are evidently connected with the fact that the sodium atom readily loses an electron but can not, apparently, take one from another atom. This may be because the positive part of the atom is so deep in its structure that it exerts little attraction for the electron and little, also, for the negative oxygen. The ease with which metals give up electrons seems to be closely connected with their properties as electrical conductors, though I am not aware that this connection has been pointed out before. It may also be connected with the character of the spectra of metals, the electron of the sodium atom being possibly in orbital motion around it, as Lorenz and others have supposed.

In hydrochloric acid the electron gained by the chlorine atom may perhaps penetrate the atom so deeply as to exert but little attraction for the hydrogen. But it is to be remembered also that while the chlorine atom may take up one electron it may give up seven electrons to other atoms, especially to oxygen.

The speculative character of the suggestions here given, is, of course, clearly recognized. It seems possible, however, that we may sometime know the structure of atoms as we now know the structure of molecules, and it is, perhaps, worth while to indicate some of the lines along which it may be possible to attach problems of this sort. W. A. NOYES.

URBANA, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI.]

A CRITICAL SURVEY OF SOME RECENT APPLICATIONS OF THE ELECTRON CONCEPTION OF VALENCE.

BY HARRY SHIPLEY FRY.

Received January 2, 1912.

The purpose of this paper is to present some applications of the electron conception of valence and to discuss their bearing upon the assumptions postulated by K. George Falk[1] in his article on the electronic structure and ionization constants of the organic acids.

Falk states that the organic acids may be divided into four classes in which the ionization constants (K × 10^5) depend primarily upon the additive effects of the directive valences of the α-carbon atom. The principles upon which the direction of valences are assumed to depend are based upon the corpuscular-atomic hypothesis of Sir J. J. Thompson according to which the linkages or bonds between the atoms in a molecule are formed by the transfer of corpuscles or electrons.

Under the sub-title of "Theoretical Considerations" Falk records the following statements:

> (A) "The principles upon which the directions of valence are assumed to depend were explained in the first paper. (THIS JOURNAL, 32, 1637–54.) It may suffice to

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[1] THIS JOURNAL, 33, 1140 (1911). "The Electron Conception of Valence." II. "The Organic Acids."

state here that for a single bond the corpuscle for the carbon-hydrogen union is assumed to pass from the hydrogen to the carbon, the former becoming positively charged, the latter negatively, while for the carbon-chlorine union, the corpuscle passes from the carbon to the chlorine."

(B) "The arrangement of the elements in the periodic system serves in general to indicate the electrical relations of the elements to each other in the production of a bond."

(C) "A classification of the acids will be given here which depends upon the direction of the valences by which the α-carbon atom is combined with the other atoms in the molecule. This divides the acids into four classes which may be formulated as follows:

$$\text{I. } \substack{\rightarrow \\ \rightarrow \\ \rightarrow}\ \text{C.CO}_2\text{H; II. } \substack{\rightarrow \\ \rightarrow \\ \leftarrow}\ \text{C.CO}_2\text{H; III. } \substack{\rightarrow \\ \leftarrow \\ \leftarrow}\ \text{C.CO}_2\text{H; IV. } \substack{\leftarrow \\ \leftarrow \\ \leftarrow}\ \text{C.CO}_2\text{H.}$$

"The acids belonging to class I are those in which three electropositive groups are combined with the α-carbon atom; those belonging to class II, two electropositive and one electronegative; to class III, one electropositive and two electronegative. The ionization constants are found to increase in the order of the classes I, II, III, IV. The acids represented by formula IV, such as trichloracetic acid, are too highly ionized to give satisfactory dissociation constants, and will not be considered here."

Statements (A) and (B) constitute the principles by which Falk determines the direction of a bond in the structural formulas of the compounds under consideration. An arrow ($H \longrightarrow Cl$) serves as the symbol both for the bond of union and for the direction of the transfer of the corpuscle (electron or negative charge), from one atom to another. Accordingly, one end of a bond corresponds to a positive, while the other end corresponds to a negative charge. Therefore, it is preferable in the following discussion to indicate the polarity of each end of a bond by employing formulas of the type, $H\overset{+\ -}{\text{——}}Cl$.

Falk assumes (in statement A) that for a single bond the corpuscle for the carbon-hydrogen union passes from the hydrogen to the carbon, while for the carbon-chlorine union the corpuscle passes from the carbon to the chlorine. In other words, the hydrogen atom functions positively while the chlorine atom functions negatively in the formulas of the organic acids which he discusses. In his first paper[1] Falk has shown that from the standpoint of the electronic conception of valence, a given atom such as chlorine may function *either positively or negatively*, for Sir J. J. Thompson states[2] that atoms of one and the same kind may become either positively or negatively electrified by the loss or gain of corpuscles respectively, "and those with charges of opposite sign would combine to form a diatomic molecule." Accordingly molecular hydrogen (H_2) and molecular chlorine (Cl_2) may be represented by the electronic formulas, $H\overset{+\ -}{\text{——}}H$ and $Cl\overset{+\ -}{\text{——}}Cl$, respectively. These formulas were sug-

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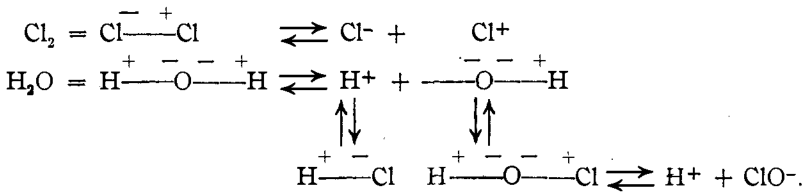
[1] THIS JOURNAL, **32**, 1637–54.

[2] "Electricity, and Matter." (*Scribner's*, **1907**), p. 139.

gested at an earlier date by W. A. Noyes,[1] in the following statement: "If we suppose, what seems not to be improbable, that all reactions involving the decomposition of molecules are preceded by an ionization of the parts of molecules, it would follow that elementary molecules as well may ionize into positive and negative parts." In the present paper experimental data will be presented, the object of which is to show that in some carbon-chlorine unions the corpuscle passes from the chlorine to the carbon. In other words, the chlorine atom may function positively. A hydrogen atom may also function negatively.

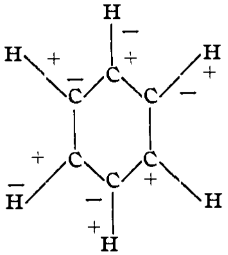
Molecular chlorine, as indicated above, possesses the formula $\overset{-}{\mathrm{Cl}}\text{——}\overset{+}{\mathrm{Cl}}$. Water, electrolytically dissociated, yields positive hydrogen ions; hence the electronic formula, $\overset{+}{\mathrm{H}}\text{——}\overset{-\;-}{\mathrm{O}}\text{——}\overset{+}{\mathrm{H}}$. The interaction of chlorine and water according to the equation, $\mathrm{Cl_2} + \mathrm{HOH} \rightleftarrows \mathrm{HCl} + \mathrm{HOCl}$, must be represented electronically as follows:



$$\begin{array}{lclcl} \mathrm{Cl_2} = \overset{-}{\mathrm{Cl}}\text{——}\overset{+}{\mathrm{Cl}} & \rightleftarrows & \mathrm{Cl^-} & + & \mathrm{Cl^+} \\ \mathrm{H_2O} = \overset{+}{\mathrm{H}}\text{——}\overset{-\;-}{\mathrm{O}}\text{——}\overset{+}{\mathrm{H}} & \rightleftarrows & \mathrm{H^+} & + & \text{——}\overset{-\;-}{\mathrm{O}}\text{——}\overset{+}{\mathrm{H}} \\ & & \updownarrows & & \downuparrows \\ & & \overset{+}{\mathrm{H}}\text{——}\overset{-}{\mathrm{Cl}} & & \overset{+}{\mathrm{H}}\text{——}\overset{-\;-}{\mathrm{O}}\text{——}\overset{+}{\mathrm{Cl}} \rightleftarrows \mathrm{H^+} + \mathrm{ClO^-}. \end{array}$$

Therefore in the oxygen-chlorine union the corpuscle passes from the chlorine atom to the oxygen atom, or in other words the chlorine atom in hypochlorous acid functions positively. Is there any evidence that chlorine may function positively when in combination with carbon?

In an earlier paper[2] I extended the electronic conception of positive and negative valences to the atoms constituting the benzene molecule. In every possible symmetrically constituted electronic formula for benzene it was shown that the hydrogen atoms in positions, 1, 3, and 5 function negatively while those in positions 2, 4, and 6 function positively. Omitting centric linkages and double bonds, the abbreviated electronic formula of benzene is represented in the following figure:



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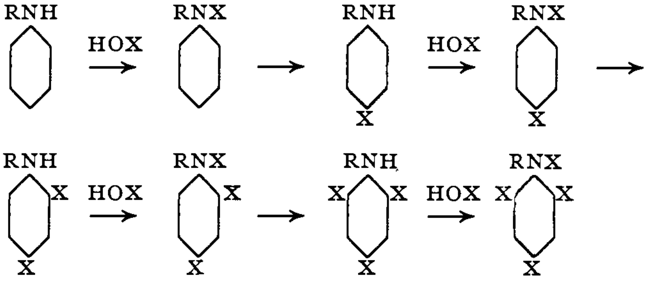
[1] This Journal, 23, 460 (1901).

[2] Fry, *Z. physik. Chem.*, 76, 385 (1911); This Journal, *Proceed.*, 30, 34 (1908).

This formula presents a structural basis for the similarity in behavior of the ortho and para positions in contra-distinction to the meta positions. If a given hydrogen atom or substituent is negative, then the hydrogen atoms or substituents ortho and para to it are positive while those meta to it are each negative; and *vice versa.* This formula rendered possible an explanation of the Crum Brown and Gibson Rule[1] for the formation of disubstitution derivatives of benzene and various rearrangement reactions.

Let it now be observed in the electronic formula of benzene that in the carbon-hydrogen unions of positions 1, 3, and 5, the corpuscle passes from the carbon to the hydrogen; in positions 2, 4, and 6, the corpuscle passes from the hydrogen to the carbon. Accordingly, chlorine atoms occupying positions 2, 4, and 6 must function positively. Some of the experimental facts, which show that chlorine atoms in positions 2, 4, and 6 are positive, are as follows:

Chattaway and Orton,[2] in a study of the characteristic rearrangements of the substituted nitrogen halides, show that acetanilide, on treatment with hypochlorous acid, yields phenyl acetyl nitrogen chloride, which is readily transformed into *p*-chloroacetanilide. Treatment of this latter compound with hypochlorous acid gives *p*-chlorophenyl acetyl nitrogen chloride, which is transformed into 2,4-dichloroacetanilide. Proceeding thus the final product is 2,4,6-trichlorophenyl acetyl nitrogen chloride, which will not undergo rearrangement. These successive changes are represented in the following formulas: (R = formyl, acetyl, or benzoyl; X = Cl, or Br).



Why does the halogen atom which wanders from the nitrogen invariably assume a position in the nucleus para or ortho to the amino group, provided these positions are unoccupied? Aniline is a derivative of ammonia. Each hydrogen atom of ammonia is equivalent and functions positively; hence the electronic formula,

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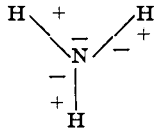
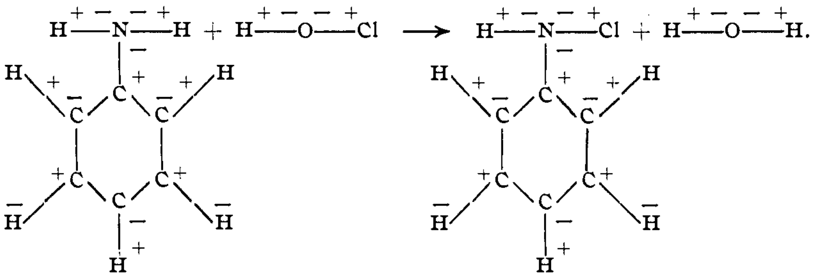
[1] *J. Chem. Soc.*, 61, 366 (1892).

[2] *Ibid.*, 75, 1046. *Ber.*, 32, 3572.



The radicle —NH_2 is therefore negative and accordingly must occupy the position of a negative hydrogen atom of the benzene nucleus. The electronic formula of aniline and its interaction with hypochlorous acid $(\overset{+}{\mathrm{H}}\overset{-}{\text{——}}\mathrm{O}\overset{-}{\text{——}}\overset{+}{\mathrm{Cl}})$ are indicated in the following equation:



Therefore in the process of transformation of phenyl acyl nitrogen halide into its less labile isomeride, it is self-evident that the halogen atom which functions positively can only exchange positions with a positive hydrogen atom of the nucleus; that is, in passing from the nitrogen to the nucleus it must enter either the para or ortho positions with respect to the attachment of the NH_2–, or RNH– radicle, which functions negatively. When the para and both ortho positions are occupied, as in 2,4,6-trichloroacyl nitrogen chloride, rearrangement is both actually and theoretically impossible. This constitutes a proof of the identity of polarity of the positions 2, 4, and 6, of the benzene nucleus, each of which is occupied by a positive chlorine atom in the compounds noted above.

Further evidence for the existence of halogen atoms, which function positively as well as negatively, is given in a previous paper.[1] In this connection Falk's second assumption (statement B), that "the arrangement of the elements in the periodic system serves in general to indicate the electrical relations of the elements to each other in the production of a bond," is subject to discussion. According to the corpuscular-atomic hypothesis a given atom may function either positively or negatively. This is actually the case with chlorine in the compounds previously discussed. How then, for instance, does the position of chlorine in the periodic system determin whether it is to function positively or negatively? Furthermore, it has been demonstrated that if the valence of an element is (n), it may function, from the standpoint of the electron

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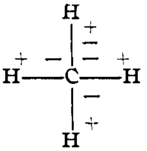
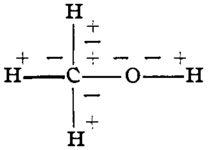
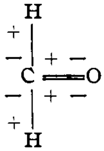
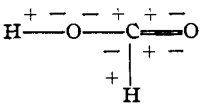
[1] Fry, *Z. physik. Chem.*, 76, 393 (1911).

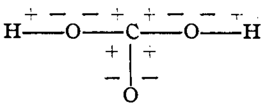
conception of valence, in ($n + 1$) different ways. For example, consider the valences of the carbon atom[1] in the electronic formulas of methane, methyl alcohol, formaldehyde, formic and carbonic acids. If in these compounds the hydrogen atoms function positively and the oxygen negatively, then the following electronic formulas result:

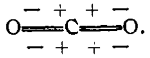

(I)


(II)

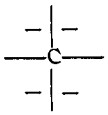

(III)

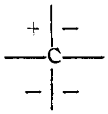

(IV)

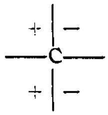

(V)

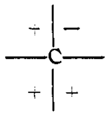


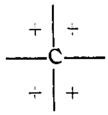
The valence (n) of carbon is 4; the number of ways in which the carbon atom may function ($n + 1$) is 5. The five types as derived from the above electronic formulas are respectively as follows:


(I)


(II)


(III)


(IV)


(V)

These types represent the successive stages of oxidation in the transition from methane to carbonic acid, or its anhydride. Hence it follows that the particular types of carbon atoms, or in other words, *the direction of the valences of the carbon atom in its compounds, can not be determined by the position of carbon in the periodic system, but depends solely upon the polarity of the atoms (or radicles) which are combined with the carbon atom.*

There now remains for consideration statement (C). Falk states that "in considering the structure of the organic acids, it is evident that the α-carbon atom (the one combined directly with the carboxyl group) influences the ionization constant of the acid to the greatest extent." A classification of the acids is then presented "which depends upon the direction of the valences by which this α-carbon atom is combined with the other atoms in the molecule." This divides the acids, according to Falk, "into four general classes which may be formulated as follows:

I. $\substack{\rightarrow\\ \rightarrow\\ \rightarrow}$ $C.CO_2H$; II. $\substack{\rightarrow\\ \rightarrow\\ \leftarrow}$ $C.CO_2H$; III. $\substack{\rightarrow\\ \leftarrow\\ \leftarrow}$ $C.CO_2H$; IV. $\substack{\leftarrow\\ \leftarrow\\ \leftarrow}$ $C.CO_2H$.

"The acids represented by formula IV are too highly ionized to give

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[1] Fry, *Z. physik. Chem.*, 76, 405 (1911).

satisfactory dissociation constants, and will not be considered in detail here." Thus Falk virtually reduces the division of the organic acids into three classes in which the ionization constants ($K \times 10^5$) depend primarily upon the additive effects of the directive valences of the α-carbon atom. Falk then proceeds to show that "the class to which any given acid belongs may readily be ascertained as the composition taken in connection with the dissociation constant shows the structure of the α-carbon atom." He then assigns for each class of acids the corresponding approximate ionization constants as follows:

$$\text{Class I.} \substack{\longrightarrow\\ \longrightarrow\\ \longrightarrow} \text{C.CO}_2\text{H}; \ (K \times 10^5) < 0.01$$

$$\text{Class II.} \substack{\longrightarrow\\ \longrightarrow\\ \longleftarrow} \text{C.CO}_2\text{H}; \ (K \times 10^5) \quad 0.10\text{–}0.40$$

$$\text{Class III.} \substack{\longrightarrow\\ \longleftarrow\\ \longleftarrow} \text{C.CO}_2\text{H}; \ (K \times 10^5) > 2.00$$

Falk then states "that substituents may exert constitutive effects resulting in constants for the acids between the values given for the classes, but a study of the composition should indicate in most cases the class to which an acid may be assigned."

The theoretical objections to Falk's classification must be considered first. Falk has plainly stated that his classification "depends upon the direction of the valences by which the α-carbon atom is combined with the other atoms in the molecule." In direct contradiction to this statement Falk has not considered the direction of the valence or bond between the α-carbon atom and the carbon atom of the carboxyl group. In other words, he considers only three of the four valences of the α-carbon atom, omitting in his discussion the fourth valence, which undoubtedly is the most important since it binds the α-carbon atom to the carboxyl group and thereby determines the polarity of the radicle attached to carboxyl. Therefore, in place of there being only four classes of organic acids, the theory demands eight which must be represented as follows:

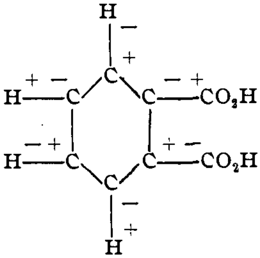
$$1. \substack{\longrightarrow\\ \longrightarrow\\ \longrightarrow} \text{C} \longleftarrow \text{CO}_2\text{H}; \ 2. \substack{\longrightarrow\\ \longrightarrow\\ \longleftarrow} \text{C} \longleftarrow \text{CO}_2\text{H}; \ 3. \substack{\longrightarrow\\ \longleftarrow\\ \longleftarrow} \text{C} \longleftarrow \text{CO}_2\text{H};$$

$$4. \substack{\longleftarrow\\ \longleftarrow\\ \longleftarrow} \text{C} \longleftarrow \text{CO}_2\text{H}; \ 5. \substack{\longrightarrow\\ \longrightarrow\\ \longrightarrow} \text{C} \longrightarrow \text{CO}_2\text{H}; \ 6. \substack{\longrightarrow\\ \longrightarrow\\ \longleftarrow} \text{C} \longrightarrow \text{CO}_2\text{H};$$

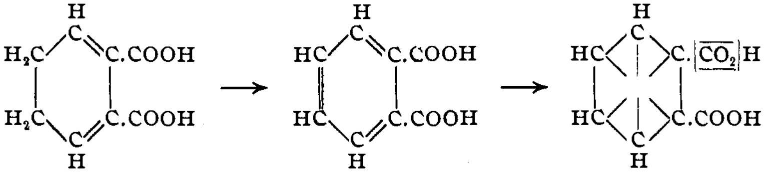
$$7. \substack{\longrightarrow\\ \longleftarrow\\ \longleftarrow} \text{C} \longrightarrow \text{CO}_2\text{H}; \ 8. \substack{\longleftarrow\\ \longleftarrow\\ \longleftarrow} \text{C} \longrightarrow \text{CO}_2\text{H}.$$

Falk has assigned approximate values of the ionization constants to only three classes of acids. What is to be done with the eight classes which are demanded by this theory?

Experimental facts will now be considered which show that the direction of the valence which binds the α-carbon atom to the carboxyl group has a definit influence upon the property of the compound, or more particularly upon the property of the carboxyl radicle itself. A compound containing two carboxyl groups should be chosen for discussion with the hypothetical requirement that the direction of the valence binding one carboxyl group be opposit to the direction of the valence binding the other. Such a condition would be fulfilled in benzene derivatives containing carboxyl radicles on adjacent carbon atoms of the nucleus. Since hydrogen atoms so attached have been shown to be of opposit polarity, it follows that in phthalic acid one carboxyl radicle functions negatively while the other functions positively, as indicated in the following formula:



Is there any experimental evidence to justify this difference in the attachment of the carboxyl groups to the nucleus? Baeyer[1] has shown that the $\Delta^{3,5}$, $\Delta^{2,4}$, and $\Delta^{2,6}$ dihydrophthalic acids yield benzoic acid on oxidation. He attributes this to a shock (Erschütterung) to the α-carbon atom which causes it to lose carbon dioxide, this effect being associated with the change from ethylene to centric linkages, thus:



Bruhl,[2] in a critical examination of Baeyer's "Erschütterung theory," asks why only one molecule instead of two molecules of carbon dioxide is removed from the acids in question, and has sought to explain the chemical behavior of the dihydro acids on the simple basis of their difference of stability, which view has the advantage of being independent of any structural hypothesis. But Bruhl, according to Cohen,[3] "fails to perceive that by avoiding any reference to structure as affecting stability, is begging the question." It must then be concluded that up to the present time there is no satisfactory structural explanation as to why only one molecule of carbon dioxide instead of two is removed from the several dihydrophthalic acids investigated by Baeyer.

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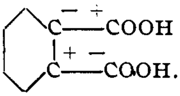
[1] *Ann.*, 269, 178 (1892).

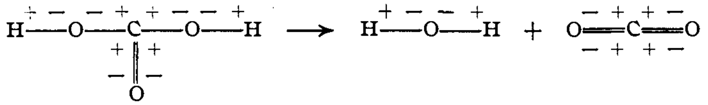
[2] *J. prakt. Chem.*, [2] 49, 229 (1894).

[3] "Organic Chemistry" (Longmans, Green and Co.), 1907, p. 461.

This anomalous behavior of the phthalic acids may be interpreted in terms of the electronic conception of positive and negative valences. As previously indicated, one of the carboxyl groups of phthalic acid is at the positive end of a bond while the other carboxyl group is at the negative end of a bond, thus, in the abbreviated formula,



How does this account for the loss of only one molecule of carbon dioxide instead of two? If reference be made to the electronic formulas of formic and carbonic acids, and carbon dioxide (see page 669), it will at once be observed that the —CO_2H radicle in formic acid is negative ($\mathrm{H}\overset{+\ \ -}{\text{——}}\mathrm{CO_2H}$) while the same radicle in carbonic acid is positive ($\mathrm{HO}\overset{-\ \ +}{\text{——}}\mathrm{CO_2H}$). Furthermore, in formic acid three of the valences of the carbon atom function positively while the fourth functions negatively. In carbonic acid and in carbon dioxide each of the four valences of the carbon atom functions positively. Therefore, it is structurally and electronically possible for carbonic acid to lose carbon dioxide, thus:



$$\mathrm{H}\overset{+\ -}{\text{——}}\mathrm{O}\overset{-\ +}{\text{——}}\underset{\substack{+\,\|\,+\\ -\,\|\,-\\ \mathrm{O}}}{\mathrm{C}}\overset{+\ -}{\text{——}}\mathrm{O}\overset{-\ +}{\text{——}}\mathrm{H} \longrightarrow \mathrm{H}\overset{+\ -}{\text{——}}\mathrm{O}\overset{-\ +}{\text{——}}\mathrm{H} + \mathrm{O}\overset{-\ +}{\underset{-\ +}{==}}\mathrm{C}\overset{+\ -}{\underset{+\ -}{==}}\mathrm{O}$$

On the other hand, the loss of carbon dioxide from formic acid, in which the —CO_2H group functions as a negative radicle, does not occur spontaneously because three of the carbon valences are positive and one is negative, whereas each of the four valences of carbon dioxide must be positive.

In terms of the electron theory the gain of electrons corresponds to reduction; the loss of electrons, to oxidation. Therefore the maximum degree of oxidation is attained when all of the valences of an element function positively, as, for instance, the carbon atom in carbonic acid and carbon dioxide. This maximum state is not yet attained in formic acid wherein three of the valences of the carbon atom are positive while the fourth valence is negative. Hence a carboxyl radicle which functions positively corresponds to the stage of oxidation represented by the carbon atom both in carbonic acid and carbon dioxide. It is therefore capable of losing carbon dioxide. A carboxyl radicle which functions negatively corresponds to the stage of oxidation represented by the carbon atom in formic acid, from which the loss of carbon dioxide is electronically impossible.

Since both a positive and a negative carboxyl radicle are present in the phthalic acids, it follows that the carboxyl group functioning positively is the one which spontaneously loses carbon dioxide in the reactions described by Baeyer. This constitutes the explanation of the fact that one molecule instead of two molecules of carbon dioxide is removed from the several phthalic acids noted above, and, furthermore, is evidence that the direction of the valence which binds a carboxyl radicle to a compound has a definit influence upon the properties of the radicle and the compound, and, therefore, is not to be disregarded in any applications of the electron conception of directive valences.

Summary.

(1) From the standpoint of the electronic conception of positive and negative valences, an atom, such as chlorine or a univalent radicle, may function either positively or negatively. Before such atom, or radicle, is assumed to be either positive or negative in any particular compound the polarity should be determined experimentally. In this connection the halogen atoms in 2,4,6-trichlorphenyl acetyl nitrogen halides and other compounds, have been shown to function positively. From the position of the halogen atoms in the periodic system they would ordinarily be assumed to function negatively.

(2) The statement that the arrangement of the elements in the periodic system serves in general to indicate the electrical relations of the elements to each other in the production of a bond is subject to extension since it has been shown that an element whose valence is (n) may function in $(n + 1)$ different ways. For instance, the tetravalent carbon atom is shown to function according to five different types depending upon its valences being all positive, all negative, or some positive and others negative. These five types are also shown to correspond to successive stages of oxidation illustrated in the compounds, methane, methyl alcohol, formaldehyde, formic acid, and carbonic acid and carbon dioxide.

(3) Falk's classification of the organic acids which he states "depends upon the direction of the valences by which the α-carbon atom is combined *to the other atoms in the molecule,*" is incomplete since he fails to take into account the direction of the valence which binds the α-carbon atom to the carboxyl group. When this valence is considered, the theory demands eight classes of organic acids: Falk postulates only four classes, and considers experimental data for only three classes.

(4) The direction of the valence which binds the α-carbon atom to the carboxyl group is of prime importance since it determines the polarity of the radicle attached to carboxyl and has a definit influence upon the behavior of the carboxyl group itself. This is evinced by the explanation given for the fact that only one instead of two molecules of carbon dioxide is removed from certain phthalic acids in the transformations described by Baeyer.

Further applications of the electronic conception of positive and negative valences are reserved for subsequent papers.