Thus the experiments with ferric chloride and cupric chloride fully corroborate, by positive results, and that with mercuric chloride, by a negative result, the conjecture expressed above. We may consider, therefore, as well established the rule that only those metallic chlorides, which more or less readily dissociate are reduced to a lower degree of chlorination when heated in a closed tube with ammonium chloride, the latter breaking up completely thereby with the setting free of nitrogen.

In the chemical literature I find only one instance which has a direct bearing on the rule in question. H. Moissan[1] prepared chromous chloride by heating chromic chloride in ammonium chloride vapor. Neither chromic nor chromous chloride being volatile below a red heat, it was not necessary to heat the reacting substances in a sealed tube, but obviously the reaction in this case has to be represented by the equation

$$3CrCl_3 + NH_4Cl = 3CrCl_2 + 4HCl + N,$$

and falls under the rule formulated above; chromic chloride is reduced by ammonium chloride because it dissociates.

In closing, I may say that while studying the action of ammonium chloride on metallic chlorides, a subject which will continue to occupy me in the immediate future, I have been devoting considerably more attention to the more interesting study of the action of ammonium chloride on the chlorides of some non-metallic elements, *viz.*, of carbon, silicon and sulphur, and I hope to be able to publish the results soon.

THE ACTION OF CHLORIC ACID ON METALS.

By W. S. Hendrixson.

Received May 16, 1904.

In the course of my work a year ago on "Silver as a Reducing Agent," in which the action of finely divided silver on chloric, iodic and chromic acids was studied quantitatively, there was occasion to study the literature regarding the action of chloric and related acids on other metals. It soon appeared clear that the amount of information to be gained about the action of chloric acid, in particular, on the metals was very meager, and it appeared

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[1] *Ann. chim. phys.* [5], **25**, 401.

also that there were several errors, whose origin in most cases could not be traced, that had apparently come down from treatise to treatise to the present time. It seemed, therefore, desirable to attempt to make some contribution to the subject, and if possible to clear up some contradictions and doubtful points, and this seemed the more desirable since chloric acid is one of the few strong oxidizing acids, which can be obtained in the free state easily and in nearly pure condition, and which is fairly stable.

So far as known to me scarcely any attempt has been made to study quantitatively the action of chloric acid on metals. It is a highly dissociated acid and it is also a strong oxidizing agent. As might be expected, its action on metals may take one or both of two courses. It may dissolve some metals with the liberation of hydrogen in about the same way as hydrochloric acid, and with very little oxidizing action; again, it may act purely as an oxidizing agent. The course depends upon the nature of the metal in any case and the concentration of the acid. Contrary to statements that have been made, I do not find any metal that dissolves in chloric acid without the reduction of at least a small portion of the acid. On the other hand, there are several metals that simply disappear in the acid and that rapidly and at ordinary temperature, without the evolution of any gas whatever. Among these are cadmium, copper, and iron.

Most of the chloric acid in the market is far from pure, and I have been able to obtain only one sample pure enough for use in this work. It was secured from Eimer & Amend, and it contained no sulphuric acid, barium, or free chlorine, and only a trace of hydrochloric acid. It was perfectly colorless and had a concentration of almost exactly 2.5N. This acid was used in nearly all of the following experiments. In a sample secured later the only impurity found was hydrochloric acid. Its amount was determined, and it was removed with a weighed amount of silver oxide.

It was very desirable in some of these experiments to hasten the action of the acid by heat. Since it is stated in the literature that chloric acid in water solution decomposes into chlorine and perchloric acid, water, and oxygen, when heated above 40°, it was deemed necessary to test the stability of the 2.5N acid at higher temperatures and this was done in the following way: A volume of 30 cc. of the acid of 2.5N strength was placed in a tube so arranged that pure air from a gas cylinder could be passed through the acid and then by a suitable exit tube into a flask containing potassium iodide. The tube was placed in a beaker of water, which could be heated. While a slow current of air was passed through the acid the temperature was slowly raised to the boiling-point of the water in the beaker, and the boiling was maintained for half an hour. At about 95° the solution of potassium iodide began to show a trace of color, due to separated iodine. At the end of the experiment the free iodine was titrated with N/10 thiosulphate and required 0.2 cc., which corresponds to 0.6 mg. of chlorine. The strength of the acid then remaining in the tube was found to be 2.65N, and on testing with silver it gave apparently only the usual slight opalescence. It seems clear, therefore, that one may heat even the strongest, pure chloric acid that is likely to be found in the market to temperatures near the boiling-point of water without fear of essential decomposition. It seems probable that the statement that chloric acid decomposes when heated above 40° might be due to that fact that the author used impure acid, containing possibly hydrochloric acid which would decompose the chloric acid, or that the statement refers to an acid of about the maximum concentration.

The methods of experiment were in general very simple. In some cases where no hydrogen was evolved, the flask or tube containing the weighed metal and measured acid was allowed to stand at room temperature. In cases where the solution was slow, the vessel was placed in water which was heated to 40° or 50°. The conditions are mentioned under the metals to which they apply. Save in two or three cases, no attempt was made to exclude the air for the two reasons, that at best the acid would contain some air, which could not with safety be expelled by heating, and that in two or three cases where the solution was carried on in an atmosphere of carbon dioxide the results were not noticeably different from those in the experiments carried out with the same metals in the presence of air. From time to time suitable means were applied to determine whether any chlorine was evolved or any hydrochloric acid was being lost. The tests were negative in every case save in one experiment in the solution of iron. By accident the temperature was allowed to reach 80° and some chlorine was evolved, and was detected by aspirating a current of air through the acid and into a solution of potassium iodide a starch. To determine the amount of reduction in any experiment the solution was made up to a known volume and portions of it were titrated with N/20 silver solution after the method of Volhard, to determine the hydrochloric acid, from which the amount of chloric acid reduced could be calculated.

ACTION OF CHLORIC ACID ON SODIUM AND POTASSIUM.

No information as to the action of chloric acid on potassium is known to me in the literature. Tommasi tried the action of sodium amalgam on the acid and stated that the acid is not reduced to the least extent. I have repeated the experiment of Tommasi,[1] using about 2 per cent. sodium amalgam freshly prepared from carefully cleaned sodium and the usual redistilled mercury. The method of experiment in this instance was to add the amalgam slowly to a measured volume of chloric acid, while the solution was kept cool. When nearly all the acid was neutralized the solution was poured off and together with the washings was acidified with nitric acid and titrated in the usual way. A blank experiment using water was made to test the freedom of the amalgam from traces of chlorine.

(1) 25 cc. 2N $HClO_3$ treated with 10 grams sodium amalgam required 1.4 cc. N/20 silver solution, corresponding to 0.0025 gram hydrochloric acid.

(2) 25 cc. 2N $HClO_3$ treated with a large excess of sodium amalgam required 6.85 N/20 silver solution, corresponding to 0.0125 gram hydrochloric acid.

Similar results were obtained with potassium, and the reduction was about twice that produced under similar conditions by sodium amalgam.

(1) 25 cc. 2N $HClO_3$ treated with about 10 grams of potassium amalgam required 2.9 cc. N/20 silver solution, corresponding to 0.0053 gram hydrochloric acid.

(2) 25 cc. N $HClO_3$ treated with 10 grams of potassium amalgam required 1.5 cc. N/20 silver solution, corresponding to 0.0027 gram hydrochloric acid.

From the results there seems to be no doubt that both sodium and potassium amalgam are capable of reducing chloric acid, though the amount of the reduction is very small. In using mercury and

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[1] *Instituto Lombardo* [2], 10, 799.

an alkali metal there is the possibility that the reduction may be caused by the mercury. In the presence of such a strongly electropositive metal as sodium, however, this does not seem probable. Moreover, on attempting to dissolve mercury in chloric acid it was found that after heating at 40° for four hours scarcely any reduction of the acid had taken place and the remaining mercury was collected, dried and weighed and corresponded within 4 mg. to the original amount taken. The smallest amount of hydrochloric acid found above corresponds to about 0.04 gram of mercury.

ACTION OF CHLORIC ACID ON MAGNESIUM.

Magnesium in the form of the ordinary ribbon of commerce was used. It was cleaned with emery paper and dissolved in an excess of normal chloric acid, 50 cc. of the acid being used in each case.

(1) 0.2918 gram of magnesium gave 0.0065 gram hydrochloric acid.

(2) 0.2170 gram of magnesium gave 0.0054 gram hydrochloric acid.

The results show in fact that about 1/20 of the magnesium was used in reducing the chloric acid. The remainder, of course, dissolved to form the chlorate with the evolution of approximately its equivalent of hydrogen. Since, as is well known, water containing salts in solution acts on magnesium with the evolution of hydrogen, it did not seem worth while to determine the amount of hydrogen produced in the solution of the metal.

ACTION OF CHLORIC ACID ON ZINC.

Concerning the action of chloric acid on zinc there are many statements in the literature and some contradictions. According to Gay-Lussac[1] and Berzelius[2] the acid dissolves zinc without decomposition and with the evolution of hydrogen; according to Vauquelin, Fordos and Gelis,[1] with the formation of hydrochloric acid, but without the evolution of hydrogen; according to Gmelin,[1] with both the reduction of the acid and the evolution of hydrogen. Tommasi[3] states that in one experiment zinc reduced 14 per cent. of the acid present in one hundred hours, and that the acid was

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[1] Gmelin's "Handbuch," Vol. I, p. 370.

[2] *J. Pharm.*, **4**, 346.

[3] *Instituto Lombardo* [2], **10**, 799.

completely reduced by an excess of zinc and sulphuric acid Though zinc has since been used as the reducing agent in the presence of sulphuric acid, in the determination of chlorates, there does not seem to be any record of later work on the action of the free acid and zinc, and none of any date with a view of determining quantitatively the nature of the reaction with reference to the relative amount of zinc that reduces the acid to that which sets hydrogen free.

In the following experiments and also in those with aluminum the reaction took place in a graduated tube filled nearly full of the acid. It was fitted with a delivery tube of small bore. The metal was supported above the acid upon a glass bulb, which could be lowered after the stopper was inserted, the objects being to prevent loss of hydrogen on the one hand and to place the metal near the middle of the mass of the acid, where the acid would have about its mean of concentration. The tube containing the acid was placed in a large beaker of water at room temperature. The zinc used was the so-called "strictly chemically pure" zinc, obtained from Eimer & Amend. It dissolved without leaving a visible residue. Other samples of zinc were tried, but the results obtained did not differ materially from those here given.

In experiments (1) and (2) 25 cc. of normal acid were used in each case. After the zinc was completely dissolved, the hydrochloric acid, resulting from the reduction of the chloric acid, was titrated in the usual way, and the hydrogen was reduced to the volumes under normal conditions, as given below. The calculation of the zinc to the hydrochloric acid, as given in the last column, is, of course, based upon the assumption that 1 molecule of chloric acid oxidizes 3 atoms of zinc, or that when the acid is reduced at all, it is completely reduced to hydrochloric acid, and the whole series of experiments support this view.

	Zinc dissolved.	H collected.	HCl found.	Zn to H.	Zn to HCl.
(1)....	0.4882	52.3	0.0627	0.1540	0.3362
(2)....	0.5412	65.3	0.0648	0.1921	0.3488

In the following experiments, (3), (4) and (5), the conditions were the same, save that the acid used was 2N.

(3)....	0.7442	14.8	0.1302	0.0435	0.7006
(4)....	0.7050	21.3	0.1203	0.0626	0.6476
(5)....	0.5532	12.4	0.0962	0.0365	0.5181

As may readily be seen, the amount of hydrogen set free is much smaller when the more concentrated acid is used and the amount of acid reduced is correspondingly greater. It is probably true that the temperature also has some influence, and this may account for the high hydrogen value in (4), which was done when the temperature of the room was unusually low. The effect of temperature will receive further attention.

ACTION OF CHLORIC ACID ON ALUMINUM.

Excepting the statement of Tommasi[1] that a solution of chloric acid, treated with aluminum, showed after six hours only a trace of hydrochloric acid, there seems to be nothing in the literature concerning the action of the acid on this metal. Aluminum slowly dissolves in cold dilute chloric acid, and whatever the concentration, hydrogen is given off and the acid is reduced, as in the case of the action of the acid on zinc.

For the following experiments the ordinary aluminum wire of commerce was used. An attempt was made to compare, as in the case of zinc, the action of the dilute acid on an excess of the metal with the action of an excess of the strong acid. In the former case, however, the metal dissolved as indicated by the loss of weight was always too small by about 5 per cent. to account for the hydrogen set free and the chloric acid reduced. Determinations of the actual amounts of metal in solution and in the residue showed that in very dilute acid the metal becomes coated with a layer of oxide, which accounts for the above-mentioned discrepancy. The ratio of the metal which replaced hydrogen to that which reduced the more dilute acid was found to be about 1 to 7, while in the experiments with the 2N acid below the ratio was about 1 to 5.

In the following experiments the aluminum was completely dissolved in 2N acid, the hydrogen was collected and reduced to normal conditions and the hydrochloric acid was titrated in the usual way.

	Al dissolved.	H collected.	HCl found.	Al to H.	Al to HCl.
(1)....	0.2435	47.8	0.1363	0.03876	0.2027
(2)....	0.2637	55.4	0.1486	0.04487	0.2210

In each experiment there was an insoluble residue of 0.7 mg.

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[1] *Loc. cit.*

ACTION OF CHLORIC ACID ON IRON.

The treatises of Graham-Otto and Dammer quote, apparently from very old but undesignated work, that zinc and iron dissolve in chloric acid with the evolution of hydrogen. Schiff[1] states, in his correspondence, that Pellagri found that iron reduces chlorates, and Tommasi[2] partially reduced copper chlorate with iron. There seem to be no other references to the action of iron on either free chloric acid or its salts.

Contrary to the statements mentioned, iron dissolves readily in dilute or strong chloric acid without the evolution of hydrogen or any other gas. In the following the purest, soft iron wire, such as is used in standardizing permanganate, was used. Even with two or three pieces of this large wire the action was so vigorous that a considerable rise in temperature was occasioned when 2N acid was used. The solution took place in glass-stoppered bottles standing in cold water. In several instances a brown coating was observed to form, which scaled off and was soon dissolved in the excess of acid. The iron goes directly into the ferric condition, and in no instance, even while the solution was going on, could ferrous iron be detected by the usual tests. The solution has the usual brown color characteristic of ferric salts, but remains perfectly clear so long as the acid is in excess. With a large excess of iron, oxides and probably basic salts, are precipitated. In one such case the amount of reduction of the chloric acid was found to be approximately 95 per cent. The very ready reduction of the acid by iron suggested to the writer a method for the determination of chloric acid and chlorates by reduction with iron in the presence of sulphuric acid and the titration of the hydrochloric acid formed.

In the solution of iron, if anywhere, one might expect the oxygen of the air to exert an influence upon the relation of the metal dissolved to the amount of acid reduced. In experiment (4) the solution was carried out in an atmosphere of carbon dioxide. A distilling flask containing the acid was supported so that the neck in which the weighed iron was placed was in a nearly horizontal position. When the air had been completely expelled by carbon dioxide, the neck was raised so that the iron

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[1] *Ber. d. chem. Ges.*, 8, 1356.

[2] *Loc. cit.*

fell into the acid. The results of this experiment do not indicate that the air has any appreciable influence. In the following experiments the iron in column (3) is, of course, calculated on the basis that it was all oxidized to the ferric condition. In all cases the amounts of iron thus calculated and added to the residues of carbon and silica, found in the respective experiments, are somewhat smaller than the corresponding amounts of iron weighed. I am not at present able to account for this small difference, and the subject will receive further attention. In (1) of the following experiments 35 cc. of normal acid were used at 40° and in the others 20 cc. of 2N acid were used in each case and the acid was kept at about room temperature.

	Iron weighed.	HCl found.	Iron calculated.	Residue.
(1).......	0.1609	0.0518	0.1592	0.0011
(2)........	0.2262	0.0699	0.2148	0.0046
(3)........	0.3010	0.0949	0.2916	0.0006
(4)........	0.3220	0.1023	0.3143	0.0014

ACTION OF CHLORIC ACID ON TIN.

The tin used was so-called pure tin, obtained from Schuchardt, and the solution took place in glass-stoppered bottles at room temperature. In the first experiment 25 cc. of the 2N acid were used and the solution occupied about thirty minutes. In the second case 50 cc. of normal acid were used and the action occupied several hours. Contrary to what might be expected, very little tin oxide or stannic acid remained. In each case the residue, which did not increase on long standing, weighed 0.0022 gram. The solution remained clear for a long time, even after it had been diluted preparatory to titration. As in the case of iron, no hydrogen was set free, and the tin went at once into the stannic condition, as shown by appropriate tests.

(1) 0.3084 gram of tin gave 0.0618 gram hydrochloric acid, corresponding to 0.3027 gram tin.

(2) 0.3572 gram tin gave 0.0721 gram hydrochloric acid, corresponding to 0.3531 gram tin.

ACTION OF CHLORIC ACID ON COPPER.

After the work on copper had been done, there came to my notice the communication of Brochet on the solvent action of chloric acid on copper, which appeared in *Comptes Rendus,* January 25th of this year.[1] His paper came into my hands after the next paragraph had been written. While granting to Brochet the priority in several particulars, since he gave no analytical data, I deem it best to submit, for record, the paragraph as originally written.

The action of chloric acid on copper offers no peculiarities. It is just what one in view of the foregoing would expect. The copper simply disappears, and this gives rise to a clear blue solution due to salts of copper. The copper used was in the form of bright wire gauze such as is commonly used in the combustion in organic analysis. The metal dissolves rapidly in 2N acid at 50°.

(1) 0.2778 gram copper gave 0.0528 gram hydrochloric acid, corresponding to 0.2766 copper.

(2) 0.5288 gram copper gave 0.1000 gram hydrochloric acid, corresponding to 0.5236 gram copper.

ACTION OF CHLORIC ACID ON CADMIUM.

The action of chloric acid on cadmium is in every way similar to its action on copper, it being one of simple oxidation and the solution of the oxide in the excess of acid, no gas being given off. Ordinary commercial cadmium was used. The acid was twice normal. In the first case the reaction went on at room temperature and in the second at 50°.

(1) 0.4732 gram cadmium gave 0.0520 gram hydrochloric acid, corresponding to 0.4810 gram cadmium.

(2) 0.4091 gram cadmium gave 0.0438 gram hydrochloric acid, corresponding to 0.4052 gram cadmium.

The action of chloric acid on certain other metals has been studied to some extent. It acts with exceeding slowness on mercury and antimony, even when at full strength and at 70°, and no attempt was made to determine the quantitative relationship. Nickel dissolves readily and apparently in quite the same way as copper and cadmium. Bismuth is rather slowly oxidized and only a small portion of the product goes into solution. In one experiment 0.3693 gram of bismuth gave 0.0282 gram hydrochloric acid, corresponding to 0.3624 gram bismuth. Finely divided arsenic readily dissolves in 2N $HClO_3$, forming arsenic acid, though, as Gooch and Blake[2] found, chloric acid in dilute solution is scarcely reduced by As_2O_3.

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[1] See also *Bull. Soc. Chim.*, **31**, 257.

[2] *Ztschr. anorg. Chem.*, **33**, 104.

In a recent communication on silver as a reducing agent it was shown that silver reduces chloric and iodic acid directly to hydrochloric and hydriodic acids, and according to the equation as there given for chloric acid.

$$6Ag + 6HClO_3 = 5AgClO_3 + AgCl + 3H_2O.$$[1]

The same general reaction has since been found to hold true in the case of bromic acid and silver. There was no evidence in any case of the formation of any intermediate product in the reduction of the acid, but in each case the reduction ran smoothly, as above represented. Omitting the matter of the evolution of hydrogen, the same reaction holds true in general of the action of chloric acid on other metals. In no case when the temperature has been kept moderately low has there been evidence of the formation of a lower acid, an oxide of chlorine or free chlorine. Except in the case of iron, where the question of impurity is uncertain, the amount of metal dissolved has been accounted for by the amount of reduction of the acid, or the reduction and the hydrogen set free. It is possible that some irregularity in the reaction took place in the case of iron and in other instances, even though it was not detected. Since chloric acid is almost as highly dissociated as hydrochloric acid, it must be that a large portion of the hydrochloric acid formed by the reduction exists in the solution in the free condition, and it might be expected that the two acids would act upon each other according to some one of their known reactions. If such action occurs, its extent must evidently be quite small.

There is yet a persistent tendency, as shown in chemical literature, to regard the reduction of an acid in its action on a metal, as in the case of the action of hot sulphuric acid on copper, as due to the nascent hydrogen first set free. Thus,

$$Cu + H_2SO_4 = H_2 + CuSO_4,$$

$$H_2 + H_2SO_4 = 2H_2O + SO_2.$$

In the case of chloric acid, however, we have all varieties of reaction, from that of the action of the acid on sodium and potassium, where nearly the full equivalent of the hydrogen is set free and the reduction of the acid is extremely small, to that of the action of the same acid on iron, tin and copper, in which no

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[1] Hendrixson : This Journal, **25**, 637.

hydrogen is set free and nearly, or quite, the full equivalent of the metal appears in the amount of reduced acid. It would seem, therefore, since the temperature is practically the same in all cases, as well as the concentration of the acid, that the reduction cannot be accounted for on the basis of nascent hydrogen. In each case it seems to be rather a mere question of the tendency of the metal, under the conditions, to oxidize at the expense of the oxygen of the acid, or, to go into solution at the expense of the hydrogen which is set free. In the cases of iron, tin and bismuth it seems evident to the eye that oxides are first formed, and in all cases where reduction occurs the view is simplest and most nearly in accord with the facts, that the metal is oxidized and that the oxide dissolves in the excess of the acid or remains insoluble, as in the case of bismuth.

Work is now in progress on the action of chloric acid on arsenic and it will be extended to other metals.

IOWA COLLEGE, GRINNELL, IOWA,
May 11, 1904.

SOME COMPOUNDS OF CHROMIC CHLORIDE WITH SUBSTITUTED AMMONIAS.

BY W. R. LANG AND C. M. CARSON.

Received April 18, 1904.

IT HAS already been shown that dry liquid ammonia forms with violet chromic chloride a pink powder which, when extracted with water, gives crystalline compounds containing 12, 10 and 8 molecules of ammonia respectively.[1] In addition to this, compounds with methylamine were also obtained and described in a previous paper.[2] The authors have made a series of experiments with other substituted ammonias, the results of which are as follows:

(1) *Ethylamine*, $C_2H_5NH_2$, acts on the chloride with great energy at temperatures between 0° and 18°, producing a dark red powder. On extracting this compound with water and evaporating carefully, red crystals are obtained which, on analysis, give:

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[1] Lang and Carson: This Journal, April, 1904, pp. 414-417.

[2] Lang and Jolliffe: *Ibid.*, p. 417.