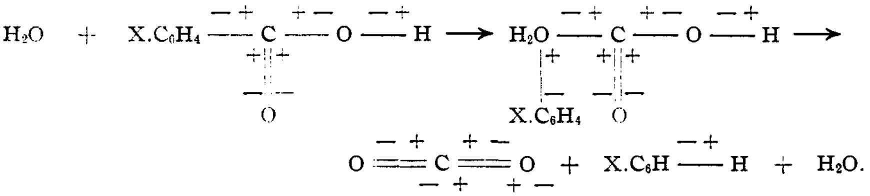
from three to five. Similarly, the action of water in effecting the elimination of carbon dioxide would depend upon the formation of an unstable oxonium compound through an increase in the valence of the oxygen atom from two to four as indicated in the following equations, which are perfectly analogous to those above:



$$H_2O + X.C_6H_4 \overset{-+}{—} \underset{\underset{O}{\overset{+\|+}{\underset{-\|-}{}}}}{C} \overset{+-}{—} O \overset{-+}{—} H \longrightarrow H_2O \overset{-+}{—} \underset{\underset{X.C_6H_4 \quad O}{|+ \quad +\|+ \quad |- \quad -\|-}}{C} \overset{+-}{—} O \overset{-+}{—} H \longrightarrow$$

$$O \overset{-+}{\underset{-+}{=}} C \overset{+-}{\underset{+-}{=}} O + X.C_6H \overset{-+}{—} H + H_2O.$$

Thus the electronic conception of positive and negative valences not only indicates the nature of the radicals which, through the action of amines or water, lose carbon dioxide but it also affords a possible interpretation of the way in which the reactions proceed. The theoretical deductions are based upon experimental facts and data afforded by the analogous action of pyridine upon chlorocarbonic ethylester.

In conclusion it may be remarked that the electronic conception of positive and negative valences and the electronic formula of benzene, afford explanations of certain anomalous properties and reactions which are generally classed as stereochemical problems. The possibility of interpreting some of these properties and reactions indicates that they are not necessarily anomalous or irregular. Hence it is hoped that a further extension of the principles and methods herewith presented may lead to the interpretation and solution of other problems.

The following article may be regarded as a continuation of the present paper, but only in so far as it relates to the electronic formula of benzene, which involves the question of the existence of negatively functioning hydrogen.

CINCINNATI, OHIO.

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

POSITIVE AND NEGATIVE HYDROGEN, THE ELECTRONIC FORMULA OF BENZENE, AND THE NASCENT STATE.

BY HARRY SHIPLEY FRY.

Received December 15, 1913.

That a univalent atom, chlorine for example, may function either positively or negatively has been conclusively demonstrated from several different standpoints.[1] The other halogens, bromine and iodine, also have been shown to dissociate into positive and negative parts in their inter-

---

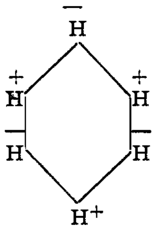
[1] W. A. Noyes, THIS JOURNAL, **23**, 460 (1901); **35**, 767 (1913); Stieglitz, *Ibid.*, **23**, 796 (1901); Walden, *Z. physik. Chem.*, **43**, 385 (1903); Fry, *Ibid.*, **76**, 387, 395 (1911).

actions with silver benzoate.[1] Accordingly, if X_2 represent molecular halogen, dissociation from the standpoint of the electronic conception of positive and negative valences is represented thus:

$$X_2 = X \overset{+\ -}{\text{——}} X \rightleftarrows \overset{+}{X} + \overset{-}{X}.$$

From the same standpoint, one may assume that molecular hydrogen dissociates into positive and negative hydrogen. While the existence of positive hydrogen (hydrogen ion, $\overset{+}{H}$) is indisputable the question of the existence of negative hydrogen is open to discussion.

In previous papers it has been shown that the occurrence of three positive and three negative hydrogen atoms in the electronic formula of benzene



is a necessary consequence of the application of the electronic conception of positive and negative valences to the constituent atoms of the benzene molecule. Hence, the purpose of the present paper is threefold: (1) To offer theoretical arguments for, and experimental evidence of the existence of negative hydrogen; (2) to consider the facts which require the assumption of the existence of positively and negatively functioning hydrogen atoms in the benzene nucleus; and (3) to propose a definition of the so-called "nascent state."

A rigid application of the conception of positive and negative valences to the molecular formulas of hydrogen and chlorine has led to conclusions which have not as yet been completely verified by experiment. For instance the molecular formulas of these gases and their chemical combination, preceded by dissociation, may be represented as follows:

$$\begin{array}{lllll}
C_2 = H \overset{+\ -}{\text{——}} H & \rightleftarrows & \overset{+}{H} & + & \overset{-}{H} \\
Cl_2 = Cl \overset{-\ +}{\text{——}} Cl & \rightleftarrows & \overset{-}{Cl} & + & \overset{+}{Cl} \\
 & & \downarrow\uparrow & & \downarrow\uparrow \\
 & & H \overset{+\ -}{\text{——}} Cl & & H \overset{-\ +}{\text{——}} Cl
\end{array}$$

Thus, when two or more types of a structural formula are possible I have termed them, for the sake of reference, "electronic isomers" or, more briefly, "electromers."[2] In order to account for the existence of only one elec-

---

[1] Fry, preceding paper.

[2] Fry, *Z. physik. Chem.*, 76, 387 (1911).

tromer, when theoretically two (or more) are possible, the following assumptions have been made: One electromer may revert to another through the transposition of electrons as indicated in the scheme: $\mathrm{H}\overset{+\ \ -}{\text{——}}\mathrm{Cl} \rightleftarrows \overset{+}{\mathrm{H}} + \overset{-}{\mathrm{Cl}} \rightleftarrows \overset{+}{\mathrm{H}} + (\ominus) + \mathrm{Cl} \rightleftarrows \mathrm{H} + \mathrm{Cl} \rightleftarrows \mathrm{H} + (\ominus) + \overset{+}{\mathrm{Cl}} \rightleftarrows \overset{-}{\mathrm{H}} + \overset{+}{\mathrm{Cl}} \rightleftarrows \mathrm{H}\overset{-\ \ +}{\text{——}}\mathrm{Cl}$; or the one electromer may be the predominating or sole type, depending upon certain physical conditions. For example an aqueous solution of hydrogen chloride yields positive hydrogen and negative chlorine ions. Therefore, the dissociating molecules are presumably of the type $\mathrm{H}\overset{+\ \ -}{\text{——}}\mathrm{Cl}$.

The assumed existence of two types of hydrogen chloride, $\overset{+}{\mathrm{H}}.\overset{-}{\mathrm{Cl}}$ and $\overset{-}{\mathrm{H}}.\overset{+}{\mathrm{Cl}}$, is paralleled by the two possible types of chlorobenzene, $\overset{+}{\mathrm{C_6H_5}}.\overset{-}{\mathrm{Cl}}$ and $\overset{-}{\mathrm{C_6H_5}}.\overset{+}{\mathrm{Cl}}$, which in turn may be regarded as derivatives of $\overset{+}{\mathrm{C_6H_5}}.\overset{-}{\mathrm{H}}$ and $\overset{-}{\mathrm{C_6H_5}}.\overset{+}{\mathrm{H}}$, respectively. Notwithstanding the fact that only one monochlorobenzene is known, it has been shown in the preceding paper that the benzene nucleus is united to negative chlorine in ortho and in para chloronitrobenzenes ($\mathrm{NO_2}\overset{+\ \ -}{\text{——}}\mathrm{C_6H_4}\overset{+\ \ -}{\text{——}}\mathrm{Cl}$), and to positive chlorine in metachloronitrobenzene ($\mathrm{NO_2}\overset{+\ \ -}{\text{——}}\mathrm{C_6H_4}\overset{-\ \ +}{\text{——}}\mathrm{Cl}$). Why then are there not two monochlorobenzenes? One is compelled to assume, either that the one electromer is unstable (under ordinary physical conditions) and that it reverts to the known stable electromer through the transposition of electrons, thus,

$$\mathrm{C_6H_5}\overset{-\ \ +}{\text{——}}\mathrm{Cl} \longrightarrow \mathrm{C_6H_5Cl} \longrightarrow \mathrm{C_6H_5}\overset{+\ \ -}{\text{——}}\mathrm{Cl};$$

or that monochlorobenzene is an equilibrium mixture of two tautomeric electromers, thus,

$$\mathrm{C_6H_5}\overset{-\ \ +}{\text{——}}\mathrm{Cl} \rightleftarrows \mathrm{C_6H_5}\overset{+\ \ -}{\text{——}}\mathrm{Cl}.$$

This latter assumption could be verified if it were possible to hydrolyze chlorobenzene and thereby obtain two different products, namely, phenol and benzene, according to the following equations, (1) and (2), respectively:

$$(1)\quad \overset{+}{\mathrm{C_6H_5}}.\overset{-}{\mathrm{Cl}} + \overset{+}{\mathrm{H}}.\overset{-}{\mathrm{OH}} \longrightarrow \overset{+}{\mathrm{C_6H_5}}.\overset{-}{\mathrm{OH}} + \overset{+}{\mathrm{H}}.\overset{-}{\mathrm{Cl}}$$

$$(2)\quad \overset{-}{\mathrm{C_6H_5}}.\overset{+}{\mathrm{Cl}} + \overset{+}{\mathrm{H}}.\overset{-}{\mathrm{OH}} \longrightarrow \overset{-}{\mathrm{C_6H_5}}.\overset{+}{\mathrm{H}} + \overset{-}{\mathrm{HO}}.\overset{+}{\mathrm{Cl}}$$

But, as a matter of fact, monochlorobenzene does not undergo hydrolysis either by acids or bases. In other words, it has been impossible so far to prove directly whether the chlorine atom in monochlorobenzene is positive or negative. This, however, is not the case with all monosubstituted derivatives of benzene. For instance, in the preceding paper, it has been shown that the carboxyl radical in benzoic acid is positive. Furthermore, the (SO_3H) radical in phenylsulfonic acid may function either positively or negatively. This follows from the fact that phenylsulfonic acid on hydrolysis *in alkaline solution*[1] yields phenol and sulfurous acid while *in acid solution* or with superheated steam the products are benzene and sulfuric acid. The equations for these reactions (perfectly analogous to equations (1) and (2) above), are as follows:

$$(1)\quad \overset{+}{C_6H_5}.\overset{-}{SO_3H} + \overset{+}{H}.\overset{-}{OH} \longrightarrow \overset{+}{C_6H_5}.\overset{-}{OH} + \overset{+}{H}.\overset{-}{SO_3H}$$

$$(2)\quad \overset{-}{C_6H_5}.\overset{+}{SO_3H} + \overset{+}{H}.\overset{-}{OH} \longrightarrow \overset{-}{C_6H_5}.\overset{+}{H} + \overset{-}{HO}.\overset{+}{SO_3H}.$$

L. W. Jones was the first to consider the hydrolysis of phenylsulfonic acid from an electronic standpoint, regarding the transfer of electrons between the carbon and sulfur atoms as an intramolecular oxidation or reduction.[2] Subsequently, Bray and Branch[3] interpreted this behavior of phenylsulfonic acid as an example of tautomerism:

$$C_6H_5 \overset{+\;-}{\relbar\joinrel\relbar\joinrel\relbar} SO_3H \rightleftarrows C_6H_5 \overset{-\;+}{\relbar\joinrel\relbar\joinrel\relbar} SO_3H.$$

The experimental facts, interpreted from either of the above viewpoints, lead to the conclusion that the electromers of phenylsulfonic acid may be regarded as derivatives of $\overset{+}{C_6H_5}.\overset{-}{H}$ and $\overset{-}{C_6H_5}.\overset{+}{H}$, respectively. Furthermore the hydroxybenzoic acids, ortho and para, have been shown to contain positive carboxyl radicals, while the metahydroxybenzoic acid contains a negative carboxyl radical. These compounds may likewise be regarded as derivatives of $\overset{-}{C_6H_5}.\overset{+}{H}$ and $\overset{+}{C_6H_5}.\overset{-}{H}$, respectively.

The formulas of the various derivatives of benzene heretofore considered may now be tabulated in two columns. Those in the first column are to be regarded as derivatives of $\overset{-}{C_6H_5}.\overset{+}{H}$, those in the second column as derivatives of $\overset{+}{C_6H_5}.\overset{-}{H}$.

$\overset{-}{C_6H_5}.\overset{+}{H}$	$\overset{+}{C_6H_5}.\overset{-}{H}$
($\overset{-}{C_6H_5}.\overset{+}{Cl}$) ?	($\overset{+}{C_6H_5}.\overset{-}{Cl}$) ?
$\overset{-}{C_6H_5}.\overset{+}{SO_3H}$*	$\overset{+}{C_6H_5}.\overset{-}{SO_3H}$*
meta-$(NO_2)\overset{-}{C_6H_4}.\overset{+}{Cl}$*	ortho-$(NO_2)\overset{+}{C_6H_4}.\overset{-}{Cl}$*
	para-$(NO_2)\overset{+}{C_6H_4}.\overset{-}{Cl}$*
ortho-$(HO)\overset{-}{C_6H_4}.\overset{+}{COOH}$*	meta-$(HO)\overset{+}{C_6H_4}.\overset{-}{COOH}$*
para-$(HO)\overset{-}{C_6H_4}.\overset{+}{COOH}$*	

---

[1] It is noteworthy that phenol is formed in the presence of negative hydroxyl ion while the hydrocarbon, benzene, is formed in the presence of positive hydrogen ion. This feature will be considered more fully in a subsequent paper.

[2] Jones, *Am. Chem. J.*, **48**, 26 (1912).

[3] THIS JOURNAL, **35**, 1445 (1913).

It should be noted that the polarity of the radicals followed by an asterisk has been confirmed either directly or indirectly by experimental observations described in previous papers, from which it is evident that certain substituents in the benzene nucleus function sometimes positively, sometimes negatively. It may then be concluded that those atoms or radicals which function positively have substituted positive hydrogen atoms of the nucleus. On the other hand, those atoms or radicals which function negatively have substituted negative hydrogen atoms of the nucleus. This, of course, is only an indirect proof of the existence of positive and negative hydrogen atoms in the benzene nucleus. In like manner we speak of the existence of carbonic and sulfurous acids when as a matter of fact chiefly their derivatives, that is to say their substitution products, are known. A direct proof of the existence of negative hydrogen will be presented after some theoretical arguments have been considered.

It has been observed that only one electromer of hydrogen chloride is known, namely, $(\overset{+}{H}\text{——}\overset{-}{Cl})$, since its aqueous solution yields positive hydrogen and negative chlorine ions. It has also been shown on theoretical grounds that this fact does not preclude the possible existence of negative hydrogen and positive chlorine ions in an aqueous solution.[1] For instance, during the electrolysis of hydrochloric acid, negative hydrogen may result by cathodic reduction, and positive chlorine ions arise by anodic oxidation: A hydrogen atom carrying a unit positive charge may lose it on contact with the cathode; $\overset{+}{H} + \ominus \longrightarrow H$. The resulting neutral atom immediately acquiring a negative charge becomes a negative hydrogen ion; $H + \ominus \longrightarrow \overset{-}{H}$, which is then immediately repelled from the cathode to combine with one of the approaching positive hydrogen ions, thus forming a molecule of hydrogen; $\overset{-}{H} + \overset{+}{H} \longrightarrow \overset{+}{H}\text{——}\overset{-}{H} = H_2$. An analogous and simultaneous process may take place at the anode:

$$\overset{-}{Cl} + \oplus \longrightarrow Cl;\quad Cl + \oplus \longrightarrow \overset{+}{Cl};\quad \overset{+}{Cl} + \overset{-}{Cl} \longrightarrow \overset{+}{Cl}\text{——}\overset{-}{Cl} = Cl_2.$$

Are there any facts to warrant the assumption of the existence of positive chlorine ions at the anode? The existence of positive chlorine ions is substantiated by the apparently anomalous facts, that on electrolysis concentrated solutions of hydrochloric acid yield equal volumes of hydrogen and chlorine while very dilute solutions yield hydrogen at the cathode, but no free chlorine at the anode. Instead an equivalent amount of oxygen is evolved. Ostwald[2] states that "This is due to the fact that the water is decomposed by the chlorine with the formation of hydrogen chloride and oxygen according to the equation $2\ H_2O + 2\ Cl_2 = 4\ HCl +$

---

[1] Fry, *Z. physik. Chem.*, 76, 387 (1911).

[2] "Principles of Inorganic Chemistry," p. 195 (1902).

O_2. This process, it is true, takes place with measurable velocity only in light; we may, however, assume here, as in similar cases, that the process takes place without light, only very slowly." This explanation may be modified and extended since the liberation of oxygen from solutions of chlorine in water is due to the decomposition of the intermediately formed hypochlorous acid according to the generally accepted equations:

$$Cl_2 + HOH \rightleftarrows HCl + HOCl; \quad 2HOCl \longrightarrow 2HCl + O_2.$$

To admit the existence of hypochlorous acid is to admit the existence of positive chlorine, $(\overset{-}{\mathrm{HO}}.\overset{+}{\mathrm{Cl}})$. The decomposition of water by chlorine may be regarded as an oxidation of the hydroxyl ion by the positive chlorine ion as follows:[1]

$$\left.\begin{array}{l} 2\overset{-}{\mathrm{HO}} \longrightarrow 2\overset{+}{\mathrm{H}} + 2\overset{--}{\mathrm{O}} \\ 2\overset{+}{\mathrm{Cl}} \longrightarrow 2\overset{-}{\mathrm{Cl}} + 4\,\oplus \end{array}\right\} \longrightarrow \overset{--}{\mathrm{O}} + \overset{++}{\mathrm{O}} = O_2$$

or summarized more briefly, $2\overset{-}{\mathrm{HO}} + 2\overset{+}{\mathrm{Cl}} \longrightarrow 2\overset{+}{\mathrm{H}} + 2\overset{-}{\mathrm{Cl}} + O_2$. It is evident that this oxidation could take place only in the presence of a very low concentration of hydrogen ions since concentrated solutions of hydrochloric acid on electrolysis yield no oxygen. A high hydrogen ion concentration obliterates the hydroxyl ion concentration. Consequently the positive chlorine ions combine with the negative chlorine ions to form molecular chlorine in concentrated solutions: $\overset{+}{\mathrm{Cl}} + \overset{-}{\mathrm{Cl}} \longrightarrow Cl_2$. Thus, the existence of positive chlorine ions at the anode accounts for the fact that dilute solutions of hydrochloric acid yield oxygen while concentrated solutions yield chlorine. Accordingly, if positive chlorine ions result from anodic oxidation of negative chlorine ions, then negative hydrogen ions may arise by cathodic reduction of positive hydrogen ions and, therefore, precede the liberation of molecular hydrogen according to the equation: $\overset{-}{\mathrm{H}} + \overset{+}{\mathrm{H}} \longrightarrow H_2$.

Analogously, negative hydrogen ions may be formed and function in the production of molecular hydrogen when metals interact with water or acids according to the general equation: M (a divalent metal) + $2\overset{+}{\mathrm{H}} \longrightarrow \overset{++}{\mathrm{M}} + H_2$, which is represented from the electronic standpoint as follows:

$$\mathrm{M} = \overset{++}{\mathrm{M}} + 2\,\ominus; \quad \overset{+}{\mathrm{H}} + \ominus \longrightarrow \mathrm{H}; \quad \mathrm{H} + \ominus \longrightarrow \overset{-}{\mathrm{H}}; \overset{+}{\mathrm{H}} + \overset{-}{\mathrm{H}} \longrightarrow H_2.$$

---

[1] Nernst ("Theoretical Chemistry," English trans., 1911, p. 767) regards the action of chlorine upon oxygen ions, molecular oxygen being liberated, as analogous to action of chlorine on bromine ions. Electronic equation for latter: $(Cl_2 = \overset{+}{\mathrm{Cl}}.\overset{-}{\mathrm{Cl}}) + 2\overset{-}{\mathrm{Br}} \longrightarrow 2\,\overset{-}{\mathrm{Cl}} + (\overset{+}{\mathrm{Br}}.\overset{-}{\mathrm{Br}} = Br_2)$.

In this connection, direct evidence of the existence of negative hydrogen is afforded by the hydrides of the metals, for example, sodium hydride, NaH. Reference should be made to the interaction of sodium, on the one hand, and of sodium hydride on the other, with water according to the equations (1) and (2), respectively:

$$(1)\quad 2Na + 2HOH \longrightarrow 2NaOH + H_2$$

$$(2)\quad NaH + HOH \longrightarrow NaOH + H_2$$

From an ionic standpoint these reactions are represented as follows:

$$(1)\quad 2Na + 2\overset{+}{H} \longrightarrow 2\overset{+}{Na} + H_2$$

$$(2)\quad NaH + \overset{+}{H} \longrightarrow \overset{+}{Na} + H_2$$

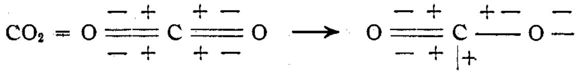
A further analysis of these reactions from an electronic standpoint requires that sodium be regarded as a compound of positive sodium with a negative electron, (Na $\ominus$), the interaction of which with water (or positive hydrogen ions) yields molecular hydrogen according to the general electronic scheme indicated above. Analogously sodium hydride is a compound of positive sodium with negative hydrogen, $(\overset{+\,-}{NaH})$, and the ionic equation (2) above is represented electronically as follows:

$$NaH = \overset{+}{Na} \text{——} \overset{-}{H} \longrightarrow \overset{+}{Na} + \overset{-}{H};\ \ \overset{+}{H} + \overset{-}{H} \longrightarrow H_2.$$

In other words, sodium hydride may be regarded as an ionogen which, dissociating yields positive sodium and negative hydrogen.[1]

Further evidence that the hydrogen of sodium hydride functions negatively is shown by the formation of sodium formate according to the equation: $NaH + CO_2 \longrightarrow HCO_2Na$.[2] It has been shown previously that each of the four valences of the carbon atom in carbon dioxide is positive while in formic acid one of the carbon valences is negative. It follows, therefore, that when sodium hydride combines with carbon dioxide one of the positive valences of the carbon atom in carbon dioxide is reduced to a negative valence by the negative hydrogen of sodium hydride. The negative hydrogen naturally tends to become positive and accordingly yields two electrons which are just sufficient to reduce one positive valence of carbon to a negative valence which, in turn, binds the resultant positive hydrogen atom:

$$NaH \longrightarrow \overset{+}{Na} + \overset{-}{H};\ \ \overset{-}{H} \longrightarrow \overset{+}{H} + 2\,\ominus$$

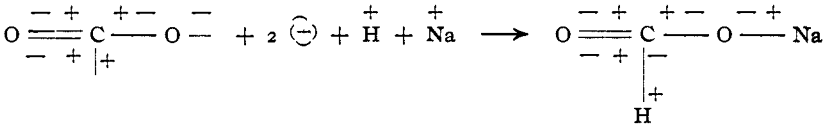


$$CO_2 = O \overset{-\;+}{\underset{-\;+}{=\!=\!=}} C \overset{+\;-}{\underset{+\;-}{=\!=\!=}} O \longrightarrow O \overset{-\;+}{\underset{-\;+}{=\!=\!=}} \underset{|+}{C} \overset{+\,-}{\text{——}} O \overset{-}{\text{—}}$$

---

[1] Results of experiments on the electrolysis of hydrides of metals will be presented in a subsequent paper.

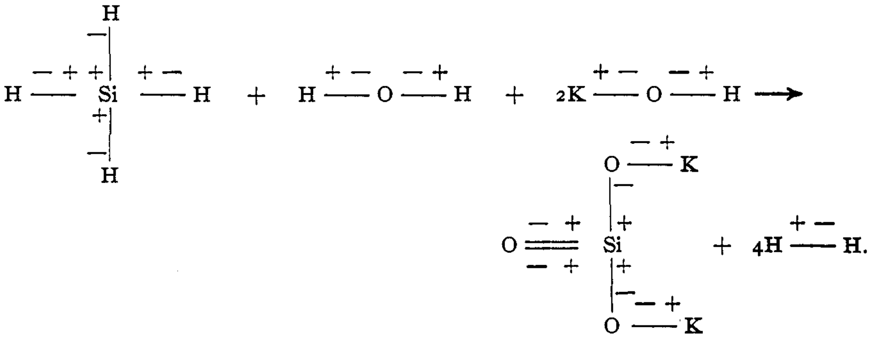
[2] Moissan, *Compt. rend.*, 136, 723 (1903).



Again, the existence of negatively functioning hydrogen is shown by the interaction of silicon hydride and aqueous potassium hydroxide. One volume of the former yields four volumes of hydrogen according to the equation:

$$SiH_4 + HOH + 2KOH \longrightarrow K_2SiO_3 + 4H_2.$$

Now, potassium silicate is analogous in composition to potassium carbonate a derivative of carbonic acid in which each of the valences of the carbon atom functions positively. Therefore each of the valences of the silicon atom in potassium silicate functions positively. Furthermore since neither water nor potassium hydroxide acts as a reducing agent in the above equation, one must conclude that each of the four valences of silicon hydride is also positive. Therefore, the hydrogen atoms function negatively and the above reaction from an electronic standpoint may be represented as follows:

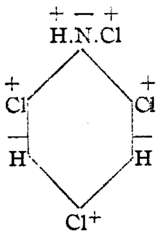


In this connection it is worthy of note that silicon and carbon, from the standpoint of the periodic classification, belong to the same natural family. Therefore, since silicon may be united to negative hydrogen as shown above, it is natural to conclude that carbon also may hold in combination negatively functioning hydrogen. In other words, an interpretation of the evidence presented leads to the conclusion that hydrogen may function not only positively but also negatively. The possibility of negative hydrogen being held in combination by positive valences of the carbon atom is also warranted by the electronic formula for benzene, which renders possible interpretations of many apparently anomalous phenomena presented in previous papers. In this connection it should be recalled that in the rearrangement reactions which characterize the substituted nitrogen halides[1] the positive halogen atom, on passing from the nitrogen atom

---

[1] Fry, This Journal, 34, 667–8 (1912).

to the nucleus, invariably assumes a position para or ortho to the negative amino radical, and when the para and both ortho positions are occupied as in 2,4,6-trichloroacyl nitrogen halide, rearrangement is both experimentally 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 halogen atom. Accordingly, the hydrogen atoms in positions 2, 4 and 6 must be assumed to function positively.



Now negatively functioning hydrogen has just been shown to act as a reducing agent, but *benzene in this sense is neither an oxidizing nor a reducing agent. Therefore, the number of positive hydrogen atoms of the nucleus must be equal to the number of negative hydrogen atoms of the nucleus.* In other words, if positions 2, 4 and 6 are occupied by positive hydrogen atoms, then positions 1, 3 and 5 must be occupied by negative hydrogen atoms. This conclusion may be regarded as a further substantiation of the proposed electronic formula for benzene.

The possibility of formulating a new definition for the so-called "nascent state" may now be considered. "Nascent action" according to common usage is a term[1] for "all those phenomena in which a substance at the moment of its liberation from compounds performs reactions it is incapable of in its ordinary condition. Thus, to cite a simple and well-known case: Hydrogen has no action on silver chloride suspended in a liquid through which it is bubbled; hydrogen evolved within the liquid (electrolytically or by action of metals) produces metallic silver, hydrochloric acid being formed at the same time." Such action has been attributed to the liberation of hydrogen in the atomic state. Accordingly, changes are effected by the atoms before they have coalesced to form molecules.

A more comprehensive view of the nascent state and nascent action may be developed by applications of the electronic conceptions of oxidation and reduction.

Ordinarily, hydrogen functions positively, while chlorine functions negatively ($HCl \rightleftarrows \overset{+}{H} + \overset{-}{Cl}$), but in certain compounds, or under special

---

[1] Freund, "Study of Chemical Composition," Cambridge Physical Series, 1904, p. 327.

conditions, hydrogen may function negatively and chlorine positively. Furthermore, negative hydrogen has been shown to act as a reducing agent, since it naturally tends to revert to its ordinary state, positive hydrogen, which change is accompanied by the liberation of electrons. On the other hand, positive chlorine acts as an oxidizing agent, since it naturally tends to become negative by acquisition of electrons. In terms of the atomistic conception of electricity the latter change is equivalent to the liberation of the so-called "positive electrons." The following equations (1) and (2) illustrate, respectively, these natural tendencies:

$$(1)\quad \overset{-}{\mathrm{H}} \longrightarrow \overset{+}{\mathrm{H}} + 2\,\ominus\,; \qquad (2)\quad \overset{+}{\mathrm{Cl}} \longrightarrow \overset{-}{\mathrm{Cl}} + 2\,\oplus$$

An electrically neutral state, *i. e.*, the atomic state, may be encountered intermediately in each of the above changes and is indicated in the following equations (3) and (4), respectively:

$$(3)\quad \overset{-}{\mathrm{H}} \longrightarrow \mathrm{H} + \ominus\,; \qquad \mathrm{H} \longrightarrow \overset{+}{\mathrm{H}} + \ominus\,.$$

$$(4)\quad \overset{+}{\mathrm{Cl}} \longrightarrow \mathrm{Cl} + \oplus\,; \qquad \mathrm{Cl} \longrightarrow \overset{-}{\mathrm{Cl}} + \oplus\,.$$

Now, if the atomic state and nascent state are to be regarded as synonomous then they may be defined, from the electronic standpoint, as an unstable condition which manifests not only an adaptability but also a tendency to either gain or lose electrons and thereby attain a more stable condition. *This condition can not be limited to the atomic state of an element,* since not only atomic or neutral hydrogen, but also negative hydrogen tends to lose electrons. A comparison of equations (1) and (3) indicates that a negative hydrogen atom may be more potent as a reducing factor than a neutral hydrogen atom since the former yields two electrons while the latter yields only one in the transition to the positive state. The activity of negative hydrogen as a reducing agent has been illustrated by the action of sodium hydride upon carbon dioxide. It is the negative hydrogen, that is to say, nascent hydrogen, which in this case reduces carbonic acid to formic acid.

On the other hand, positive chlorine is a more active oxidizing agent than is atomic or neutral chlorine since the former unit may combine with two electrons while the latter unites with only one electron in the transition to negative chlorine, as indicated in equations (2) and (4) above. It has been shown that the formation of positive chlorine ions at the anode[1] would account for the liberation of oxygen during the electrolysis of very dilute hydrochloric acid (low hydrogen ion concentration) according to the abbreviated equation: $2\overset{+}{\mathrm{Cl}} + 2\overset{-}{\mathrm{OH}} \longrightarrow 2\overset{+}{\mathrm{H}} + 2\overset{-}{\mathrm{Cl}} + \mathrm{O}_2$. The same reaction may be involved in the oxidizing reactions of hypochlorous acid.

---

[1] From this standpoint either negative or neutral hydrogen atoms produced at the cathode may be the active reducing agent in the so-called electrolytic reductions.

Therefore, from these points of view, the "nascent state" may be defined more comprehensively as *an unstable condition of a substance which manifests an adaptability and a tendency to lose electrons or to gain electrons and thereby revert to a more stable condition. If the substance (ion, atom, or compound) lose negative electrons it acts as a reducing agent. If it combines with negative electrons it acts as an oxidizing agent.* As a matter of fact practically all actions classed as "nascent" are of an oxidation or a reduction type.

CINCINNATI, OHIO.

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

THE MOLECULAR REARRANGEMENT OF TRIARYLMETHYLHYDROXYLAMINES AND THE "BECKMANN" REARRANGEMENT OF KETOXIMES.[1]

BY JULIUS STIEGLITZ AND PAUL NICHOLAS LEECH.[2]

Received December 23, 1913.

Acid halogen amides[3] RCONH(Hal), hydroxamic acids RCONHOH, dihydroxamic acids[4] RCO.NH.OCOR, and acid azides[5] $RCON_3$ undergo readily, under the influence of appropriate reagents, molecular rearrangements as the result of which derivatives of the amines RNH_2 are formed. According to the theory of one of us[6] all of these rearrangements may be interpreted as resulting from the primary formation and subsequent rearrangement of a *univalent* nitrogen derivative, acyl imide, RCO.N<. The reagents used for effecting the rearrangement are in each instance those one would expect to use on the basis of this theory to facilitate the formation of the univalent nitrogen derivative and bring about the re-

---

[1] See a preliminary report (abstract) by Stieglitz, Reddick and Leech, *VIII Internat. Congr. Appl. Chem.*, **25**, 443 (1912), and by Stieglitz and Leech, *Ber.*, **46**, 2147 (1913).

[2] The work presented in this paper forms the basis of a dissertation by Leech presented to the University of Chicago in part fulfilment of the requirements for the Ph.D. degree.

[3] A. W. Hofmann, *Ber.*, 14, 2725 (1882); **15**, 408 (1883); Hoogewerff and van Dorp, *Rec. trav. chim.*, **6**, 373 (1887); **8**, 173 (1889), etc.; Lengfeld and Stieglitz, *Am. Chem. J.*, **15**, 215, 504 (1893), etc.

[4] Lossen, *Ann.*, **161**, 359 (1872), etc.; Thiele and Pickard, *Ibid.*, **309**, 189 (1899); and especially L. W. Jones, *Am. Chem. J.*, **48**, 1 (1912).

[5] Curtius, *Ber.*, **27**, 778 (1895); *J. prakt. Chem.*, **50**, 289 (1894), etc.

[6] Stieglitz, *Am. Chem. J.*, **18**, 751 (1896); **29**, 49 (1903); Stieglitz and Earle, *Ibid.*, **30**, 399, 412 (1903); Stieglitz and Slossen, *Ber.*, **34**, 1613 (1901); Slossen, *Am. Chem. J.*, **29**, 289 (1903); Hilpert, *Ibid.*, **40**, 155 (1908); Stieglitz and Peterson, *Ber.*, **43**, 782 (1910); Peterson, *Am. Chem. J.*, **46**, 325 (1911); Stieglitz and Leech, *loc. cit.*; Stieglitz and Vosburgh, *Ber.*, **46**, 2151 (1913); Schroeter, *Ber.*, **42**, 2340 (1909); **44**, 1207 (1911); Stoermer, *Ibid.*, **42**, 3133; Wieland, *Ibid.*, **42**, 4207 (1909); Montague, *Ibid.*, **43**, 2014 (1910); L. W. Jones, *Am. Chem. J.*, **48**, 1 (1912).