

**A Possible Reconciliation of the Octet and Positive-Negative Theories of Chemical Combination.**—I have recently had the opportunity of reading, in proof, the monograph by Professor G. N. Lewis on "Valence and the Structure of Atoms and Molecules" which has just appeared as a volume of our Scientific Series of Monographs. One of the most fundamental concepts of the theory proposed by Professor Lewis is that a pair of electrons forms the bond which holds two atoms in combination. In nearly all reactions, whether those of electrolytes in solutions or of organic or other compounds, two atoms of one compound separate and combine with two atoms of some other compound. The atoms of the second compound must also separate. Professor Lewis has not, I think, discussed what happens to the electrons in these processes of separation and recombination.

Two methods of separation between two atoms held together by a pair of electrons seem possible: one electron may remain with each atom, leaving both atoms electrically neutral; or the pair of electrons may remain with one of the atoms, which will in that case be negative, while the other atom will be positive. It will be admitted by everyone that electrolytes react in the second manner. There are many considerations which point to the conclusion that many other compounds react in a similar manner.

In the case of hydrogen, it is generally agreed that the hydrogen atoms of acids separate from oxygen, or some other element with which they are combined, without any electron. Since we have among the organic compounds all degrees of ionization from that of strong acids to that of substances like ethyl alcohol, which ionize even less than water, and since ionic hydrogen is very easily transferred from oxygen to carbon and *vice versa*, in tautomeric compounds, we seem to be justified in assuming that in nearly or quite all reactions hydrogen atoms separate from carbon in the positive form and the carbon atoms from which they separate must, therefore, be left in the negative form. In this sense that they either cling to or give up easily the pair of electrons which unites them to other atoms, carbon and other atoms in organic compounds are either positive or negative. This point of view is often useful in predicting the course of a reaction. For instance, in the addition of ammonia, hydroxylamine, phenylhydrazine or the Grignard reagent to aldehydes or ketones, the hydrogen or magnesium always adds itself to the oxygen atom, which clings obstinately to the pair of electrons. In the hydrolysis of cyanides,  $R-C\equiv N$ , the nitrogen atom clings to the electrons and the hydrogen atoms attach themselves to that, while the negative hydroxyl adds itself to the carbon.

In the separation of two carbon atoms in breaking the double union of the type  $R-CH : : CH_2$ , the pair of electrons clings chiefly to the end

carbon atom, which becomes, in that way, negative and the hydrogen adds to that, while the bromine or iodine of hydrobromic or hydriodic acid adds to the second, positive carbon atom. In a similar manner, when nitrogen trichloride adds to the same compound, the positive chlorine adds to the end carbon atom while the negative nitrogen atom of the nitrogen dichloride group adds to the second carbon atom.<sup>1</sup>

The theory here presented does not require us to assume that in a molecule of chlorine,  $\text{Cl} : \text{Cl}$ , one of the chlorine atoms is positive and the other negative. It does assume, however, that when the molecule separates into two atoms, in a reaction with some other compound, the pair of electrons usually remains with one of the atoms, which is therefore negative, while the atom which separates without the electrons is positive.

The theory does not require us to suppose, either, that an atom which enters a molecule in a positive form must necessarily leave the molecule in the same form. Thus, in the addition of hypochlorous acid to ethylene the positive chlorine atom is added to one of the carbon atoms and the negative hydroxyl to the other.<sup>2</sup> But the ethylene chlorohydrin,  $\text{CH}_2\text{Cl}-\text{CH}_2\text{OH}$ , formed hydrolyzes to glycol,  $\text{CH}_2\text{OH}-\text{CH}_2\text{OH}$ , and hydrochloric acid. The chlorine adds in the positive form and splits off in the negative. Such a result seems quite natural according to the theory as here presented, but it is rather difficult to account for by the positive-negative theory as it has often been interpreted.

The view here presented is closely related to a suggestion made in the author's address before the St. Louis Congress of Arts and Sciences, namely, that molecules separate into positive and negative ions *as they react with each other*.<sup>3</sup>

In the foregoing, no attempt has been made to consider the kinetics of the binding pairs of electrons. The success which has attended the application of the theories of Bohr and Sommerfeld to explain the spectral lines of hydrogen and helium inclines most physicists to the view that the electrons of atoms are rotating in orbits around positive nuclei. At a meeting of the Faraday Society in Cambridge, England, in July, Professor Sidgwick suggested that two atoms may be held together by two electrons rotating about the positive nuclei of the two atoms. A somewhat similar suggestion was made by the author some time ago.<sup>4</sup> It is possible that some such hypothesis may ultimately be put on a sound basis and connected accurately with experimental facts, but at present it can be considered only as a very wild guess. It is somewhat in line with the theories

<sup>1</sup> G. H. Coleman, private communication.

<sup>2</sup> For reasons for believing that hypochlorous acid may easily separate into positive chlorine and negative hydroxyl, see Noyes and Wilson, *THIS JOURNAL*, **44**, 1630 (1922).

<sup>3</sup> Noyes, *Chem. News*, **90**, 228 (1904).

<sup>4</sup> Noyes, *THIS JOURNAL*, **39**, 879 (1917).

of the physicists and it seems quite certain that at some future time our theories of chemical combination must be brought into harmony with the known facts about spectral lines, absorption bands, color and other phenomena of light and radiation.

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**A Method for Reproducing Graphs in Quantity.**—Graphs, etc., are plotted with waterproof india ink on the ordinary graph (or coördinate) paper. This is dipped in a saturated solution of purified, colorless paraffin oil (such as Stanolind-Liquid Paraffin) in chloroform and allowed to stand for  $\frac{1}{2}$  to 1 minute. It is then removed from the solution and allowed to drain as long as convenient. The excess of oil is wiped off and the sheet allowed to dry in the air until ready to use.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

## THE BEHAVIOR OF MERCURIC SALTS OF ORGANIC ACIDS TOWARD HEAT<sup>1</sup>

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In a previous communication Kharasch<sup>4</sup> called attention to the fact that mercuric salts of certain aromatic carboxylic acids when heated split off carbon dioxide and the mercury becomes attached to the carbon originally bound to the carboxyl group. That reaction is applicable only to those aromatic carboxylic acids which split off carbon dioxide at their respective melting points or at slightly higher temperatures. In the case of the mercury salts of aromatic carboxylic acids, which do not split off carbon dioxide

<sup>1</sup> Read before the Organic Division of the American Chemical Society at the Pittsburgh Meeting, September, 1922.

<sup>2</sup> National Research Fellow in Organic Chemistry.

<sup>3</sup> The material presented here is used by F. W. Staveley in his dissertation presented in partial fulfilment of the requirements for the Degree of Doctor of Philosophy at the University of Chicago.

<sup>4</sup> Kharasch, *THIS JOURNAL*, **43**, 2238 (1921).