(5) Two solutions of arsenic acid containing 32% of HCl were treated a few minutes with a *rapid* stream of H_2S, and the determination of arsenic carried out as usual.

Weights of arsenic sulfide: (*a*) 0.2367 g. (*b*) 0.2369 g.

Again there was no reduction of arsenic acid, for the yield of As_2S_5 was quantitative.

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A THEORY OF MULTIPLE IONIZATION: A MODIFICATION OF THE ELECTROLYTIC DISSOCIATION THEORY.

I. INTRODUCTORY AND QUALITATIVE STATEMENT OF THE THEORY, WITH APPLICATIONS.[1]

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In the extended application of the electrolytic dissociation theory to general and analytical chemistry which has been made and has been embodied in many textbooks, certain difficulties have been encountered. These have been satisfactorily met by making assumptions at variance with the original propositions of the theory. As such assumptions as have, from time to time, been proposed are widely scattered throughout the literature and are only occasionally alluded to in the textbooks, it seems that a comprehensive theory should be developed to embody the new conceptions as well as to show their relation to the original hypothesis.

The phenomena which the ionic theory, as it is most widely understood, fails to explain, or in regard to which further explanation is to be desired, will now be enumerated under five classes, and then a modification of the theory will be suggested which, it is hoped, will sufficiently explain most of the hitherto obscure facts.

1. We should like to have some insight into the cause of the different degrees of ionization of electrolytes. Why is one acid strong and another weak? The ionic theory offers no hypothesis to explain this.

2. There are certain types of reactions and certain compounds that seem to find no place in the theory. Such compounds are nitrosyl chloride, sulfuryl chloride, phosgene, nitrogen chloride, compounds of the halogens with each other, and practically all acid anhydrides. Nitrogen tetroxide dissolves in water to form a mixture of acids. In all the reactions of these compounds with water ionogens are formed. Are they not formed by ionic actions? Abegg[2] says:

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[1] This paper, read before the Cincinnati Section on May 12, 1915, forms the basis of a thesis submitted to the Ohio Mechanics Institute for the Degree of Bachelor of Science.

[2] Abegg, "The Theory of Electrolytic Dissociation," 1907, p. 161.

"The observation that all reactions in which ions participate in measurable amounts—even the hydrolytic actions of the extremely weakly dissociated water—proceed to their equilibria with an immeasurably great velocity, has induced the assumption that indeed every capacity to react is to be attributed to the presence of ions. A basis for this assumption has been thought to exist in the fact that reactions between non-electrolytes usually proceed with extreme slowness corresponding to an immeasurably small, but not absolutely lacking, dissociation."

If this is true, the development of an ionic theory which includes them would be highly desirable.

3. The oxidizing actions of hot, concentrated sulfuric and nitric acids are not explained by the theory. The writing of the formulae of oxygen acids as hydroxides is frequently necessary in the interpretation of these reactions and has become common in the textbooks. There must be an ionic basis for these actions, although they have not yet been satisfactorily brought within the bounds of the ionic theory.

4. It is well known that only weak electrolytes obey the law of mass action.

5. **Amphoterism.**—In his "Qualitative Analysis,"[1] Stieglitz devotes an important chapter to the amphoteric electrolytes, as aluminium hydroxide. He develops, by the usual methods, equilibrium equations to show what would result if their acid and basic qualities neutralize each other.

Although amphoterism is found most prominently in the middle families of the periodic system, it is a much more common property than we usually believe it to be. Arrhenius[2] in his "Immuno-Chemistry" credits the albumins with being amphoteric. Some careful work in connection with the application of the ionic theory to amphoterism has been done by Winkelblech[3] and by Walker,[4] working chiefly with organic compounds, especially those in which "zwitter-ion"[5] formation occurs. To quote Stieglitz[6] again, "Pronounced amphoterism is shown by a large number of metal hydroxides; it is, perhaps, the rule rather than the exception." He even suggests that NaO' ions exist in immeasurable quantities in solutions of $NaOH$.

Theory of Multiple Ionization.—These considerations allow of but one conclusion, which may be stated in the form of a question. May not amphoterism be a property common to all electrolytes? This leads to the statement: When substances undergo electrolytic dissociation in solution they tend to dissociate into ions in at least two ways, the ratio between the different ionization constants varying from 1:1 to very nearly 1 : ∞, and depending on the nature of the solvent, the concentration of

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[1] Stieglitz, "Qualitative Analysis," **1912**, Theoretical Part, p. 171.

[2] "Immuno-Chemistry," **1907**, pp. 161–3.

[3] *Z. physik. Chem.*, **36**, 546 (1901).

[4] *Ibid.*, **49**, 82 (1904); **57**, 706 (1905).

[5] Moore in Lehfeldt's "Electro-Chemistry," **1904**, Part 1, p. 145.

[6] *Loc. cit.*

the solution and the average structure of the molecules dissociating. This forms the basis, then, of a theory of multiple ionization. For example, when nitric acid dissociates, X molecules may dissociate as follows:

$$HNO_3 \rightleftarrows H^+ + NO_3^-$$

Y molecules may dissociate in another manner

$$HNO_3 \rightleftarrows OH^- + NO_2^+.$$

The familiar mathematical expression for the degree of dissociation,[1] γ, of an electrolyte is

$$\gamma = \frac{i-1}{n-1}.$$

Considered in the light of the theory outlined in the preceding paragraph it would be better to write it

$$\alpha + \beta = \frac{i-1}{n-1},$$

in which α and β are the degrees of dissociation according to the two schemes of ionization which the salt, acid or base is capable of following.

Applications.—It is now necessary to apply this new hypothesis to the points outlined above in which the theory in its present form fails to give entirely satisfactory explanations.

Amphoterism.—It is scarcely necessary to add anything here. Walker, Bredig, Winkelblech and others, as already mentioned, have done so much in this field that little remains to be said. They were forced to assume multiple ionization in some cases, although they did not render it broad enough to form an integral part of the theory. Stieglitz has suggested that amphoterism may account for the oxidizing action of some strong acids, although he does not seem to have fully developed the idea.

1. **Dissociation of Acids and Bases.**—Let us consider the equilibria in a fairly concentrated solution of nitric acid.

$$\begin{array}{lcccc} HNO_3 & \rightleftarrows & H^+ & + & NO_3^- \\ HNO_3 & \rightleftarrows & OH^- & + & NO_2^+ \\ & & \uparrow\downarrow & & \uparrow\downarrow \\ \hline 2HNO_3 & = & HOH & + & N_2O_5 \end{array}$$

The result is that a series of four equilibria is set up.

For sulfuric acid we would have

$$\begin{array}{lcccccc} H_2SO_4 & \rightleftarrows & H^+ & + & H^+ & + & SO_4^{=} \\ H_2SO_4 & \rightleftarrows & OH^- & + & OH^- & + & SO_2^{++} \\ & & \uparrow\downarrow & & \uparrow\downarrow & & \uparrow\downarrow \\ \hline 2H_2SO_4 & \doteq & HOH & + & HOH & + & S_2O_6\ (=2SO_3) \end{array}$$

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[1] Arrhenius, *Z. physik. Chem.*, 1, 631 (1887).

Now for nitric acid at any given concentration we have the equilibria

$$\frac{[NO_3^-] \times [H^+]}{[HNO_3]} = K_a$$

$$\frac{[NO_2^+] \times [OH^-]}{[HNO_3]} = K_b$$

When, as in the case of aluminium hydroxide as developed by Stieglitz. the product of the concentration of H-ions and of OH-ions equal K_w we have equilibrium We may combine the two equations and obtain

$$\frac{[NO_3^-] \times [NO_2^+] \times K_w}{[HNO_3]^2} = K_a \times K_b$$

$$\frac{[N_2O_5]^2}{[HNO_3]^2} = \frac{K_a \times K_b}{K_w}$$

or

$$\frac{[N_2O_5]}{[HNO_3]} = \sqrt[2]{\frac{K_a \times K_b}{K_w}}.$$

The above is the ionic method of expressing the reaction between an anhydride and an oxygen acid if the acid is monobasic. For the mathematical formulation of the equilibrium between a dibasic acid, *e. g.*, sulfuric acid, and its anhydride we obtain by similar reasoning the equation

$$\frac{2SO_3}{H_2SO_4} = \frac{1}{K_w} \sqrt[2]{K_a \times K_b}.$$

In the above examples we note that when the two types of acid radicals unite, the anhydride or its polymer is formed It is interesting to note in this connection that the anhydride of H_2SO_4 exists in two modifications, one of which has the molecular formula SO_3 and the other S_2O_6. This affords us a new definition of an inorganic anhydride: An anhydride of an oxygen acid is an oxide which, in aqueous solution, is more or less completely hydrolyzed by water, due to its dissociation into two oxide radicals, oppositely charged, which combine with the ions of water to form the acid. A more striking definition would be: An acid anhydride is a salt formed by the self-neutralization of an acid.

A strong acid is usually understood to be one which, at a definite concentration, contains a relatively great concentration of H-ions, while a weak acid is one whose ionization constant is such that at the same concentration it will yield fewer H-ions. A low concentration of H-ions is the result of one or both of two causes: either only a small concentration of H-ions results from the ionization of the acid, which would be the case when the acid is only slightly ionized, or a greater number of H-ions are formed, some of which are removed immediately after formation. The latter might be the result of multiple ionization. Most of the OH ions formed by the basic ionization of the acid would be removed by some of the H-ion formed by the acid ionization as relatively un-ionized water. So we see that multiple ionization may be one cause of the weakness of acids, and whenever it does occur must tend to lower the H-ion concentration of the acid and so be one of the factors which give the ionization constant a definite value. If the number of molecules of an hydroxide dissociating as a base exceeds the number dissociating as an acid we have a base. Let A represent the number of molecules of an hydroxide dissociating as an acid and B, the number dissociating as base. Then the limits between which an hydroxide may have acid properties at infinite dilution are $A = 1$, $B = 0$, and $A = B$. For basic properties the limits are $A = 0$, $B = 1$, and $A = B$.

Viewed in this light, determinations of the relative strengths of acids and bases by conductivity measurements are bound to be erroneous because the velocities of the ions formed by the hitherto unassumed modes of ionization are not taken into account. In his work on amphoteric electrolytes, J. Walker pointed out that, in calculating the conductance of an amphoteric electrolyte at infinite dilution, we must obtain the sum of the products of four ions into their specific conductances, and not two as is usually done. The different velocities of the ions may be such that the error is either large or small. In weak acids and bases the errors will probably be greatest, while in the strongest acids they will be insignificant, since these acids ionize, practically, in only one way. To compare the values of dissociation constants obtained hydrolytically with those obtained by conductivity measurements is very interesting. When all ionic velocities concerned are known, this may afford a method for the determination of the prevalence of multiple ionization.

If we apply these conceptions to non-oxygen acids we arrive at conclusions similar to those reached by the chemists who are elaborating electronic theories. H. S. Fry[1] formulates the ionization of hydrochloric acid exactly as the theory here advanced would lead us to formulate it.

It is unnecessary here to apply these ideas to bases, for it is obvious that such an application would present no difficulties. It is assumed that solutions of ammonium hydroxide ionize either as is usually believed, or as follows: $NH_3 \rightleftarrows NH_2^- + H^+$ This explains how it attaches the NH_2 group to mercury salts, something which cannot be explained unless multiple ionization is assumed.

The next step is to find an underlying cause for the fact that some molecules tend to ionize in only one way, while others tend to break up in more ways than one. One theory is stereochemical. All molecules of a compound do not necessarily possess the same structure. Some may have a structure which would influence them to ionize as an acid,

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

while the structure of others might lead to their basic ionization. On the relative amounts of these molecules in a solution might depend the strength of that solution as acid or base. Electronic theories, as those recently developed by W. A. Noyes,[1] L. W. Jones[2] and Fry[3] might be of assistance.

This theory explains in a very simple manner why silver and mercury oxides and not hydroxides are precipitated by NaOH. If any of these hydroxides should be formed in solution, they would yield by their acid and basic ionization some Ag^+ and AgO^- ions. These ions, being oppositely charged, would at once combine to form dissolved silver oxide. But as this is insoluble, while the hydroxide is not insoluble, it will at once be precipitated and this will continue until only a little dissolved silver hydroxide is left.

2. The second point outlined near the beginning of this paper was that a number of inorganic reactions involving ionogens did not find a place in the ionic theory. From what has gone before it is reasonable to suppose that sulfuryl chloride is formed in exceedingly small quantities when strong sulfuric and hydrochloric acids are mixed,

$$SO_2(OH)_2 + 2HCl \rightleftarrows SO_2Cl_2 + 2H_2O.$$

This is the first time we have encountered the case where the basic qualities of one acid are neutralized by another acid. So the theory of multiple ionization rationalizes the existence of the inorganic acid chlorides and the analogous anhydrides. It may even be possible to prepare compounds of this type which are not yet known. This offers a wide field for profitable research. The reaction between nitrogen tetroxide and water probably takes place in two different ways at the same time. Some molecules ionize as NO^+ and NO_3^- and these react with water to give HNO_3 and NO(OH). Others ionize, yielding NO_2^+ and NO_2^- which react with water to give HNO_2 and $NO_2(OH)$.

3. **Oxidizing Action of Acids.**—In attempting to explain oxidation-reduction reactions in terms of direct transfers of electric charges between atoms and their ions, Stieglitz[4] has suggested that oxidizing acids, as permanganic, nitric, arsenic, etc., owe their power to their capacity to ionize minimally as bases. In terms of the theory we have just developed, the oxidizing action of nitric acid is due to its basic dissociation: $HNO_3 \rightleftarrows NO_2^+ + OH^-$. The NO_2^+ ion has a definite solution tension and may pass off as a brown gas after surrendering its charge to any other atom or ion which will hold it more firmly, just as Cu^{++} gives its charges to zinc

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[1] W. A. Noyes, THIS JOURNAL, **34**, 663 (1912); **35**, 767 (1913).

[2] L. W. Jones, *Am. Chem. J.*, **50**, 414 (1913).

[3] Fry, THIS JOURNAL, **30**, 34 (1908); **34**, 664 (1912); **36**, 262 (1914); *Z. physik. Chem.*, **76**, 385 (1911).

[4] Stieglitz, "Qualitative Chemical Analysis," 1912, I, 283.

We should expect, then, that the oxidation of a ferrous salt by concentrated nitric acid might be represented ionically as follows:

$$Fe^{++} + NO_2^{+} \longrightarrow Fe^{+++} + NO_2$$

In its expanded form, we might write the equation for the action of concentrated nitric acid upon ferrous sulfate in the presence of sulfuric acid as follows:

$$2Fe^{++} + 2SO_4^{=} + 2H^{+} + SO_4^{=} + 2OH^{-} + 2NO_2^{+} \longrightarrow 2Fe^{+++} + 3SO_4^{=} + 2H_2O + 2NO_2$$

It will be noted that it is unnecessary to consider the normal ionization of nitric acid in a qualitative discussion. If the reaction is carried out without the addition of sulfuric acid, the acid ionization of nitric acid would play the part of the sulfuric acid in the above equation.

This view of the action of nitric acid is of especial importance in organic chemistry in explaining the action of the acid in nitrations where the NO_2 group becomes attached to, *e. g.*, the benzene nucleus. It is also important to note that in performing such nitrations, a mixture of concentrated sulfuric and nitric acids is employed and this is, as Stieglitz states, of importance in facilitating the basic ionization of nitric acid.

The oxidation of NO gas by concentrated nitric acid would appear to be similar to the action of zinc on a solution of a copper salt. The NO_2^{+} formed by the basic ionization of the nitric acid yields its charge to the NO molecule and passes off as a brown gas.

In the solution of copper in sulfuric acid the SO_2^{++} ions formed by the basic ionization of the acid, give up their two positive charges to the Cu, forming cupric-ion, and pass off as sulfur·dioxide gas, just as H-ions give their charges to Zn when it dissolves in HCl. The oxidation of metallic aluminium to its ion by means of NaOH with evolution of H_2 is easily explained in a similar manner:

$$2Al + 6NaO^{-} + 6H^{+} \longrightarrow 2Al^{+++} + 6NaO^{-} + 3H_2$$

A quantitative examination of some reactions of this class will, it is hoped, form the subject of later work. An important work for the future will be the insertion of the new ions into their proper places in the electromotive series by determining their solution tensions.

4. The most vulnerable point of the electrolytic dissociation theory as it stands is that the Ostwald dilution law does not give constant values for strong electrolytes. Repeated attempts have been made to remove this obstacle to an unqualified acceptance of the theory by many workers, particularly Jahn,[1] who with Nernst attempted to explain the anomaly by an application of Nernst's extended theory of solutions. Reactions between ions and undissociated molecules have been assumed by some

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[1] *Z. physik. Chem.*, 33, 545 (1900); 35, 1 (1900); 37, 490 (1901); 38, 487 (1901); 41, 257 (1902).

to be the cause of the difficulty while Hittorf,[1] Bredig,[2] Noyes[3] and Steele[4] base it upon the formation of inner complexes. Abegg and Bodlander.[5] Jones[6] and Getman and others have attempted to explain it on the basis of hydrate formation. A mathematical formula due to Rudolphi[7] has been transformed by Van't Hoff and Kohlrausch.[8] A broader attempt, though still empirical, has been made by Storch.[9] More recently important work has been done by Washburn,[10] Lewis,[11] A. A. Noyes,[12] Kendall[13] and others. In view of the fact that in spite of their labors, a satisfactory solution of the difficulty has never been reached, it would be decidedly out of place to even offer a suggestion without prolonged study. And yet it appears to the author that the factor of multiple ionization has hitherto been neglected. Possible effects of multiple ionization upon the so-called ionization constants, the effect of the velocities of the new ions upon the true values of degrees of dissociation at definite concentrations and the possibility of varying changes in the α and β dissociations with changing concentrations are at least worthy of the consideration of all who are interested in the question. Undoubtedly, the effects of multiple ionization, *i. e.*, oxidation, etc., are most apparent when dealing with concentrated solutions and it is also here that variations from the mass law are most pronounced.

Other Applications.—To render this introduction and general statement complete in a merely qualitative sense, it now remains to apply the hypothesis to some of the successful applications of the old theory.

Neutralization.—It is evident that neutralization may take place in more than one way in terms of the new conception. For example, the acid qualities of nitric acid may neutralize the basic qualities of sodium hydroxide or the acid qualities of sodium hydroxide may neutralize the basic qualities of nitric acid. A large number of molecules undergo the first reaction as compared with those which follow the second.

In considering neutralization an interesting confirmation of our theory is met. The Russian thermochemist Hess has shown that when an

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[1] *Pogg. Ann.*, **106**, 385 and 546.

[2] *Z. physik. Chem.*. **13**, 190 (1894).

[3] THIS JOURNAL, **36**, 63 (1914).

[4] *J. Chem. Soc.*, **82**, 241 (1902).

[5] *Z. anorg. Chem.*, **20**, 453 (1897).

[6] Monograph No. 60, Carnegie Institute.

[7] *Z. physik. Chem.*, **17**, 385 (1895).

[8] *Ibid.*, **18**, 301 and 662 (1895).

[9] *Ibid.*, **19**, 13 (1896).

[10] Washburn, THIS JOURNAL, **33**, 1686–1713, 1461–78 (1911); **35**, 681–74 (1912).

[11] Lewis, *Ibid.*, **30**, 668–83 (1910); **34**, 1631–44 (1912).

[12] A. A. Noyes, *et al.*, *Ibid.*, **33**, 1643, 1650, 1663, 1673, 1807, 1827 and 1836 (1911); **34**, 454 (1912).

[13] Kendall, *J. Chem. Soc.*, **101**, 1275–97 (1912); *Proc. Roy. Soc.*, (*A*) **85**, 200–19 (1912).

equivalent of a strong acid neutralizes a strong base 13,700 cal. are produced, irrespective of the strong acid or base chosen, and that with weak acids or bases less heat is produced. It now becomes clear that weak electrolytes do not give exactly this amount of heat because some of the H and OH ions formed by the weak acid or base have united before the solutions were mixed. Therefore, there is not left an equivalent of H^+ and of OH^- for combination and consequently we cannot expect exactly 13,700 cal.

Hydrolysis.—This is but a continuation of the discussion of neutralization. A typical example is the neutralization of the strong base NaOH and the weak carbonic acid. This means, if the hypothesis previously advanced is tentatively accepted, that we have a base, practically all the molecules of which dissociate in one way, and an acid in which the ratio of acid to basic ionization is more nearly one to one. For example:

$$\begin{array}{ll} 2Na^+ + 2OH^- & 2H^+ + CO_3^{=} \\ 2NaO^- + 2H^+ & 2OH^- + CO^{++} \end{array}$$

On the right there is an approximately equal number of H^+ and OH^- ions and carbonate and carbonyl ions. On the left there are a very few NaO^- and H^+ ions, and a large number of Na^+ and OH^- ions. Applying the mass law, it is seen that all of the H^+ ions would be removed as water by the relatively great number of OH^- ions. In order that the positive and negative charges on the remaining ions may balance, there must remain a large number of OH^- ions in solution. Therefore a solution of sodium carbonate reacts basic, since this is a condition of equilibrium and may be reached either by bringing together the acid and base or by dissolving the salt in water.

Summary.

1. Five points have been brought forward in which the ionic theory in its present form fails to give entirely satisfactory explanations of the observed facts, or in regard to which there may be theoretical objections.

2. To meet these points it has been suggested that ionization may take place in more ways than one. The strengths of acids and bases depend upon the relative number of molecules ionized as acid and as base. The ionic reactions between water and acid or basic anhydrides have been made clear.

3. The new hypothesis has been applied to the common reactions of neutralization and hydrolysis.

It is my endeavor to show that the hypothesis is worthy of serious consideration, and later I hope to give it quantitative examination. In conclusion, I desire to express my appreciation of the encouragement given to me by my honored friend and instructor, Dr. Sigmund Waldbott, Professor of Chemistry of the Ohio Mechanics Institute.

CINCINNATI, OHIO.