colored residue which gave on analysis 18.7 per cent. nitrogen, 36.8 per cent. zinc and 44.7 per cent. potassium. Another specimen heated to 300° for a considerable time lost 11.6 per cent. ammonia and gave a residue containing 18.8 per cent. nitrogen. The evolution of one and a half molecules of ammonia from $Zn(NHK)_2.2NH_3$ would require a loss of 12.3 per cent. in weight, while a compound of the composition $Zn(NHK)_2.\frac{1}{2}NH_3$, would contain 19.2 per cent. nitrogen, 35.8 per cent. zinc and 43.1 per cent. potassium. As the temperature is raised ammonia mixed with permanent gases is given off and at the same time rings of metallic potassium and zinc are deposited in the cooler end of the tube. When a third specimen was heated to 325° for many hours it lost 14.8 per cent. of its weight, apparently showing that even at this temperature all the ammonia of crystallization is not driven off. On emptying the tubes after heating these preparations to 250° and higher, the glass walls of the tubes were found to be much attacked by the melted salt, a fact which accounts for the divergent analytical results and at the same time discouraged any further attempts to obtain a definite compound by the elimination of ammonia from the compound, $Zn(NHK)_2.2NH_3$. In one experiment a tube lined with platinum was used in the hope that definite results might thus be obtained, but it was found that the melted salt also attacked this metal. It should be pointed out, however, that the results obtained point to the probable existence of a compound of the formula, $Zn(NHK)_2.\frac{1}{2}NH_3$.

Summary.

It is shown by the work described above that a potassium ammono-zincate, an ammonia analogue of the hypothetical water salt, potassium zincate, is obtained in the form of a definite, well crystallized compound by the action of a liquid ammonia solution of potassium amide, first, on metallic zinc, second, on zinc amide, and third, on zinc iodide, in accordance with the following respective equations :

1. $Zn + 2KNH_2 + Am. = Zn(NHK)_2.2NH_3 + H_2,$
2. $Zn(NH_2)_2 + 2KNH_2 = Zn(NHK)_2.2NH_3,$
3. $ZnI_2.4NH_3 + 4KNH_2 = Zn(NHK)_2.2NH_3 + 2KI + Am.$

STANFORD UNIVERSITY.
California, June, 1907.

THE ACTION OF HYDROCHLORIC ACID ON MANGANESE DIOXIDE.

(Preliminary Paper.)

BY WILLIS B. HOLMES.
Received June 11, 1907.

A great deal of work has been done upon the interaction of hydrochloric acid and manganese dioxide. Although the bulk of experimental

evidence seems to point to the probable formation of the trichloride and tetrachloride of manganese, a final decision in this case has not yet been reached.   None of the intermediate products of the reaction have ever been isolated and the experimental work bearing upon this subject is of an indirect nature.   Two general methods of attacking this problem have been in vogue ; the treatment of manganese dioxide with an etheral solution or with an aqueous solution of hydrogen chloride and the subsequent analyses of the solutions thus obtained.   The former method excludes the presence of water, except such as is formed by the reaction itself, while the latter method introduces it.

Manganese Dioxide Treated with an Ethereal Solution of Hydrogen Chloride.—Nicklès' treated manganese dioxide with an ethereal solution of hydrogen chloride and obtained a dark green solution, the color of which on further dilution with ether, changed to a deep violet.   On saturating this solution with hydrogen chloride he obtained a green oil which he claimed contained manganese tetrachloride.   One analysis gave results for

$$MnCl_4.12 \ (C_2H_5)_2O.2H_2O.$$
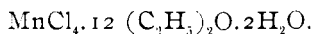
Nicklès' results, however, are not conclusive.

Christiansen[2] suspended manganese dioxide in ether, saturated the ether with chlorine and obtained a violet solution.   By decanting this violet solution he obtained a black residue[3] which also partly dissolved in ether and gave the same violet color to the solution.   He then treated manganese dioxide with ether which had been saturated with hydrogen chloride and obtained a green solution.   He considered that the violet solution and the green solution both contained the same dissolved substance, the difference in color being due to the presence of water in the former case.   For analysis a portion of the green solution was run into a solution of potassium iodine and the liberated iodide titrated with a solution of sodium thiosulphate.   From these results the available chlorine[4] was estimated.   The total manganese in this solution was then determined.   The average ratio of total manganese to available chlorine from seven analyses was 1 : 1.06.   He thus concluded that manganese trichloride was formed in both cases.   By working at a temperature of about—10° he obtained a higher ratio—approximately 1 : 1.5—and thought that the tetrachloride might be formed at lower temperatures.

Franke[5] repeated Christiansen's work and obtained the same ratio of

[1] Ann. Chem. (4), **5**, 161.

[2] J. pr. Chem,, **34**, 41, and **35**, 57.

[3] This residue is of interest, as it probubly contained some manganese trichloride.

[4] The term, available chlorine, refers to the chlorine in excess of that required for manganous chloride.

[5] J. pr. Chem., **36**, 31 and 451.

manganese to available chlorine, approximately 1 : 1, but interpreted the results differently. He thought that hydrogen chloride, instead of water, caused the difference between the blue and green solutions; that the green solution with the excess of hydrogen chloride contained chloromanganic acid, while the violet solution contained manganese tetrachloride. Manganous chloride was always present as a decomposition product, and united with the chloromanganic acid forming manganous chloromanganate

$$MnO_2 + 6HCl \longrightarrow H_2MnCl_6 + 2H_2O.$$
$$MnCl_2 + H_2MnCl_6 \longrightarrow MnMnCl_6 + 2HCl.$$
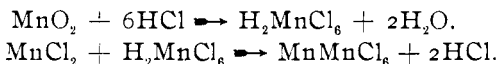
The green solution on further dilution with ether separated into manganous chloride and manganese tetrachloride, the violet color becoming evident as the tetrachloride was extracted. The ratio 1 : 1 was thus interpreted. His analysis of the violet solution gave the ratio of total manganese to available chlorine from 1 : 1.68 to 1 : 2.35. This ratio indicated the presence of the tetrachloride. The violet solution treated with a little water gave a precipitate of hydrated manganese dioxide.
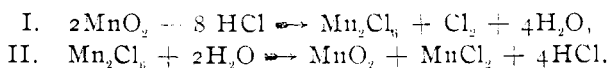
Manganese Dioxide Treated with an Aqueous Solution of Hydrogen Chloride.—Fisher[1] treated manganese dioxide with strong hydrochloric acid in the proportion of one part of the dioxide to ten parts of the acid. The resultant solution was filtered through spun glass and run into a burette. A known volume was then delivered into a solution of potassium iodide and the iodine titrated in the usual way. An equal volume was then run into a solution of sodium acetate and the precipitated manganese was separated, ignited and weighed as mangano manganic oxide. The filtrate was then treated with potassium iodide and the free chlorine estimated. This, subtracted from the result in the first solution, gave the available chlorine. The ratio of precipitated manganese to available chlorine was approximately 1 : 2, and hence the conclusion that the tetrachloride was formed. He assumed that the precipitated manganese was entirely a hydrated dioxide and that the tetrachloride, in the presence of hydrochloric acid, existed in a form analagous to chloroplatinic acid.

Pickering[2] repeated Fisher's work and obtained different results. His general method of procedure was the same, except that he used water instead of a solution of sodium acetate, and analyzed his precipitated manganese by a method whereby he could estimate not only the total manganese, but also the amount of dioxide which it contained. His results showed that the precipitated manganese was not entirely a dioxide but a mixture of different oxides; that the ratio of total manganese to available chlorine was nearly 1 : 1.64, and that the ratio of manganese

[1] J. Chem. Soc., 33, 409.
[2] J. Chem. Soc., 35, 654.

dioxide to available chlorine was 1:2. He concluded that the reaction took place as follows : —

$$\text{I.} \quad 2MnO_2 + 8\,HCl \longrightarrow Mn_2Cl_6 + Cl_2 + 4H_2O,$$
$$\text{II.} \quad Mn_2Cl_6 + 2H_2O \longrightarrow MnO_2 + MnCl_2 + 4HCl.$$

because he was never able to obtain more than half of the manganese as a precipitate. If equation II was correct then the amount of precipitated manganese should increase if the experiment was performed in the presence of manganous chloride, whereas the amount should remain stationary if the tetrachloride was formed. The amount of precipitated manganese did increase when manganous chloride was added to the solution, which indicated the presence of the trichloride. The effect of temperature upon the amount of manganese precipitated also indicated the formation of the trichloride. If the substance was a tetrachloride, at low temperatures, 100 per cent. should be precipitated, and in the case of the trichloride only 50 per cent. At 60°, less than 10 per cent. was precipitated, and at low temperatures the amount approached 50 per cent.

Vernon[1] studied the action of hydrochloric acid on manganese dioxide by estimating, at various temperatures, the rate of evolution of chlorine. If Pickering's view is correct,

$$2MnO_2 + 8HCl \longrightarrow Mn_2Cl_6 + Cl_2 + 4H_2O,$$
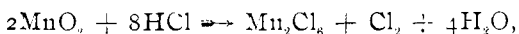
then half of the available chlorine ought to be evolved very rapidly. This was not found to be the case, especially at low temperatures. From the result of his experimental work, Vernon concluded that manganese tetrachloride is always the first product formed when manganese dioxide is dissolved in hydrochloric acid.

Wacher[2] dissolved manganese dioxide in concentrated hydrochloric acid and obtained a brown solution which, on dilution with water, gave a precipitate of hydrated manganese dioxide. He then passed chlorine into a solution of manganous chloride in concentrated hydrochloric acid, and obtained a similar brown solution. This solution also gave a precipitate of hydrated manganese dioxide when diluted with water. From these results he concluded that the tetrachloride of manganese was formed, but gave no experimental evidence to show that the precipitate was entirely hydrated manganese dioxide.

Double Salts.—Numerous double chlorides containing manganese trichloride and tetrachloride have been isolated. Rice[3] and Newman[4] obtained the double chlorides $2KCl.MnCl_3$ and $2NH_4.MnCl_3$. Meyer and Best[5] obtained similar double salts with quinoline and pyridine hydro-

[1] Phil. Mag., **81**, 469, and Chem. News, **61**, 203.

[2] Chem.-Ztg., **24**, 285.

[3] J. Chem. Soc., **73**, 258.

[4] Monatsh., **15**, 489.

[5] Z. anorg. Chem., **22**, 169.

chloride $MnCl_3.2C_9H_7NHCl$ and $MnCl_3.2C_5H_5NHCl$. They also obtained the double chlorides, $2C_5Cl.MnCl_3$, $MnCl_4.2KCl$ and $MnCl_4.MnCl_3.5KCl$. Reitzenstein[1] obtained a dipyridine manganese tetrachloride.

Experimental Part.

Previous failures to isolate the intermediate products of the interaction of hydrochloric acid and manganese dioxide probably depend upon the fact that such products are decomposed by water and heat. The reaction itself liberates water, but it seemed possible by reducing the amount of water to a minimum and at the same time keeping the temperature low, to obtain some information concerning the nature of the products formed. This proved to be the case.

The method of treating manganese dioxide with a solution of hydrogen chloride in absolute ether was not found practical. While the ratio of precipitated manganese to available chlorine could be determined from such a solution, the total chlorine could not be estimated, as it was impossible to get rid of the excess of hydrogen chloride. Attempts to precipitate the product soluble in the ethereal solution by adding a large excess of carbon disulphide or toluene, proved unavailing. A green oily liquid could be obtained, but it was impossible to do anything with it. Some medium was then sought for which would not dissolve any of the compounds of manganese formed and at the same time would dissolve hydrogen chloride and not be affected by it, or by any of the decomposition products of the reaction. Carbon tetrachloride seemed to fulfill the necessary conditions and was used throughout for the preparation of material.

The following method of procedure was followed. Five grams of precipitated manganese dioxide was mixed with 200 cc. of carbon tetrachloride and put in a long necked 500 cc. vacuum flask. This flask was then inserted in a shaking machine. The shaking machine was made of a board 40 x 15 cm., with a hole in the middle for the insertion of the neck of the flask and supported at each end by a 30 cm. upright. The neck of the flask was held in place by a perforated rubber stopper. A short shank extending from the side of the board was connected with an eccentric on a wheel run by a small motor. This gave a lateral motion to the flask, which was inserted in a pneumatic trough filled with finely ground ice and water. The shaking served the double purpose of keeping the flask and its contents cold and of agitating the mixture. Dry hydrogen chloride was then bubbled through the carbon tetrachloride. As water was formed during the reaction, no extreme precautions were taken to dry the gas, although it was passed through several towers filled with beads and sulphuric acid. Hydrogen chloride is not extremely soluble in carbon tetrachloride, so the gas was allowed to bubble through

[1] Z. anorg. Chem., 18, 290.

for an hour and a half. The reaction was then practically complete and the solid residue in the flask was separated by filtration.

The filtrate of carbon tetrachloride gave no test for manganese, but was colored yellow from the dissolved chlorine. A large amount of chlorine was always formed, and could even be detected in the wash bottle used to absorb the unused hydrogen chloride.

The solid residue consisted of a greenish black substance, which on standing slowly decomposed with the evolution of chlorine and hydrogen chloride. When it was dried in a dessicator with potassium hydroxide and sulphuric acid, decomposition set in and a substance of a reddish brown color remained ; but when dried quickly by means of filter paper and warmed, it gave off chlorine and hydrogen chloride. A little put in a large amount of water gave an immediate precipitate, probably hydrated manganese dioxide. Treated with absolute ether, it gave a solution of an intense violet color. On standing, this solution gradually lost its violet color and manganous chloride separated out ; but if kept cold the solution retained its color from twelve to forty-eight hours. If hydrogen chloride was passed into this violet solution, it turned green. On continued washing of the original residue with ether the compound which imparted the violet color was entirely dissolved out and a reddish brown residue remained. This substance which dissolved in ether with the formation of a violet solution proved to be manganese trichloride.

The reddish brown residue was much more stable than the original residue. It could be kept in a dessicator for a long time without undergoing any appreciable decomposition, but decomposed immediately on exposure to moist air. When warmed it gave off chlorine and left a residue of manganous chloride. It dissolved in absolute alcohol forming a solution of a deep wine color which slowly decolorized on standing. This substance proved to be manganese tetrachloride. About one-half of the original residue was manganese trichloride. the remainder being a mixture of manganous chloride and manganese tetrachloride.

Manganese Trichloride.—The analysis of this substance offered many difficulties. The solid could not be prepared in a condition pure enough for analysis. Attempts to obtain the trichloride from the ethereal solution by evaporating the ether by means of a current of dry cold air proved unavailing, as decomposition always set in. The analysis of the ethereal solution was then attempted. In preparing this solution for analysis the utmost care was necessary. It was very difficult to remove the last traces of hydrogen chloride, and all reagents used had to be anhydrous and kept at a low temperature. The work had to be performed as expeditiously as possible, and a dilute solution used in order to prevent decomposition.

The residue of mixed chlorides from the flask was first washed with

a large amount of carbon tetrachloride. This removed part of the hydrogen chloride. It was next washed with carbon disulphide to remove the carbon tetrachloride, and then transferred to a flask containing carbon disulphide, to which a little ether had been added, and shaken. This treatment seemed to be the most effective method of removing the last traces of the hydrogen chloride, and was repeated a second time. The residue was then transferred to a funnel and washed with ether, which had been cooled with solid carbon dioxide, until about two-thirds of the trichloride had been removed. The filter paper and residue were then put in a special funnel connected with a liter filtering flask. The funnel was surrounded with a jacket so that it could be kept cold by means of ether and solid carbon dioxide. The flask held 250 cc. of ether and was placed in a mixture of ice and salt. The residue was then washed with about 100 cc. of the cold ether, and this solution, diluted with the ether in the flask, was used for analysis.

In the analysis, three quantities were estimated; the available chlorine, the total chlorine, and the total manganese. In certain cases the precipitated manganese was also obtained. A 50 cc. pipette, protected by a drying tube, was used to run off equal portions of the solution into six receptacles. The first four consisted of liter filtering flasks fitted with rubber stoppers and carrying glass tubes large enough for the insertion of the pipette. One and two each contained about 300 cc. of a dilute solution of potassium iodide, and were used to estimate the available chlorine. Three and four each contained about 300 cc. of a dilute solution of silver nitrate to which a little nitric acid had been added, and were used to estimate the total chlorine. The arms of the flasks were connected with U tubes containing the same solutions, and these in turn were connected with an aspirator. Air was aspirated through each flask during the filling. The contents of the tubes were afterwards added to the flasks. Five and six were beakers each containing about 200 cc. of water, and were used to determine the total manganese.

The iodine was titrated with a 1/10 normal solution of sodium thiosulphate, and from the results obtained the available chlorine was estimated. The silver chloride was determined by the regular crucible method and the total chlorine estimated. Only a part of the manganese was precipitated, so ammonium hydroxide and bromine water were added to the solution to precipitate all the manganese. The precipitate was then filtered, washed, ignited in a Rose crucible and weighed as mangano-manganic oxide. It was then converted into manganous sulphide and weighed again. When the quantity of manganese was very small, the oxide and sulphide methods gave identical results, but with

larger amounts there was a slight variation. The sulphide results were used throughout as being the more reliable.

Analysis I.—This analysis was a preliminary one performed to get some idea of the ratio between the available chlorine and the total chlorine. It gave results as follows :—

Available chlorine.	Total chlorine.
0.0198 g.	0.0618 g.
0.0198 g.	

Ratio of available chlorine to total chlorine, 1 : 3.12

Analysis II.—This analysis was performed before it was realized that the manganese trichloride retained some hydrogen chloride. The results are inserted, however, as they give an indication of the amount of hydrogen chloride retained. The residue was only washed with enough carbon disulphide to insure the complete removal of the carbon tetrachloride and the ethereal solution was then prepared. This washing removed some of the hydrogen chloride, but enough remained to give an indication of the probable amount retained. Two additional portions of the ethereal solution were run into two beakers, each containing 300 cc. of water, and the filtrates were examined as follows : the first was tested for free chlorine with a negative result, and the second for manganese which had not been precipitated.

Available chlorine.	Total chlorine.	Total Manganese	Manganese in filtrate.
0.0212 g.	0.0758 g.	0.0346 g.	
0.0212 g.	0.0757 g.	0.0343 g.	0.0168 g.

0 0344 g. of manganese requires 0.0665 g. chlorine for the trichloride. Excess of chlorine 0.0093 g., equivalent to 0 0096 g. HCl. 0.1009 g. $MnCl_2$ requires 0.0228 g. HCl for the double chloride $MnCl_2HCl$. The above results suggest the double chloride $2MnCl_2.HCl$, but are indicative only and need further confirmation. The ratio of available chlorine to the calculated total chlorine is 1 : 3.13.

Analysis III.—The solution for this analysis was made with all possible precautions, but was a little too concentrated and a slight decomposition was observed. Two additional portions of the ethereal solution were used to determine the ratio between the precipitated manganese and the manganese in the filtrate. These portions were each run into 500 cc. of water and immediately filtered.

Available chlorine.	Total chlorine.	Total manganese.	Precipitated manganese.	Manganese in filtrate.
0.0209 g.	0 0684 g.	0.0348 g.	0.0167 g.	0.0183 g.
0.0209 g.	0.0684 g.	0.0346 g.	0.0167 g.	0.0179 g.

Theoretical ratio, $\dfrac{Mn}{Cl_3} = 0.517$.   Found 0.507.

0.0347 g. of manganese should require 0.0671 g. of chlorine for the trichloride.

Ratio of available chlorine to total chlorine, 1 : 3.27.

Ratio of precipitated manganese to manganese in the filtrate 1 : 1.08.

Analysis IV.—This analysis was made to determine the ratio between the total manganese and the total chlorine. Precautions were taken to wash the residue very carefully, and use a very dilute solution to insure a minimum of decomposition.

Total chlorine.	Total manganese.
0.0519 g.	0.0164 g.
0.0320 g.	0.0165 g.

Theoretical ratio, $\dfrac{Mn}{Cl_3} = 0.517$. Found 0.515.

Properties of the Trichloride:—Manganese trichloride is a solid, almost black in color, with a slight greenish tinge. Heat breaks it up with the evolution of chlorine, and it is immediately decomposed by water. Absolute ether is the best solvent yet found for the trichloride. When allowed to stand in a desiccator it decomposes into manganous chloride and manganese tetrachloride. All samples thus treated gave the reddish brown substance characteristic of the tetrachloride. The trichloride dissolves in absolute alcohol, giving a wine colored solution which answered all tests for the tetrachloride. A small amount of this wine colored solution treated with a large amount of absolute ether and kept cold soon assumed the violet color characteristic of the trichloride. It is thus possible to pass from one chloride to the other and back again. This, together with the fact that only half of the manganese is precipitated when the ethereal solution is run into water indicates that the breaking down of the trichloride takes place in two stages as Pickering[1] observed.

I. $Mn_2Cl_6 \rightleftharpoons MnCl_2 + MnCl_4$.

II. $MnCl_4 + 2H_2O \rightleftharpoons MnO_2 + 4HCl$.
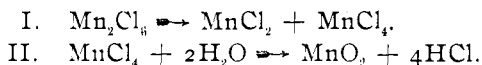
The composition of the precipitate has not yet been determined. This will be done, however, when the quantitative study of this reaction is taken up.

Manganese Tetrachloride.—The tetrachloride was prepared by treating manganese dioxide, suspended in carbon tetrachloride, with hydrogen chloride. The same method of procedure as was used in preparing the trichloride was followed, and the same precautions observed. The residue was washed with absolute ether to remove the trichloride. Persistent washing with ether failed to remove the last traces of the trichloride, so the residue was dried by means of filter paper and put in a desiccator to allow the remaining trichloride to decompose. This failure to remove the last traces of the trichloride was probably due to the slight decomposition of the tetrachloride when some halogen absorbent was present. Samples of the tetrachloride when first suspended in ether gave no coloration, but the ether soon assumed the violet color of the trichloride. Attempts to prepare pure manganese tetrachloride by the above method

[1] J. Chem. Soc., **35**, 654.

proved unavailing, as manganous chloride was always formed.   Absolute alcohol was the only solvent found in which the tetrachloride was soluble, and such a solution was analyzed.   Manganese chloride is soluble in absolute alcohol, so the amount present had also to be determined.

The solution for analysis was prepared in the following way : The residue after standing in the desiccator was transferred to the funnel of the special filtering flask previously described.   The funnel was kept cold by means of ether and solid carbon dioxide.   The flask held 250 cc. of absolute alcohol, and was surrounded with a mixture of ice and salt. About 100 cc. of absolute alcohol, which had been cooled with solid carbon dioxide, was then filtered through this funnel.   Four portions of the resultant solution were then pipetted off, and run into the same flasks as were used with the trichloride for the estimation of available and total chlorine.   Two additional portions were run into two beakers, each holding 500 cc. of water and the precipitated manganese then determined. This result gave the amount of manganese contained in the tetrachloride. The filtrate contained manganous chloride and this manganese was then precipitated and estimated.   The sum of the two gave the total manganese.   In the analysis one precaution had to be observed.   The precipitated manganese dioxide and alcohol interact unless the precipitation is made in a large volume of water and the filtration performed immediately.

Analysis I.—In this analysis the manganese was precipitated in 300 cc. of water, and the filtration was delayed for a short time.   The results consequently are a little irregular.

	Found.	Calculated.
Available chlorine	0.0192 g.	. . . . . .
	0.0192 g.	. . . . . .
Total chlorine	0.0872 g.	0.0874 g.
	0.0874 g.	0.0850 g.
Chlorine in $MnCl_4$	. . . . . .	0.0428 g.
	. . . . . .	0.0389 g.
Chlorine in $MnCl_2$	. . . . . .	0.0446 g.
	. . . . . .	0.0461 g.
Precipitated manganese	0.0164 g.	. . . . . .
	0.0151 g.	. . . . . .
Manganese in $MnCl_2$	0 0346 g.	. . . . . .
	0.0358 g.	. . . . . .
Total manganese	0.0510 g.	. . . . . .
	0.0509 g.	. . . . . .

$$\frac{\text{Available chlorine}}{\text{Total chlorine}} = \frac{0.0192}{0.0408} = 0.470$$

$$\frac{\text{Precipitated manganese}}{\text{Chlorine in } MnCl_4} = \frac{0.0157}{0.0408} = 0.385. \qquad \text{Theory, 0.387.}$$

Analysis II.—In this analysis the manganese was precipitated in 500 cc. of water and the filtration performed immediately.

	Found.	Calculated.
Available chlorine	0.0059 g.	......
	0.0060 g.	......
Total chlorine	0.0442 g.	0.0440 g.
	0.0442 g.	0.0443 g.
Chlorine in $MnCl_4$	......	0.0140 g.
	......	0.0140 g.
Chlorine in $MnCl_2$	......	0.0300 g.
	......	0.0303 g.
Precipitated manganese	0.0054 g.	......
	0.0054 g.	......
Manganese in $MnCl_2$	0.0233 g.	......
	0.0235 g.	......
Total manganese	0.0287 g.	......
	0.0289 g.	......

$$\frac{\text{Available chlorine}}{\text{Total chlorine}} = \frac{0.0060}{0.0140} = 0.429$$

$$\frac{\text{Precipitated manganese}}{\text{Chlorine in } MnCl_4} = \frac{0.0054}{0.0140} = 0.386. \quad \text{Theory, } 0.387.$$

Properties of the Tetrachloride.—This chloride is a solid of reddish brown color, stable at ordinary temperature, if kept dry, but it quickly decomposes on exposure to moist air. Samples have been kept for several weeks in a desiccator without undergoing appreciable decomposition. But in a large amount of water the tetrachloride gives an immediate precipitate, probably hydrated manganese dioxide. Heated to 100° it gives off chlorine, and a residue of manganous chloride remains. When the tetrachloride is suspended in ether and kept cold it slowly decomposes into the trichloride, imparting the characteristic violet color to the solution. If an excess of alcohol is added to this solution, some tetrachloride is again formed. Suspended in ether with mercurous chloride it decomposes more rapidly, but all the ordinary reducing agents such as can be used in a solution nearly anhydrous cause immediate decomposition without the intermediate stage. Absolute alcohol seems to be the only solvent which will dissolve the tetrachloride without rapid decomposition. If the alcohol contains a little water the solution is decolorized more quickly.

Summary.

1. When manganese dioxide, suspended in carbon tetrachloride, is acted upon by hydrogen chloride, manganese trichloride and manganese tetrachloride are formed.

2. Manganese trichloride has been isolated and its properties described.

3. When an ethereal solution of manganese trichloride is mixed with a large volume of water only half of the manganese is precipitated.

4. Manganese tetrachloride has been isolated and its properties described.

5. When an alcoholic solution of manganese tetrachloride is diluted with a large volume of water, all the manganese is precipitated.

6.   Manganese tetrachloride is probably the first product formed when manganese dioxide and hydrochloric acid interact.

ON THE NON-EXISTENCE OF β-CADMIUM IODIDE.

By J. F. SNELL.

Among the specific gravities determined by Bödeker and published in his monograph, "Die Beziehungen zwischen Dichte und Zusammensetzungen bei festen und liquiden Stoffen" (Leipzig, 1860), that of cadmium iodide was given as 4.576. Fullerton having obtained a much higher result in this laboratory. F. W. Clarke and E. A. Kebler[1] in 1883 (also in this laboratory) determined the densities of specimens of the salt prepared by a number of different methods. Portions prepared (a) by union of the elements in presence of water (b) by action of potassium iodide on cadmium sulphate with recrystallization from alcohol and (c) by action of hydriodic acid on cadmium carbonate (without removal of the free iodine present in the acid) gave results varying between 5.61 and 5.73 at temperatures of 10.5° to 18.2°; a slightly impure specimen prepared by heating equivalent quantities of the elements in an evacuated sealed tube gave 5.54 at 20°, a practically identical result. But portions prepared by the action of hydriodic acid on metallic cadmium and by the action of hydriodic acid on cadmium carbonate with the addition of metallic cadmium to remove the coloration due to free iodine had specific gravities of only 4.60 to 4.69 at 14.0° to 19.0°—results almost as low as Bödeker's. From these results Clarke and Kebler inferred the existence of two forms of cadmium iodide, the common or α-form and the form of low specific gravity, which they designated β-cadmium iodide. They pointed out that an extraordinary expansion is represented in the formation of cadmium iodide of sp. gr. 4.63 (mean of all measurements), either from the α-salt or from the elements, the respective molecular volumes being : β-salt 79.2, α-salt 64.8, mean of elements 64.3.

The present investigation was undertaken with the object of determining more precisely the conditions of formation of β-cadmium iodide and of studying the relation of this substance to the α-salt. The latter question presented some interest, since there was, on the one hand, the possibility of a dimorphism, similar to that of mercuric iodide and, on the other hand, a possibility of the one salt's being a polymer of the other, Hittorf's classical work on migration ratios having afforded evidence of the polymerization of cadmium iodide in aqueous and alcoholic solutions. The

[1] Am. Ch. J., 5, 255 (1883).