6. The products of the reaction are the sulfates of potassium, chromium, and iron, and the colloidal hydrous oxides of iron and chromium. The latter are precipitated by the sulfate ion, and adsorb a large quantity of ferric sulfate and smaller quantities of the other two sulfates.

7. The equations for the reaction have been formulated.

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THE ELECTRONIC CONCEPTION OF POSITIVE AND NEGATIVE VALENCES.

BY HARRY SHIPLEY FRY.

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A paper recently published by Roger F. Brunel,[1] presents some general and some specific criticisms of the electronic conception of valence. The author states that the object of his paper[2] "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."

Brunel then subjects to criticism, either directly or indirectly, the opinions of a number of authors who have contributed to this subject None of Brunel's specific criticisms have any bearing upon the applications in which I am principally interested, namely the problem of substitution in the benzene nucleus[3] and the development of relationships between chemical constitution and absorption spectra.[4] But, on the other hand, some of his general criticisms call for comment, especially certain statements presented in a paragraph on page 718.[5] In quoting this paragraph, the assertions which it embodies have been numbered 1, 2, and 3 for facility in comment. Brunel states:

"Of the other applications of the theory to the more complex problems the author [Brunel] would mention only that of Fry to the question of substitution in the benzene ring. (1) The rule governing the positions of substituents which Fry puts forward with the utmost confidence is so simple as to arouse distrust at once. (2) It would appear sufficient to say that, in view of the extensive investigations carried on in this field in recent years by Holleman, Flürscheim, Obermüller and others, if any such rule could cover the facts it would have been discovered long ago empirically, even if not expressed in the same terms. (3) Holleman

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[1] THIS JOURNAL, **37**, 709 (1915).

[2] *Loc. cit.*, p. 710.

[3] Fry, THIS JOURNAL, **30**, 34 (1908); *Z. physik. Chem.*, **76**, 385 (1911); THIS JOURNAL, **34**, 664 (1912); *Ibid.*, **36**, 243, 262. 1035 (1914); *Ibid.*, **37**, 855, 863, 883 (1915).

[4] Fry, *Z. physik. Chem.*, **76**, 398, 591 (1911); *Ibid.*, **80**, 29 (1912); *Ibid.*, **82**, 665 (1913).

[5] *Loc. cit.*

has, however, recently called attention to a number of cases of substitution where it is quite impossible to apply Fry's rule."

This paragraph can not be regarded as fulfilling in any sense the above noted purpose of Brunel's paper. Furthermore, it embodies assertions (1, 2, and 3) which call for comment. (1) Brunel's statement that Fry's rule "*is so simple as to arouse distrust at once*" is purely arbitrary because it has no bearing whatever upon the numerous and extended applications of the rule published by Fry.

Consider briefly Brunel's assertion (2):

"It would appear sufficient to say that in view of the extensive investigations carried on in this field in recent years by Holleman, Flürscheim, Obermüller 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."

In this statement Brunel not only imposes a limitation upon the possibility of the discovery of new rules and relationships but he also completely ignores the well-known fact that the Brown and Gibson Rule is itself a purely empirical rule for determining whether a given mono-substituted derivative of benzene will yield chiefly a mixture of ortho and para diderivatives, or chiefly the meta diderivative. Moreover, Fry's rule is the direct result of his interpretation of the empirical Brown and Gibson rule in terms of the electronic conception of positive and negative valences in conjunction with his electronic formula for benzene.

Consider next Brunel's assertion (3):

"Holleman[1] has, however, recently called attention to a number of cases of substitution reactions where it is quite impossible to apply Fry's rule." This assertion can not be accepted as final, since Fry[2] has published "A Reply to A. F. Holleman" showing that Holleman's inability to correlate Fry's rule with certain cases of substitution was due to Holleman's failure to apply to the principle of the electronic tautomerism of benzene derivatives the generally accepted principle that, in a tautomeric equilibrium mixture, either one, or the other, or both tautomers (depending upon conditions), may interact with a given reagent. Thus from the standpoint of the electronic tautomerism of benzene derivatives, the simultaneous formation of ortho, para, and meta substituted derivatives was readily explained.[3] Furthermore, those cases of substitution which Holleman regarded as opposed to Fry's rule were shown to conform to the rule and to serve as direct experimental evidence substantiating the principle of the electronic tautomerism[4] of benzene derivatives.

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[1] THIS JOURNAL, 36, 2495 (1914).

[2] *Ibid.*, 37, 883 (1915).

[3] Fry, *Ibid.*, 37, 863 (1915).

[4] Brunel objects to the use of the conception of electronic tautomerism on the grounds that electronic isomers (electromers) have not as yet been isolated. This ob-

Passing from the foregoing assertions, it will be found that some of Brunel's general conclusions also invite comment. Consider the statement on page 721:[1]

"In conclusion the author would 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."

To this it may be replied, and justly maintained, that *the electronic conception of valence as a formulative hypothesis* (*i. e.*, the conception of positive and negative valences as applied to structural formulas) is, at its present status of development, neither primarily nor necessarily concerned with the question of the ultimate cause of chemical affinity. Such questions inevitably lead into a field where speculation predominates. An illustration of this is afforded by the recent and varied hypotheses of J. J. Thomson which manifest little, if any, discernable *utility* in the interpretation of the mechanism of chemical reactions and the correlation of the various phenomena of Organic Chemistry.

Brunel closes his paper with this statement:

"A number of questions are proposed which should be answered—at least, the hypotheses regarding them should be explicitly stated—before the theory is applied to the most perplexing problems of organic chemistry." In reply, *the hypothesis of positive and negative valences has been explicitly stated.* A careful study of most of the published applications of the hypothesis shows that it is used primarily to qualify, or to differentiate, the valences of an atom as positive or negative in the same manner that we may regard a positive hydrogen ion as a hydrogen atom possessing a positive valence; or a negative chlorine ion as an atom possessing a negative valence. In applying these conceptions we are entitled to assume, *symbolically* at least, that an atom with zero valence develops a unit positive valence through the loss of an electron. Another atom with zero valence develops a unit negative valence through the acquisition of an electron. From this point of view I have suggested a general rule[2] for applying the conception of positive and negative valences to various atoms, namely, that if the valence of an atom equals (n) in the ordinary meaning of the term, then that atom, from the standpoint of the con-

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jection is unwarranted because the use of the conception of tautomerism neither involves nor demands the immediate possibility of the isolation of the tautomers. Strictly speaking, the term *tautomeric* is applied to substances in which *only the equilibrium mixture of the structural isomers is known;* the term *desmotropic* is employed in cases where *the isomers have been shown to be capable of independent existence.* (Experiments are now in progress in this laboratory, the object of which is to establish the independent existence of "*electronic desmotropes.*")

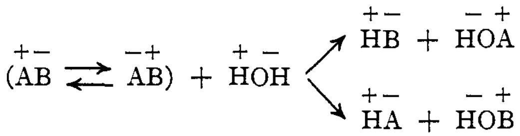
[1] *Loc. cit.*

[2] Fry, THIS JOURNAL, **30,** 34 (1908); *Z. physik. Chem.*, **76,** 388 (1911).

ception of positive and negative valences, may function in $(n + 1)$ different ways.[1]

Furthermore, the development of a positive valence by an atom (*schematically* through the loss of an electron) corresponds to oxidation. When an atom develops a negative valence (*schematically* through the acquisition of an electron) it is reduced. *The extensive field of oxidation and reduction reactions thus affords an experimental justification for the use of the electronic conception of positive and negative valences.* This phase of the hypothesis also possesses an added significance, since Stieglitz[2] has demonstrated by means of the chemometer that there is involved an actual transfer of electrical charges in certain oxidation and reduction reactions involving carbon compounds.

Again, if we admit that the hydrogen ion is positive and that the hydroxyl ion is negative under normal conditions, *i. e.*, provided that the hydrogen ion is not reduced and that the hydroxyl ion is not oxidized, then it is natural to conclude that *hydrolysis reactions constitute an experimental method for designating the polarity of the radicals of a compound under the particular conditions of the hydrolysis.* The following general scheme (in contradistinction to the scheme presented by Brunel on page 718,[3] embodies the theoretical and the actual possibilities presented by hydrolysis reactions:



$$(\overset{+\,-}{\mathrm{AB}} \rightleftarrows \overset{-\,+}{\mathrm{AB}}) + \overset{+\,-}{\mathrm{HOH}} \begin{array}{l} \nearrow \overset{+\,-}{\mathrm{HB}} + \overset{-\,+}{\mathrm{HOA}} \\ \searrow \overset{+\,-}{\mathrm{HA}} + \overset{-\,+}{\mathrm{HOB}} \end{array}$$

If the compound AB on hydrolysis yields only HB and HOA, then AB is *qualified* by the formula $\overset{+\,-}{\mathrm{AB}}$. If, on the other hand, conditions are such that the products of hydrolysis are HA and HOB, then AB is *qualified* by the formula $\overset{-\,+}{\mathrm{AB}}$. In some reactions four products of hydrolysis are obtained, and accordingly, the compound AB presents an illustration of electronic tautomerism,[4] *i. e.*, the existence of both electromers $(\overset{+\,-}{\mathrm{AB}} \rightleftarrows \overset{-\,+}{\mathrm{AB}})$ in dynamic equilibrium. Many instances[5] have been recorded in which reactions proceed according to the above and analogous schemes, and therefore substantiate not only the existence of electromers but also electronic tautomerism. Hence, *as a corallary to the experimental*

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[1] This rule has been repeatedly illustrated in various papers by Fry (*Loc. cit.*). Its application to the valences of the nitrogen atom and its various compounds has been presented in detail by L. W. Jones, *Am. Chem. J.*, 50, 414 (1913).

[2] *Qual. Chem. Anal.*, 1, Chaps. XIV and XV (1911).

[3] *Loc. cit.*

[4] Fry, *Z. physik. Chem.*, 76, 390 (1911).

[5] Fry, THIS JOURNAL, 37, 864 (1915).

facts, it seems justifiable to maintain that the ordinary structural formula for AB, namely A—B, is qualified when it is written $\overset{+}{\text{A}}\text{——}\overset{-}{\text{B}}$, or $\overset{-}{\text{A}}\text{——}\overset{+}{\text{B}}$, or both $(\overset{+}{\text{A}}\text{——}\overset{-}{\text{B}} \rightleftarrows \overset{-}{\text{A}}\text{——}\overset{+}{\text{B}})$, depending upon the conditions of the experiments and the products obtained. Therefore, *in designating the ends of a bond as positive or negative, one is not concerned primarily or necessarily with the question of the nature of chemical affinity* (a point upon which Brunel has insisted). The chief value and claim for recognition of electronic formulas (and for the existence of electronic tautomers in dynamic equilibrium) should and does lie in the fact that *in numerous instances they are more precise and more significant in the explanation of chemical phenomena and the mechanism of reactions than are the ordinary structural or graphic formulas.*

In conclusion, consider briefly a significant statement made in 1867 by Kekulé which illustrates the principle at issue:

"The question whether atoms exist or not has but little significance from a chemical point of view: its discussion belongs rather to metaphysics. In chemistry we have only to decide whether the assumption of atoms is an hypothesis adapted to the explanation of chemical phenomena. More especially have we to consider the question whether a further development of the atomic hypothesis promises to advance the knowledge of the mechanism of chemical reactions."

Kekulé's efforts to develop a knowledge of the mechanism of chemical reactions are today embodied in the structure theory, the recognized foundation of the extensive achievements of organic chemistry, both theoretical and applied. The established utility of *the structure theory* (which in reality is *a formulative hypothesis*) is not dependent upon the existence of atoms nor upon the fundamental nature of valence or chemical affinity. Similarly, the utility of *the electronic conception of positive and negative valences* (which is also *a formulative hypothesis* with the structure theory as its foundation), is not primarily dependent upon the existence of electrons nor upon the fundamental nature of chemical affinity. The significance of this viewpoint may become more evident if the words of Kekulé (quoted above) be paraphrased in modern terms: In chemistry we have to decide whether the electronic conception of positive and negative valences is an hypothesis adapted to the explanation of chemical (and physical) phenomena. More especially have we to determine whether the further development of this hypothesis of positive and negative valences promises to advance our knowledge of the mechanism of chemical reactions. In view of the fact that electronic formulas, in many instances, have proven to be more precise and more significant than the ordinary structural formulas in the explanation of chemical phenomena and the mechanisms of reactions, the hypothesis of positive and negative valences may possibly become a necessary adjunct to the structure theory. This, as I have stated before,[1] must depend upon the extent of its applications and experimental verifications, and upon the part that is played by just criticisms in bringing to light the relative merits and demerits of its *applications*.

From these and the preceding points of view noted in this paper, the general criticisms and conclusions of Brunel have little, if any, bearing upon the *electronic conception of positive and negative valences as a formulative hypothesis*.

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NEPHELOMETRIC ESTIMATION OF PHOSPHORUS.

BY PHILIP ADOLPH KOBER AND GRETE EGERER.

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I. Introduction.

The estimation of phosphorus in biological and industrial sciences, especially of minute amounts, is becoming of increasing importance A large number of volumetric and colorimetric methods have been proposed but thus far none has been satisfactory for micro-quantitative work. While looking for a suitable nephelometric precipitant[2] for phosphorus in connection with our nuclease technic[3] our attention was called[4] to the reagent developed by Pouget and Chouchak.[5] This reagent consists of a nitric acid solution of strychnine and molybdic acid and produces a very sensitive reaction with phosphates (one milligram of phosphorus in 2 liters giving a very marked suspension of insoluble substance) similar in sensitiveness to the Nessler or the Graves[6] reaction for ammonia. The authors found it will detect 1 part of phosphorus in 20 million parts

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[1] THIS JOURNAL, 37, 892 (1915).

[2] Uranium acetate and magnesia mixture were tried as nephelometric precipitants, but as preliminary experiments, especially with the latter, were not successful, these reagents were abandoned.

[3] P. A. Kober and S. S. Graves, THIS JOURNAL, 36, 1304 (1914).

[4] Dr. I. Greenwald of this laboratory, after making an attempt to apply this reagent directly for nephelometric work, abandoned it. Subsequently (see *J. Biol. Chem.*, 21, 29 (1915)) he recommended the original reagent for a colorimeter method, although, according to him, the color of the opalescent liquid is so slight that it is not apparent until it is put into the instrument. It is obvious that any defect in the suspension for nephelometric work will make a defect for colorimetric, and our experiments, as indicated elsewhere, show that the reagent as recommended by the original authors, although usable, is not satisfactory.

[5] *Bull. soc. chim.*, 5, 104 (1909); 9, 649 (1911).

[6] THIS JOURNAL, 37, 1181 (1915).