation of a complex molecule by the reacting substances has recently been taken into consideration by numerous investigators, for example, Fischer,[1] Kauffmann,[2] Gadamer,[3] Schmidlin,[4] Baume,[5] Berthoud,[6] and others. Electrolytic dissociation is thus considered as a special phenomenon occurring with certain substances in certain solvents. Furthermore, the process of electrolytic dissociation, even when it occurs, is no longer regarded as necessarily the step through which the electrolyte reacts, as is evidenced by many recent investigations of Acree, Stieglitz, Bredig and others.

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[1] *Ann.*, 394, 350 (1913).

[2] *Die Valenzlehre*, p. 336 (1911).

[3] *J. prakt. Chem.*, [2] 87, 312 (1913).

[4] *Ber.*, 45, 899 (1912).

[5] *J. chim. phys.*, 12, 206 (1914).

[6] *Ibid.*, 10, 578 (1912).

The author finds another strong objection to the electron conception of valence, perhaps shared by others, in the assumption that all decompositions of molecules are processes of ionization. When one considers the very great difference between the equilibrium in the reaction $HCl \rightleftarrows H + Cl$, under the influence of heat, and that in the reaction $HCl \rightleftarrows \overset{+}{H} + \overset{-}{Cl}$ as it occurs in aqueous solution, it seems strange to assume that in both cases we have charged hydrogen and chlorine atoms moving about in the neighborhood of each other, under the influence of the same attractive force except for a certain difference in the dielectric constant of the medium.

For any direct evidence as to whether or not atoms of elementary substances are electrically charged during reaction, we must for the present turn to physical investigations of gases. Here, as pointed out by Bates,[1] such evidence as can be found is against the hypothesis. In addition to the opinion expressed by J. J. Thomson we would also note that Le Blanc and Volmer[2] have recently added to the evidence that in a reacting mixture of hydrogen and chlorine the atoms of these elements are not present in the charged conditions except when under specific ionizing influences.

In conclusion the author would again call attention to the fact that the "electron conception of valence" cannot avoid dealing with the question of chemical affinity, *i. e.*, the attractive force between atoms. It has already developed into a complex mass of hypotheses, both fundamental ones dealing with the existence of electromeric substances, etc., and supplementary ones regarding the electronic formulas of particular substances. Many statements made very categorically are really only hypothetical. It appears to the author quite unjustifiable to go further without explicit statements regarding such questions as the following:

Do atoms which have not gained or lost electrons attract each other? If so, by what means?

What is supposed to be the magnitude of this force existing before the exchange of electrons as compared with that after such an exchange?

What fundamental principle controls this tendency of atoms to gain and lose electrons? That is, what is the fundamental principle on which we are to determine the electronic formulas of substances?

What is the relation, if any, between this tendency and what we usually speak of as the affinity between various atoms?

It could well be said that such questions carry us too far into detail in a field where everything is speculation, if it were not for the fact that assumptions regarding them are involved in every application of the electron conception and that the lack of explicit hypotheses permits inconsistencies to remain concealed too easily. That the whole theory is

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[1] *Loc. cit.*

[2] *Z. Elektrochem.*, **20**, 494.

quite hypothetical is quite clear from the fact that there is not a single well established case of the existence of such electrical isomers as we are constantly being asked to assume in great numbers. We must at least ask that the hypotheses involved shall be made very explicit.

Summary.

In the above paper the following objections are raised to the electron conception of valence:

1. The chemical evidence advanced in support of this hypothesis, in as far as it deals with simple phenomena is quite unconvincing.
2. Any application of the theory involves the constant use of assumptions that render it too elastic to be proved or disproved by these applications.
3. The electromeric formulas assigned to chemical cmpounds are inconsistent with any rule that can be proposed.
4. No single well-established case of electroisomerism is yet known.
5. The evidence of physical experiments is at present opposed to the assumptions on which it is based.
6. The conception necessarily involves assumptions regarding the attractive force between atoms, the attraction of various atoms for electrons, and the relation of this last property to chemical affinity. A number of questions are proposed which should be answered—at least, the hypotheses to be adopted regarding them should be explicitly stated—before the theory is applied to the most perplexing problems of organic chemistry.

[Contribution from the Chemical Laboratory of the University of Illinois.]

A METHOD FOR THE CALCULATION OF THE HYDRATION OF THE IONS AT INFINITE DILUTION, AND THE IDEAL DIFFUSION COEFFICIENT AS APPLIED TO THE HYDRODIFFUSION OF ELECTROLYTES.

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Introduction.

If, in the formula for the diffusion coefficient, $dS = -Dq\, dc/dx\, dt$, we regard D as the quantity of the dissolved substance in grams or mols which in unit time, t, passes through the unit distance x in unit cross-section, q, with unit fall of concentration,—c, occurring in this distance, likewise expressed in grams or mols, and if we divide D by M, the molecular weight of the compound in question, then D/M ($= I$, the ideal diffusion coefficient) indicates the quantity of the substance which would pass under the above conditions, provided that each molecule while retaining