ON POSITIVE AND NEGATIVE HALOGEN IONS.

By Julius Stieglitz.

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At the end of an article on "The Reaction between Chlorine and Ammonia," published by W. A. Noyes and A. C. Lyons in a recent number of this Journal,[1] the interesting suggestion is made, that the chlorine may dissociate, before action, into positive as well as negative ions; the suggestion is accompanied by an invitation for discussion and further consideration.

The writer is induced to open the discussion because for a number of years the hypothesis of the existence of positive as well as negative ions of the three halogens, chlorine, bromine, and iodine, and notably of the formation of positive halogen ions by hypochlorous, hypobromous, and hypoiodous acids, with its consequences, has been publicly presented before the student and the professional body at the University of Chicago. The theory was supported, among other things, by the behavior of the above hypo-acids towards acids and by the strongly marked basic properties of the iodoso[2] and iodonium bases.[3]

As far as the former is concerned, the reaction

$$HOCl + HCl \rightarrow Cl_2 + H_2O$$

was considered as a purely ionic reaction,

$$\overset{-}{HO} + \overset{+}{Cl} + HOCl + \overset{+}{H} + \overset{-}{Cl} \rightarrow Cl_2 + H_2O, \text{ etc.};$$

hypochlorous acid ionizes very little but, like so many nearly neutral hydroxides, it ionizes both as a weak acid,

$$HOCl \rightleftarrows \overset{+}{H} + \overset{-}{ClO},$$

and at the same time as a still weaker base,

$$HOCl \rightleftarrows \overset{-}{HO} + \overset{+}{Cl},$$

much like aluminum hydroxide, the relative size of whose ionization constants is reversed. In the same way the action of chlorine on alkalies in aqueous solution was considered as a purely ionic reaction:

$$\overset{+}{Cl} + \overset{-}{Cl} + Cl_2 + \overset{+}{K} + \overset{-}{OH} \rightarrow \overset{+}{K} + \overset{-}{Cl} + HOCl, \text{ etc.}$$

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[1] This Journal, **23**, 463.

[2] Willgerodt: *Ber. d. chem. Ges.*, **25**, 3494, etc.; V. Meyer: *Ibid.*, **25**, 2632, etc.

[3] Hartmann and V. Meyer: *Ibid.*, **27**, 426, etc.

The chief object of these lines is, however, to point out that the existence of *positive chlorine ions*, in aqueous solutions both of chlorine and of hypochlorous acid, can no longer be considered as a mere hypothesis, but must be accepted as proved experimentally by the splendid, quantitative experiments of Jakowkin[1] on the action of water on chlorine, although this consequence of his work has not heretofore been recognized.

Jakowkin's experiments prove conclusively that the reaction

$$HOCl + HCl \rightleftarrows H_2O + Cl_2\ ^1$$

is reversible; and also that it is an *ionic* reaction. A condition of equilibrium is produced according to

$$HOCl + \overset{+}{H} + \overset{-}{Cl} \rightleftarrows H_2O + Cl_2,^2$$

and is dependent consequently on the concentrations of the hydrogen and chlorine ions as well as of the hypochlorous acid and chlorine. It is obvious, however, that if the reaction as far as the hydrochloric acid is concerned is an ionic one (which is rigidly proved) and also as far as the water is concerned (which is universally recognized), it must of necessity be an ionic reaction also for the *hypochlorous acid* (which must therefore dissociate, at least to a very slight extent, into hydroxyl and *positive chlorine ions*), and also be an ionic reaction for *chlorine*, which must dissociate partially into *positive* and negative ions. The very cause of hydrolysis as in all such cases and of the reversibility lies, not more in the minimal, but actual, ionization of water, than in the formation of these ions of hypochlorous acid and of chlorine, if the theory of ionization means anything at all.

It is curious that neither Jakowkin, nor any of the chemists who have commented on his work, seem to have drawn this obvious conclusion from it,—in the author's opinion the most important truth growing out of his fine experiments. Jakowkin assumes in his calculations that the hypochlorous acid is not dissociated into ions. Its dissociation constant undoubtedly is so small that, as in the case of water, it may well be neglected in these calculations; but, as in the well established ionization of water, no matter how small the ionization constant for hypochlo-

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[1] *Ztschr. phys. Chem.*, **29**, 613.

[2] Substances occurring in minimal quantities, *e. g.*, the ions of water, chlorine and hypochlorous acid, are, for the sake of simplicity, not represented in the equation.

rous acid (for $\overset{-}{HO} + \overset{+}{Cl}$) may be, it involves the *fact* of the existence of *positive chlorine ions.*

It must be added that these views would have been published long ere this, if it had not been the hope of the author to report at the same time on other direct experimental confirmations of them. Circumstances have made it impossible to undertake before this the delicate work involved ; but in the ensuing year it is intended at least to study the behavior, of solutions of chlorine, hypochlorous acid, iodine chloride, etc., towards the electric current, in the hope of proving that, under suitable conditions, the migration of positive halogen ions to the negative pole will take place. Such a migration would decide the question, it seems to me, in the most direct and unquestionable fashion. I regret that the interesting paper of Professor Noyes and Mr. Lyons has made it necessary to publish these lines rather prematurely ; but their invitation for discussion encourages me to do so before the completion of my own experiments.

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THE PHOTOMETRIC DETERMINATION OF SULPHATES.

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THE time element enters largely into most transactions in the industrial world and chemistry as a pure science is not always to be considered. Exact methods, if time-consuming, must give place, in many cases, to rapid tests that give practical knowledge in the shortest possible limit of time.

If a trainload of coal is detained for inspection it is not feasible to wait a day or two for an ultimate analysis by organic combustion. The heating power is obtained in an hour and a half by calorimetry. By this same process, using the Mahler bomb, the determination of volatile sulphur, which would take two hours by ordinary chemical methods, may be accomplished by photometry in five minutes,—not with great accuracy, but with sufficient accuracy for practical purposes.

The physician in analyzing urine does not desire to know the exact percentage of sulphates present, but merely to what extent the amount present is below or above the normal. Photometry tells him this in a few minutes.