

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

THE ATOMIC WEIGHT OF TANTALUM.

[SECOND PAPER.]¹

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No very satisfactory agreement or concordance has been obtained in the investigations which have been carried out for the determination of the atomic weight of tantalum. In 1906 Hinrichsen and Sahlborn² published five determinations of the ratio $2\text{Ta} : \text{Ta}_2\text{O}_5$, but with a variation amounting to more than a unit in the atomic weight. Yet, these determinations, without doubt, were the most accurate up to that time. In 1910, Balke³ published a series of eight determinations of the ratio $2\text{TaCl}_5 : \text{Ta}_2\text{O}_5$, in which he obtained an average of 181.5 ± 0.098 for the constant, and in the following year Chapin and Smith,⁴ in a series of eight determinations of the ratio $2\text{TaBr}_5 : \text{Ta}_2\text{O}_5$, obtained 181.8 ± 0.199 .

Since both Balke, and Chapin and Smith must have had a very pure salt, and since its conversion to the oxide is attended with very little manipulation, it would seem that the principle involved is at fault. The object of this investigation, therefore, was to study the ratios $2\text{TaCl}_5 : \text{Ta}_2\text{O}_5$ and $\text{TaCl}_5 : 5\text{Ag}$, with respect to their values for the determination of the atomic weight of tantalum, as well as to establish a more accurate value of the constant if possible.

Preparation of Materials.

Chlorine.—The chlorine used throughout this investigation was prepared by allowing hydrochloric acid to drip upon potassium permanganate contained in a large flask. The acid used was prepared by distilling the constant boiling mixture from a large Jena retort. Small quantities of potassium permanganate were put in during the first part of the distillation, and the first portions of the distillate were rejected. The chlorine was passed through three towers filled with glass beads. In the first tower the beads were kept moist with water, while in the other two concentrated sulfuric acid was allowed to drip from time to time. To remove the last traces of moisture, the chlorine was finally passed through a tube about a half meter long, containing glass wool interspersed with phosphorus pentoxide. With the exception of two ground-glass joints at the generator, all the apparatus employed for the

¹ The work described in this paper furnished the basis for a thesis by Mr. Sears presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Illinois.

² *Ber.*, **39**, 2600 (1906).

³ *THIS JOURNAL*, **32**, 1127 (1910).

⁴ *Ibid.*, **33**, 1497 (1911).

preparation or use of chlorine or hydrogen chloride throughout this investigation was made continuous.

In order to make sure the chlorine would not be contaminated by the phosphorus pentoxide, the gas was passed for several hours through the above drying train into water, which was subsequently found to give no test for phosphorus.

Sulfur Monochloride.—This compound was prepared by passing a stream of chlorine over molten sulfur, which had been twice recrystallized from freshly distilled carbon disulfide. The apparatus was constructed in such a way that the sulfur monochloride could be redistilled directly from the receiver. The first portions of the distillate were rejected, and the final product distilled directly into sealing bottles through which a current of dry, filtered air had been passed to remove all traces of moisture.

Nitric Acid.—The nitric acid used was distilled from a quartz distilling flask, the middle third being collected in a quartz receiver and retained for use.

Water.—The ordinary distilled water was redistilled, after the addition of alkaline permanganate, from the still used in this laboratory for conductivity water.

Sodium Chloride.—Chemically pure sodium chloride was dissolved in water, filtered, precipitated three times with hydrogen chloride, then recrystallized from water, dried and fused in a platinum crucible in an electric furnace.

Sodium Hydroxide.—The sodium hydroxide used in the absorption flask, was prepared by electrolyzing a solution of Kahlbaum's sodium hydroxide, using a silver anode and a mercury cathode, arranged according to the manner of the Castner-Kellner process. This was found to contain no chloride when tested in the nephelometer.

Hydrofluoric Acid.—The ordinary C. P. hydrofluoric acid was distilled after the addition of small amounts of silver nitrate and potassium hydroxide. A platinum still and receiver were used and the middle portion was retained for use. The acid treated in this way gave no opalescence with silver nitrate.

Silver.—The silver used in this investigation was prepared in essentially the same manner as that used by Richards and Wells¹ in their work on the atomic weights of sodium and chlorine.

Chemically pure silver nitrate was recrystallized three times from nitric acid and reduced with ammonium formate, which had been prepared by distilling ammonia gas into redistilled formic acid until the solution was neutral or slightly acid. The silver was then fused in porcelain crucibles lined with pure carbon² in an electric furnace. The fused silver was cleaned

¹ *Pub. Carnegie Inst. Wash.*, No. 28 (1905).

² Richards and Wells, *Ibid.*, No. 28 (1905).

with sand, etched with nitric acid, carefully washed, dissolved in nitric acid, and again reduced with ammonium formate. This was washed by decantation, dried, and fused in porcelain crucibles lined with pure lime¹ in an electric furnace. It was then carefully cleaned with a bristle brush, etched with nitric acid, and electrolyzed, using a pure silver wire as cathode, the fused silver as anode, and silver nitrate, made by dissolving some of the fused silver in nitric acid, as the electrolyte. This electrolytic silver was carefully washed, dried, and again fused in the pure lime-lined boats in a tube furnace through which was passed hydrogen, prepared from zinc and hydrochloric acid, and purified by passing through wash bottles containing alkaline permanganate; silver sulfate, caustic potash and finally through tubes containing heated platinized quartz and glass wool interspersed with phosphorus pentoxide. The bars of silver thus obtained were carefully cleaned, etched with nitric acid and preserved in a desiccator over solid potassium hydroxide. Before weighing, these bars were cut into pieces, etched to the desired weight with nitric acid, carefully washed and dried by heating for several minutes to approximately 120°.

Tantalum Oxide.—Tantalum oxide free from chloride was prepared by once recrystallizing the potassium fluotantalate from pure water to which had been added a small amount of hydrofluoric acid prepared as above. The oxide obtained from this salt, as described below, was tested for chloride by dissolving it in dilute hydrofluoric acid, contained in a platinum dish, using just enough of the acid to obtain a clear solution, adding silver nitrate and allowing the solution to stand for two days. No precipitate could be detected.

Tantalum Chloride.—Potassium fluotantalate which had been prepared for the earlier investigation was used as the starting point for the preparation of tantalum chloride. The fluotantalate was placed in a platinum dish and covered with sulfuric acid which had been distilled from quartz. The mass was slowly heated till all the hydrofluoric acid had disappeared and sulfuric acid fumes had begun to come off freely. The mixture was then evaporated to dryness, transferred to a large rubber dish and washed by decantation with large amounts of pure water. The material was finally dried, placed in quartz crucibles and strongly ignited in an electric furnace. The apparatus used for the preparation of the chloride is shown in Fig. 1. About 30 g. of the tantalum oxide were placed in the tube F, by means of a funnel through D, and the apparatus sealed together at B, D, H, and L, so that it formed a continuous piece of glass through O. A stream of chlorine was passed through the apparatus by means of the tube A, for several hours, the entire apparatus being warmed with a free flame from time to time, in order to remove any traces of mois-

¹ Richards and Wells, *Pub. Carnegie Inst. Wash.*, No. 28 (1905).

ture that might be present. Sulfur monochloride was then introduced into the bulb E, through C, and heated to boiling, the oxide at the same time being heated to a temperature just below the softening point of the glass. The tantalum chloride formed, together with the excess of sulfur monochloride, collected in Bulb I. When all the oxide had been converted into chloride the excess of sulfur monochloride was driven through the ap-

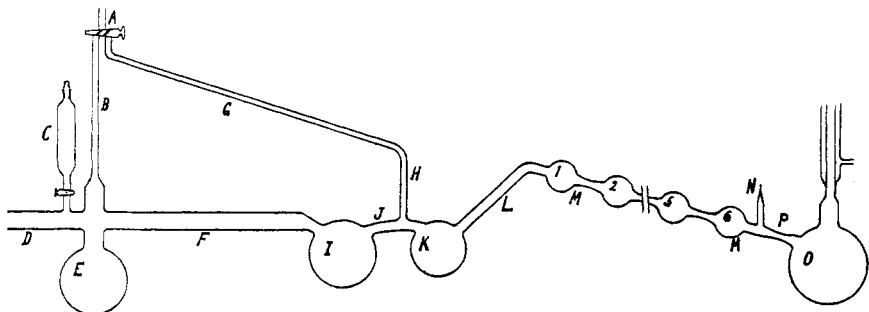


Fig. 1.

paratus and collected in O. The tantalum chloride was then distilled into K and the apparatus sealed off at J. The two-way stopcock A was then turned so that the chlorine passed through G. The tantalum chloride was then heated to boiling and kept at nearly that temperature while the remainder of the apparatus was heated so that any remaining sulfur monochloride and some tantalum chloride were driven over into O. The apparatus was then sealed off at P and, after cooling, at H.

Considerable difficulty was encountered during the process of distilling off the excess sulfur monochloride on account of a tendency of the mixture to explode. The force of these explosions varied considerably. Sometimes only a slight flash was noticed, but on several occasions the whole apparatus was destroyed. The explosions seemed to occur most frequently when the sulfur monochloride was practically all distilled over and the temperature raised to the boiling point of the tantalum chloride. It was also noticed that their occurrence depended on the rate at which the chlorine had been passed through the apparatus during the formation of the tantalum chloride. The more rapid the current, the less danger was there of an explosion. The cause of these explosions was not definitely determined, though it seems probable that they were due to a spontaneous combustion of the free sulfur which was always present in the mixture when a rapid current of chlorine was not kept up.

In order to replace the chlorine with dry air the tip N was broken off and quickly attached by means of a rubber cement to a glass tube leading through a two-way stopcock to two phosphorus pentoxide tubes, the bulbs M being heated previously in order to prevent the entrance of air when the tip N was broken off. The apparatus was then evacuated by means of

a good water-pump attached to one of the pentoxide tubes. The two-way stopcock was then turned and air was allowed to enter slowly through the other pentoxide tube to which a wash-bottle containing sulfuric acid had been attached. This process was repeated until all the chlorine was replaced with dry air. The tantalum chloride was then heated to the boiling point while air was being drawn slowly from the apparatus. After cooling, the evacuation process was continued for two or three times, after which the tantalum chloride was distilled into the small bulbs M, and each sealed off for analysis. The chloride in these bulbs was pure white.

Experimental.

Ratio : $2\text{TaCl}_5 : \text{Ta}_2\text{O}_5$.—In order to test this ratio the purified chloride was transferred from the sealed bulbs to the quartz reaction flask shown in Fig. 2. The transfer in this and all succeeding cases was made as follows: By means of a knife and a hot file a crack was drawn about two-thirds around the neck of the bulb containing the chloride. This, together with the weighed flask, into the mouth of which had been inserted a wide necked funnel, was introduced into an air-tight box, provided with a removable glass top and a pair of rubber gloves fitted into two holes in the sides of the box. In order to insure a perfectly dry atmosphere, dishes containing pumice stone moistened with sulfuric acid were kept in the box and a stream of dry filtered air was passed through it for several hours before the transfer was made. By slipping the hands into the rubber gloves it was possible to break the neck off the bulb and transfer the chloride to the reaction flask without soiling the neck of the flask. After replacing the stopper it was removed from the box and again weighed.

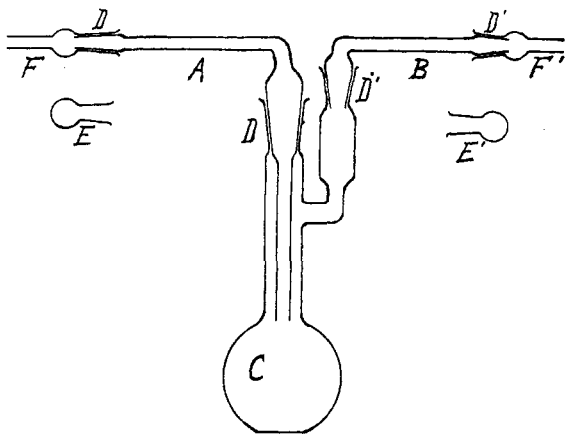


Fig. 2.—A, B, and C are fused transparent silica, D, D', D', are carefully ground joints. Caps E, E', and tubes F, F', are made of soft apparatus glass.

The flask was then connected through an absorption train to an aspirating bottle in such a way that a slow current of moist air was drawn through it for several hours. Then water and a few drops of nitric acid were added and the tantalum oxide evaporated to dryness. The evaporation was repeated two or three times, after which the oxide was ignited

to bright redness. This was done by means of an electric resistance furnace made by winding Ni-chrome wire around an unglazed porcelain cup and insulating with powdered magnesia. By use of a rheostat the temperature was gradually increased to 900° to 1000° . During the ignition a very slow current of dry filtered air was drawn through the flask.

Three determinations were made in this way, but in no case could a constant weight be obtained, though in one case sixteen ignitions of about two hours each were made. On close examination a fine deposit was found in the exit tube, which showed that some of the oxide was being lost, either by volatilization or by being mechanically carried over by the slow current of air that was drawn through the flask. The latter seemed the more probable. In order, however, to test this point two more determinations were carried out in the same way, with the exception that no air was passed through the flask after evaporating to dryness. In the first, after eight ignitions of a half hour each a fairly constant weight was obtained, but on examining the exit tubes a fine deposit was quite noticeable. In the second, nineteen ignitions of a half hour each were made without obtaining a constant weight. The loss during any one ignition varied from a few hundredths to almost a milligram. A fine, white deposit was found in the exit tubes in this determination also.

The result of these two series showed quite conclusively that it would be impossible to obtain a satisfactory ratio by trying to hydrolyze the chloride and ignite to the oxide, since the result depended wholly on the time of heating, a fact which might have escaped detection if the reaction flask had not been supplied with the horizontal exit tubes. In order to determine more satisfactorily the reason for this, the following experiment was carried out: A sample of tantalum chloride was carefully hydrolyzed and evaporated with nitric acid two or three times and finally ignited in the quartz flask, Fig. 2, for two hours in the electric furnace. A part of the resulting oxide was then removed from the flask and fused with potassium pyrosulfate. The gases present in the mixture were at the same time conducted into a solution of silver nitrate. No opalescence in the silver solution was detected, though the melt was boiled for some time after a clear fusion had been obtained. From this it was assumed that the tantalum oxide contained no chloride. The remainder of the tantalum oxide in the flask was weighed and ignited for two-hour periods. The following weights were obtained: 1.2256, 1.2241, 1.2240. A little nitric acid was then added and the mixture evaporated to dryness and ignited for one-hour periods. The weights were as follows: 1.22440, 1.22407.

The result of this experiment, together with the fact that a fine, white deposit was always found in the exit tubes on ignition, shows that tantalum oxide is certainly lost during ignition and also that it occludes a part of

the nitric acid giving it up, if at all, only after long ignition. Ruff and Schiller¹ have shown that when tantalum oxide is ignited with sulfuric acid a part of the acid is held, even after repeated ignitions.

As a result of these experiments it was concluded that the ignition and weighing of tantalum oxide obtained from the chloride could not be used for work of the highest accuracy and, therefore, the method was abandoned.

Ratio : TaCl_5 : 5Ag.—In the beginning of the investigation of this ratio an attempt was made to hydrolyze the tantalum chloride and precipitate the hydrochloric acid formed, with silver in the presence of the tantalic acid. It was soon evident, however, that the silver was being used up by a continual displacement of the equilibrium. In one experiment to determine the nature of this reaction a sample of tantalum oxide was boiled with water and allowed to stand for several days, when the supernatant liquid, which still had a faint opalescence, was poured off and tested with silver nitrate. The opalescence was quite noticeably increased, a fact which indicated that it would be necessary to remove the tantalic acid before precipitating the chloride with silver.

The method which seemed most suitable for the separation of the tantalic acid was to hydrolyze the tantalum chloride as before and distill off the hydrochloric acid. With the idea in mind that it might be possible to obtain the chloride-oxide ratio and the chloride-silver ratio from the same sample of tantalum chloride the quartz reaction flask, Fig. 2, was designed. The apparatus first used for the hydrolysis was the same as that already described in the study of the ratio $2\text{TaCl}_5 : \text{Ta}_2\text{O}_5$. The tantalum chloride was hydrolyzed in the quartz flask and the hydrochloric acid drawn into a liter flask where all but the last traces were absorbed. In order to prevent the escape of any acid, a series of twelve small bulbs was attached to the large absorbing flask. These were arranged with a gentle slope so that the gas was forced to bubble through the liquid in each of the bulbs. A solution containing a little excess of the calculated amount of sodium hydroxide to react with the hydrochloric acid was placed in the absorbing train. As a final guard against loss of chloride a bulb was sealed to the end of the absorbing train in such a way that the liquid in it could be removed and tested for any hydrochloric acid that might escape absorption. The analysis was made in a three-liter Erlenmeyer flask, by precipitation with a weighed amount of silver dissolved in nitric acid. The nephelometer was used here and in all succeeding analyses with silver to obtain the final end point. Standard solutions of silver nitrate and sodium chloride were used for this purpose.

In Table I are the results obtained in the analyses that were carried to completion without the known loss of hydrochloric acid.

¹ *Z. anorg. Chem.*, **72**, 329 (1911).

TABLE I.

Cl = 35.46.		NaCl : Ag = 0.54185.		Ag = 107.88.	
No.	Wt. of TaCl ₅ , (vac.).	Wt. of Ag, (vac.).	100 parts of TaCl ₅ equivalent to parts of Ag.	Atomic weight.	
5.....	11.66795	17.51344	66.622	182.06	
9.....	7.61398	11.42585	66.638	182.14	
11.....	4.09519	6.15647	66.518	181.50	
12.....	8.09039	12.16628	66.498	181.40	

The poor agreement was thought to be due to the amount of manipulation necessary for the transfer of the solution from the rather extended absorption train, since in none of these did any hydrochloric acid reach the test bulb. To obviate this difficulty it was determined to carry out the whole process of hydrolyzing the tantalum chloride and distilling off the hydrochloric acid in a sealed apparatus under reduced pressure. In order to determine the possibility of completely hydrolyzing the tantalum chloride under these conditions the following experiment was carried out:

A weighed amount of pure sodium chloride was suspended in a glass weighing bottle above a sulfuric acid solution (1 : 1) in a 500 cc. distilling flask which was sealed by means of a glass tube to another flask, used as a receiver. In the receiver was placed the calculated amount of pure sodium hydroxide solution required to neutralize the hydrochloric acid formed. The neck of the reaction flask was then sealed off, the receiver connected with a good water pump and the whole apparatus evacuated, and then closed by sealing the capillary connection between the receiver and the pump. By tipping the apparatus slightly the bottle containing the sodium chloride was dropped into the acid solution. The hydrochloric acid formed was then distilled over into the receiving flask where it was absorbed in the alkali. One determination made in this way gave 0.54189 for the ratio NaCl : Ag, which agrees very well with the value obtained by Richards and Wells¹ (0.54185). In a second experiment two or three grams of tantalum oxide, free from chloride, were placed in the reaction flask with the sodium chloride and the analysis carried out as before. Repeated distillation, however, failed to remove all the hydrochloric acid, though it was finally evaporated to dryness twice after moistening with one or two cubic centimeters of sulfuric acid each time.

From this it was evident that the hydrochloric acid could not be completely removed from the tantalum oxide at the temperature of boiling sulfuric acid. Therefore, a second analysis of sodium chloride in the presence of tantalum oxide was made as before, with the exception that the residue, obtained by twice evaporating the mixture to a syrupy consistency with sulfuric acid, was transferred to a 500 cc. platinum dish by rinsing out the flask with as little water as possible. Enough hydrofluoric

¹ *Pub. Carnegie Inst. Wash.*, No. 28 (1905).

acid was then added to form a clear solution and the chloride determined by adding an excess of silver nitrate and comparing the opalescence to that of standard sodium chloride solution treated in the same manner. The value obtained for the ratio $\text{NaCl} : \text{Ag}$ was 0.54211. A great deal of difficulty was encountered in transferring the residue from the reaction flask because of the fact that it formed with the sulfuric acid a mass of gummy particles which clung so tightly to the walls of the flask that it was impossible to remove it completely. This undoubtedly would account for a considerable part of the variation from the accepted ratio but the result seemed to indicate that the principle involved in the method might be used.

Not yet satisfied, however, that the silver nitrate would not form an insoluble compound with the tantalum under these conditions a sample of tantalum oxide, free from chloride, was dissolved in hydrofluoric acid and silver nitrate was added. No opalescence appeared within twelve hours.

The results obtained from this series of experiments indicated that it would be possible to determine the chloride by precipitation with silver nitrate in the presence of the tantalum fluoride, if enough hydrofluoric acid was used, to hold the tantalum in solution. If too little hydrofluoric acid was used, however, the silver formed an insoluble compound, probably a tantalate. Platinum was the most satisfactory material in which to carry out this reaction. Accordingly, a platinum Erlenmeyer flask having a capacity of about one and three-fourths liters and fitted with a platinum stopper, together with a small platinum weighing bottle was obtained for this work.

The method of analysis was as follows: The weighed platinum bottle together with a bulb containing the purified tantalum chloride was placed in the dry-box and the transfer made as described above. The stopper, also of platinum, was carefully replaced in the bottle and the whole transferred to the balance and weighed. One of Ruprecht's best balances was used throughout the investigation and the weights were carefully standardized. All weighings were made by substitution, using a platinum crucible of approximately the same weight as the bottle for tare. Sufficient pure water to make an approximately fifth normal solution with the tantalum chloride and enough hydrofluoric acid to dissolve the tantalic acid were placed in the platinum flask and warmed to a temperature slightly above that of the surrounding atmosphere. The stoppered bottle was then dropped into the solution and the flask quickly closed. The warm solution soon caused an expansion of the air within the bottle sufficient to force the stopper out and allow the hydrolysis of the tantalum chloride to take place. The calculated amount of silver to precipitate the chloride was weighed out to within one or two milligrams, dissolved in nitric acid

(1 : 1) and the solution made up to about fifth normal. The silver nitrate solution was then poured slowly into the chloride solution while the latter was being gently agitated. After a complete transfer to the silver nitrate, the flask was shaken for some time to insure a thorough mixing and then allowed to stand until the next day, when a sample of the clear supernatant liquid was removed for a nephelometric test. The flask and contents were cooled with ice for several hours before removing the sample in order to reduce the solubility of the silver chloride. The transfer was made to platinum crucibles by means of a pipet coated with pure paraffin. Excess of silver nitrate was added to one and sodium chloride to the other, after which they were allowed to stand for about eight hours before the nephelometric readings were taken.

Considerable difficulty was encountered in obtaining nephelometric tubes that would be sufficiently transparent and yet resistant to the action of the hydrofluoric acid. The ordinary glass tubes were coated with pure paraffin, collodion, etc., but with little success. It was found that they either diffused the light or dialyzed too readily. Finally, however, tubes were constructed by cementing together the edges of strips of celluloid and closing the ends of the cylindrical tubes thus formed with carefully cleaned rubber stoppers over which a thin layer of paraffin was placed. These tubes were found to be very satisfactory.

Table II contains the results of three analyses carried out by this method.

TABLE II.

	Cl = 35.46.	NaCl : Ag = 0.54185.	Ag = 107.88.	
Preparation.	Wt. of TaCl ₅ (vac.).	Weight of Ag. (vac.).	100 parts of TaCl ₅ equivalent to parts of Ag.	Atomic weight.
I.....	3.53605	5.31834	66.488	181.34
II.....	2.99083	4.49851	66.485	181.32
III.....	6.21118	9.34345	66.476	181.27

Although the agreement here is much better than any previously obtained it did not seem to be as good as the method should produce. The only reason for this that presented itself was that there was something about the equilibrium of the reaction that was not understood. So a study of this was taken up as follows:

Standard solutions of sodium chloride and silver nitrate were prepared, and equivalent amounts of these were mixed and allowed to stand for three days when a portion of the clear liquid was tested in the nephelometer. No difference was detected. In a second determination in which the same solutions were used enough hydrofluoric acid was added to make a 4.4% solution. The nephelometer again showed exact equivalence, which indicated that hydrofluoric acid alone did not affect the equilibrium.

A sample of sodium chloride was then weighed out, dissolved and precipitated with a weighed amount of silver in the usual manner. On the

following day a portion of the clear liquid tested in the nephelometer showed a slight excess of chloride. The calculated amount of silver was added from the standard solution and allowed to stand until the following day when a nephelometric test showed exact equivalence. In this experiment 1.78135 g. of sodium chloride required 3.28748 g. of silver for precipitation which gave 0.54185 for the ratio NaCl : Ag. This is in exact agreement with the value obtained by Richards and Wells. A second determination was carried out in the same way, using 1.79253 g. of sodium chloride to which had been added 0.31 g. of tantalum oxide dissolved in enough hydrofluoric acid to make a 5.5% solution. After a thorough mixing, the whole was set aside till the next day when a nephelometric test was made. This showed a considerable excess of sodium chloride though exact equivalents had been added. This seemed to indicate that equilibrium had not yet been reached, so the solution was again shaken for some time and set aside for another day when a nephelometric test showed a greater excess of sodium chloride than before. The shaking was repeated and a nephelometric test made on the next day showed only a very slight excess, which entirely disappeared on the fourth day. A third determination was made in which the percentage of hydrofluoric was kept the same but the amount of tantalum oxide added was doubled. Nephelometric tests made on the third and fifth days after precipitation showed exact equivalence. Other determinations were made in which the percentage of hydrofluoric acid was decreased but without obtaining satisfactory results.

These experiments indicated that it would be possible to determine accurately the amount of chloride present in a hydrofluoric acid solution containing a sufficient amount of the latter, but that a longer time would be required for the equilibrium to be reached than in the case of sodium chloride. With this in mind five analyses of tantalum chloride prepared by the method already described, but further treated as described below, were carried out and the results are given in Table III.

TABLE III.

	Cl = 35.46.	NaCl : Ag = 0.54185.	Ag = 107.88.	
Preparation.	Weight of TaCl ₅ (vac.).	Weight of Ag. (vac.).	100 parts of TaCl ₅ equivalent to parts Ag.	Atomic weight.
A.....	4.03892	6.07417	66.493	181.36
B ₃	3.32164	5.00133	66.417	180.96
B ₄	2.68304	4.04002	66.412	180.93
B _a	3.01453	4.53953	66.406	180.90
B _b	3.95846	5.95931	66.425	181.00

In preparation A the chlorine was replaced with dry air and the tantalum chloride was redistilled under atmospheric pressure. Preparation B was treated in the same manner except that it was redistilled under slightly reduced pressure. In preparation B five samples were obtained of which the third and fourth (B₃ and B₄) were analyzed without further treatment.

Samples 1 and 2, however, were subjected to a further distillation under atmospheric pressure and formed preparation B_a. Sample 5 was treated in as nearly the same manner as was possible at different times and formed preparation B_b.

The results obtained in this series seem to indicate that tantalum chloride either occludes some chlorine which may be removed only with the greatest care or that it is partially decomposed by distillation in dry air. The former would tend to give a low value for the atomic weight while the latter would undoubtedly give a value too high.

Summary.

During the present study of the ratios $2\text{TaCl}_5 : \text{Ta}_2\text{O}_5$ and $\text{TaCl}_5 : 5\text{Ag}$, the following observations were made:

1. Tantalum oxide, prepared from the chloride, not only occludes the nitric acid but is lost on ignition.
2. Silver forms with tantalic acid an insoluble compound, probably a tantalate.
3. Hydrochloric acid cannot be removed completely from tantalic acid by boiling with sulfuric acid either under atmospheric or reduced pressure.
4. Silver can be used to determine hydrochloric acid in the presence of tantalum fluoride if the precipitation is carried out in an approximately 5.5% solution of hydrofluoric acid. Three to four days, however, are necessary for equilibrium to become established.
5. Tantalum chloride, purified by replacing the chlorine atmosphere with dry air and by distilling either under atmospheric or reduced pressure, apparently varies slightly in composition.

In conclusion it may be pointed out that there is now available for the first time a method of analysis sufficiently accurate to detect slight differences in the composition of tantalum chloride. It now remains to make a careful study of the preparation of the chloride with regard to the definiteness of its composition. This problem is now under investigation and as soon as a satisfactory solution is obtained a final series of determinations will be published. It may be added that the possible value of this method of analysis for the determination of the atomic weights of other elements will be investigated.

URBANA, ILL.

[CONTRIBUTION FROM THE UNITED STATES GEOLOGICAL SURVEY.]

SOLUBILITY OF MIXTURES OF SODIUM AND POTASSIUM CHLORIDES IN SOLUTIONS OF HYDROCHLORIC ACID.¹

By W. B. HICKS.

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Some experiments conducted by Dr. R. C. Wells of the Geological Survey on the brines from Great Salt Lake indicated that potassium

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