[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 10.]

DERIVATIVES OF COLUMBIUM AND TANTALUM.[1]

BY MARY ENGLE PENNINGTON.

Received November 29, 1895.

Among the more metallic members of Group V of the Periodic System are the elements columbium and tantalum, which, though almost a century old and counting among their devotees such investigators as Rose, Hermann, Marignac, Rammelsberg, and others of equal fame, still offer many interesting problems to the student of inorganic chemistry. Comparatively few of the compounds of these elements have been prepared. Those which have been studied narrowly enough to afford an accurate knowledge of their chemical behavior form a much shorter list. The early literature is, in many instances, very contradictory, due to the supposed existence of such elements as pelopium and ilmenium, engendering as they did the fruitful controversy between Hermann and Marignac, which controversy resulted in the tacit acceptance by the chemical world of Marignac's statement, that columbium is elementary. The old doubt, however, appears to have been revived through the very careful work of Krüss in 1887, on the oxides of these metals, their separation from each other and also from the oxides which accompany them in their apparent minerals.

He found through the fractional crystallization of the double fluoride of columbium and potassium, and by determining the atomic value of the various fractions, that something apparently contaminated the columbium. In some fractions the values obtained were far too low. This he accounted for by proving the presence of titanium. Other portions, however, were much too high, and this, it was carefully proved, was not due to adhering tantalum. Just what the substance was which gave in one fraction an R^V having almost double the accepted atomic mass was left undecided.

A careful consideration of this question in the light of the various researches, makes it seem not improbable that the compounds of columbium, as we know them, are not perfectly free

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[1] From the author's thesis presented to the University of Pennsylvania for the degree of Ph.D., 1895.

from contaminating substances. The many difficulties encountered in the separation of this oxide from others usually occurring with it, and the insufficiency of the prevailing methods of separation, seem to demand a more exact knowledge of the behavior of the element in the purest condition obtainable, and also when mixed with the oxides of tantalum and titanium which usually adhere to it.

It was with the hope that some additional light might be thrown upon the general deportment of the derivatives of these elements that this research was undertaken.

The material used was obtained from a columbite from Wakefield, N. H. An abundant supply of the mineral was secured through the kindness of Professor S. P. Sharples, of Boston, in whose possession it had been for some years though it had never been analyzed. Wakefield is a new locality for columbite. The deposit was discovered while mining for feldspar. Near the columbite is quite a deposit of beryl.

ANALYSIS OF WAKEFIELD COLUMBITE.

The mineral occurs in large, black, lusterless masses. Scattered over the surface are little patches of a bright yellow substance. These proved to be uran-ochre and gave evidence of the presence of the uranium which was later found in the mineral. Feldspar occasionally penetrated the mass, though in small quantity. The specific gravity of picked material was found to be 5.662 at 4° C.

Decomposition was effected by the method usually employed for this class of minerals.

Fusion with Acid Potassium Sulphate.—The finely divided mineral was allowed to stand over calcium chloride for some hours. The desired amount of this dry, and almost impalpable, powder was weighed off and mixed with at least nine times its weight of fused potassium bisulphate. This must be an intimate mixture. Great care should be exercised when the heat is first applied, else loss by spattering will occur. Frequent stirring tends to prevent this, and also hastens the decomposition.

Some trouble was experienced by the fusion "climbing" and leaving far up on the sides of the crucible particles of mineral which could neither be driven down by heat or forced down by a platinum rod. To collect these particles the crucible containing the clear, quiet fusion was slightly tilted and the adhering portions covered with a little bisulphate. Then by gently heating the whole mass was driven down until it met the main portion of the fusion. All decompositions by this method were made in a large platinum crucible or platinum dish. The latter was preferred. If the mineral is fine enough the fusion is complete in about five hours.

The fused mass was taken up in a large quantity of water, and boiled out with water several times. The insoluble portion consisted of the oxides of columbium, tantalum, titanium, tin, tungsten, and any silica which was present. Small quantities of these oxides invariably remained dissolved although the solution was boiled for a long time ; it is, therefore, advisable to let the filtrate stand twenty-four hours, then refilter.

The moist oxides, according to Headden,[1] should "be digested with yellow ammonium sulphide" to remove all tin, tungsten, etc. Rose recommends that yellow ammonium sulphide should be simply poured over them, and that this solution should be evaporated to dryness, and gently ignited, to render the columbium and tantalum oxides which have been dissolved by the alkali, insoluble. Wöhler[2] claims that it is sufficient to treat the metallic oxides upon the filter with yellow ammonium sulphide. As some uncertainty existed as to the best course to pursue, the effect of ammonium sulphide when mixed with these oxides for a longer or shorter period of time was studied.

Heating in a porcelain dish on the water-bath for three hours gave 1.15 per cent. of the mixed oxides ; one and one-half days, 1.60 per cent. ; three days, 1.85 per cent. ; one week, 2.24 per cent. By pouring the sulphide over the oxides on the filter, as Rose and Wöhler advise, 0.24 per cent. of the mixed oxides was obtained.

Apparently, the moist metallic oxides are more readily dissolved by ammonium sulphide than is generally supposed, and,

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[1] *Am. J. Sci.*, 41, 91, *1891*.

[2] Mineral Analyze, p. 140.

therefore, when working with columbites containing the acid oxides care must be taken, or a very appreciable error may result.

The ammonium sulphide solution was precipitated by dilute hydrochloric acid, and the precipitate was filtered, and washed with hydrogen sulphide water, alcohol, ether, carbon disulphide and ether. The mixed sulphides were carefully heated in the air, then reduced in a current of hydrogen gas. The residue treated with dilute hydrochloric acid gave tin in solution and left undissolved a small quantity of a black compound which proved to be the tetroxide, Cb_2O_4, with possibly a little tantalum.

The moist oxides when treated with ammonium sulphide have not only the acids removed, but the iron contained in them is changed to sulphide. This is dissolved out by dilute sulphuric acid. Filter off the oxides and wash them thoroughly with boiling water. A pump is usually necessary because of the precipitate being finely divided, and having a tendency to clog the pores of the filter. By this treatment the oxides should be entirely freed from iron and manganese. Nevertheless ignition gave a powder having a distinct pinkish yellow hue, showing the presence of these elements. The oxides were, therefore, re-fused with potassium bisulphate and treated as before. The second fusion gave a product lighter in color, yet not perfectly white. Another fusion was resorted to, and no loss in weight was observed, as a small amount of iron still adhered to the oxides. In fact, a *perfectly white* mixture of the oxides has not been obtained by this method.

The sulphuric acid solution of the iron which remained with the insoluble oxides, was added to the aqueous extraction of the fusion. This solution now contained iron, manganese, uranium, and calcium, with a large excess of sulphuric acid and alkali salt. Yttrium, cerium, and calcium were looked for according to the plan presented in Rose's Handbuch der analytischen Chemie, **2,** 335, which is, in brief, this: The greater part of the free acid is neutralized with sodium carbonate; sodium acetate is added, so that acetic acid is in large excess. The earths are precipitated by ammonium oxalate, the precipitate being allowed to stand twenty-four hours. From three grams of mineral only a very small amount was obtained. This was too small a quantity to investigate further, so that if any rare earths are present in the mineral they exist in traces.

To the filtrate which contained iron, manganese and uranium were added ammonium sulphide and ammonium carbonate. The iron and manganese were precipitated as sulphides, while uranium was held back by the ammonium carbonate. Beryllium, if present, would have been found here. This element was sought for, since the locality from which the mineral came made it a probable constituent, but none was detected. The sulphides having been filtered out, the filtrate was made acid with hydrochloric acid, the carbon dioxide boiled off, then the uranium precipitated by ammonium hydroxide. The uranium hydrate was filtered, washed, ignited, and weighed as U_3O_8. The sulphides of iron and manganese were dissolved off the filter in hydrochloric acid, oxidized, and separated by the basic acetate method, the manganese being finally weighed as manganese pyrophosphate.

The water contained in this columbite was determined by heating in a boat in a glass tube, and collecting the aqueous vapor in a weighed calcium chloride U tube.

In the literature relating to columbites and allied minerals, while a ferrous content is given, the method by which it was determined is omitted. Perhaps this is due to the fact that the customary decomposition with sulphuric acid in a sealed tube naturally suggests itself, yet in applying this course to the columbite under examination unexpected difficulties were encountered. The experience is at least interesting.

The mineral was ground very fine and heated in sealed tubes with sulphuric acid (one part of concentrated acid to two parts water), the resulting decomposition being titrated with permanganate with the following results:

	Per cent. FeO.
0.5 gram heated one day at 210° C	1.316
0.5 gram heated two days at 230° C	1.416
0.5 gram heated five days at 230° C	5.50

It seemed probable that this was not the total amount of ferrous iron in the columbite, hence attention was directed to an old method which is rarely used, yet seems to be worthy of greater attention than has been given it. Berzelius first suggested the method, though it is generally credited to Hermann. The finely ground mineral is mixed with fused and finely divided borax. A small platinum crucible is completely filled with this mixture, then covered with a platinum lid, and the whole placed in a larger platinum crucible. Dry magnesium oxide is packed around and over the inner crucible until it is completely covered and so excluded from air contact. The heat of a good Bunsen lamp is applied for one-half hour, when the decomposition is complete. Longer heating, or too rapid cooling, causes the fusion to adhere very tightly to the crucible, and loss may result on endeavoring to remove it. When the whole is quite cold, the small crucible is taken out, freed from adhering magnesium oxide, and weighed. The fusion, which is a clear green glass, is then freed from the crucible by sharply tapping ; a piece may be broken off, weighed, ground in a mortar, dissolved in water and sulphuric acid, and titrated with potassium permanganate. Or, if the amount of ferrous iron is not large, it is better to crush the whole fusion in a diamond mortar, then place in a flask provided with a Bunsen valve, dissolve in water and sulphuric acid, and titrate. To prevent the oxidation of the iron during its solution, a quantity of sodium carbonate was placed in the flask with the ground fusion, and the water and sulphuric acid added carefully to this mixture. When a strong evolution of carbon dioxide had continued for several minutes, the cork carrying the Bunsen valve was quickly inserted, and the flask put aside until solution had taken place. It is necessary to shake the flask from time to time, otherwise the finely divided oxides which separate will enclose some particles of the fusion, and the result will be low. In one or two hours the insoluble residue should be a perfectly white, fine, homogeneous mass. The flask is then opened, more sulphuric acid added if necessary, and the iron titrated with permanganate. A number of fusions were made according to this method, the amount of ferrous oxide found being 6.426 per cent. The method seems to be, so far as columbite is concerned, perfectly trustworthy. It is rapid, and the manipulation is not difficult. The oxides which separated out were perfectly white. In one experiment they were filtered off, washed with hot water, ignited, and weighed. The percentage of mixed oxides, 77.94 per cent., agrees quite well with that obtained by the bisulphate method.

The quantitative analysis of this columbite by fusing with bisulphate, as above described, gave the following results :

	A.	B.	C.	D.	E.
Ta_2O_5 Cb_2O_5 TiO_2	78.61	79.04	79.00	77.96	78.70
Fe_2O_3	12.30	13.83	13.62	13.58	....
SnO_2 WO_3	1.15	1.60	1.85	2.24	1.84
MnO	8.96	8.32	....	8.08	....
	101.02	102.79	....	100.86	....

One-half gram of material was used in each case. The ferric oxide, as given above, includes the ferrous, which, estimated by the method of Berzelius, equals 6.42 per cent.

In a sixth analysis three grams of material were taken, and due attention was paid to those constituents which former analyses had shown to be present, but in such small quantities that their determination was not trustworthy. The results in this case were :

	Per cent.
Ta_2O_5 Cb_2O_5 TiO_2	78.04
WO_3 SnO_2	0.24
U_3O_8	0.48
Fe_2O_3	5.22
FeO	6.42
CaO	0.02
MnO	8.96
H_2O	1.22
Total	100.60

An interesting point in the composition of this columbite is the ferric oxide. Hermann records one analysis of some fragments of a columbite from Miask containing several per cent. of it, and so far as I am aware this is the only columbite in which this constituent is mentioned. He also gives a Miask columbite containing 0.50 per cent. of uranium oxide. Genth mentions a trace of uranium in a columbite analyzed by him.

While no effort was made to separate the metallic oxides quantitatively, it was found from the preparation of pure material that the columbium was in decided excess. Titanic acid was proved to be present, and silica was found in very small quantities.

Many of the recorded analyses in which separations of columbic and tantalic oxides are given, fail to state whether any attempt had been made to eliminate or to prove the presence of titanium or silica. Given a mixture of tantalum, columbium, and titanium, the analyst will have no difficulty in separating tantalum from columbium by Marignac's double fluoride method. But the titanium double fluoride, when mixed with the columbium salt, shows an abnormal solubility which makes its separation very doubtful. This point will be more fully discussed later.

Fusion with Sodium Thiosulphate.—It occurred to me to try the decomposition of the mineral by fusion with sodium thiosulphate, believing that in this way tungsten and tin would be converted into sulpho salts, and could then be more effectually removed from the other constituents. Without entering into detail, I may say the attempt was fruitless.

Decomposition by the Gibbs Method.—Some years ago Dr. Gibbs published a procedure[1] for the decomposition of the columbite minerals; and as my desire was to investigate the different methods of decomposition, I naturally turned to this suggestion. In mineral literature this course is given a second place to the bisulphate decomposition. My own experience compels me to prefer it to the latter method. The details of the Gibbs method are, in brief, as follows:

The mineral must be fine, yet need not be in an impalpable powder, as is necessary in the bisulphate decomposition. It was intimately mixed, by grinding in a mortar, with three times its weight of potassium fluoride; the mixture was transferred to a platinum crucible and made into a paste with concentrated

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[1] *Am. J. Sci. Arts.*, 37, 357. *1864.*

hydrofluoric acid. The mass heated up at once, and for some minutes the decomposition proceeded without the application of heat. It was found advantageous to let this mixture of acid salt and mineral stand for several hours, stirring occasionally, and adding more acid if the mass became hard. It was then heated on a water-bath until the excess of acid was driven off. After thoroughly drying on an iron plate, the free flame was applied. Hydrofluoric acid was driven out of the acid potassium fluoride, and at length the whole mass fused and formed a clear, quiet, easily handled fusion, which, upon cooling, became a beautiful pink-violet in color.

The decomposition is not complete until every part of the mixture has assumed this color, which does not change on further heating. In the early part of the fusion a deep blue color appears. If the action be interrupted at this point, an incomplete decomposition will result.

The violet mass was taken up with water and hydrofluoric acid in a platinum dish, then boiled and filtered. This extraction should be repeated several times. If the decomposition is not quantitative, the solution in water is much hastened by first grinding the fusion. Any silica which may have been present in the mineral will remain as potassium silicofluoride. This being a gelatinous compound, it is likely to enclose fine particles of the fusion and prevent their solution. If the amount of silica is not large, a separation may usually be effected by treating with concentrated hydrofluoric acid; but if much silica be present it is safer to evaporate to dryness with a little sulphuric acid, and take up the remaining potassium sulphate with water. If any insoluble substance is left it may be dissolved in hydrofluoric acid and added to the main portion of the solution.

If an analysis of the mineral is desired, hydrogen sulphide gas may now be passed through the acid filtrate, whereby any tin, tungsten, or molybdenum present will be precipitated as sulphide. Filter, and separate as usual.

The filtrate was evaporated to dryness, and enough sulphuric acid added to expel all the hydrofluoric acid. The excess of acid was driven off on an iron plate, not over a free flame, and the oxides of columbium, tantalum, and titanium precipitated by boiling with a large quantity of water. The boiling must be continued for several hours to insure a complete precipitation, but it is not so difficult to bring down the metallic oxides under these conditions as in the bisulphate decomposition. Filter, and wash the oxides with hot water, first by decantation, then on the filter. The ignition of the oxides gave a *perfectly white*, fine powder; and this fused with sodium carbonate or potassium fluoride yielded a colorless mass when cold. The oxides obtained from the bisulphate never did so, but formed with the carbonate a tinge of green, and with the fluoride a tinge of pink, showing the presence of manganese and probably of iron.

The filtrate from the mixed oxides contained iron, manganese, and uranium. These were separated by ammonium sulphide and ammonium carbonate, following the plan given under the bisulphate method.

When the object is simply the extraction of pure mixed oxides, the above procedure may be somewhat varied. The fusion is made just as usual, then taken up with water insufficient for perfect solution, and a small quantity of hydrofluoric acid, boiled, and filtered. On cooling, the filtrate will be found to be an almost solid mass of the columbium double fluoride, $2KF.CbOF_3.H_2O$, which separates as a beautiful shining salt and consists of thin laminæ. At first the tantalum double fluoride remains undissolved, or is dissolved only in small quantity, as it is a very insoluble salt compared with the columbium compound, but if too much hydrofluoric acid is added the tantalum will be discovered with the columbium potassium fluoride, and larger amounts of iron and manganese will also contaminate it. From a very concentrated solution of the columbium double fluoride, such as would be obtained by this method, any tantalum double fluoride will, if present, separate almost immediately. These needles should be examined under a microscope for the thin transparent plates of the columbium salt. When these begin to appear, filter at once and use a pump. The plates are a good indication that all tantalum is separated. The filtrate, on standing, will usually give the columbium salt, but it may have to be concentrated a little. The first crop of crystals may be colored pink by manganese or iron. Recrystallization, however, removes this. The next crop is fairly pure. When working with large quantities, a very satisfactory approximate separation of columbium from tantalum may be obtained by this method of extraction.

As boiling with pure water, or even with water containing a small amount of hydrofluoric acid decomposes the tantalum potassium fluoride and leaves an insoluble compound,

$$2(2KF.TaF_5)Ta_2O_5,$$

while the columbium double salt is practically unaffected, this treatment leaves us in the end a white, finely divided mass, which is almost free from columbium. By heating this residue on a water-bath with a rather concentrated solution of hydrofluoric acid and a little potassium fluoride, the tantalum potassium fluoride is obtained and may be purified by recrystallization.

The Gibbs method was used for the preparation of rather large quantities of tantalum and columbium potassium fluorides. I think it preferable to the bisulphate decomposition and subsequent solution of the oxides in hydrofluoric acid, in that it does not consume so much time, and iron and manganese are more readily eliminated. The only objection is that large platinum vessels are needed; as a substitute for these, rubber beakers and funnels were sometimes used.

The method finally adopted is as follows:

Separation of Columbium and Tantalum by their Potassium Double Fluorides.—The pure mixed oxides were placed in a platinum crucible with three times their weight of potassium fluoride, then moistened with hydrofluoric acid as described under the decomposition of the mineral by the Gibbs method. By treating the fusion with water and hydrofluoric acid an almost perfect solution was obtained since only a trace of silica was present. Concentration gave the long pointed needles of tantalum potassium fluoride, $2KF.TaF_5$. These were filtered and the solution again concentrated. The crystal crop should be examined under the microscope as it may be a mixture of tantalum and columbium. Usually it is only tantalum.

If a considerable excess of hydrofluoric acid and potassium fluoride is present in the mother-liquor, the next crop of crystals may be a complex mass about which the analyst can come to no definite conclusion. The fraction consists principally of long crystals much like the titanium double fluoride, and to make the matter more puzzling these crystals are not so soluble as those separating at the same time. They may be obtained pure by treating the mixture with a few drops of water and quickly filtering. Recrystallization from pure water gives the laminated salt $2KF.CbOF_3.H_2O$. If the acid and potassium fluoride are not in large excess, usually two, and sometimes three, crops of the laminated salt are formed, but in time the long needles are almost sure to make their appearance. These needles were tested for titanium, but no satisfactory evidence of its presence was obtained.

When the solution is very concentrated large, thin plates separate from it. These do not give the reaction with gallotannic acid, but they react with zinc, hydrochloric acid, and potassium thiocyanate. This test for columbium compounds will be noticed later. Recrystallization does not give the laminated salt. The crystals are always found, and are by no means in small quantity. With zinc and hydrochloric acid they give a greenish color which quickly becomes brown. They were repeatedly recrystallized, then decomposed with sulphuric acid. The oxide obtained was white and at 19° C. had a specific gravity of 4.57.

The oxide was placed in a platinum retort connected with a platinum condenser; hydrofluoric acid was poured over it and a free flame was applied. The volatile products were collected in water in a platinum dish. Several evaporations were necessary for the volatilization of this oxide. The solution in the dish was then treated with a small quantity of potassium fluoride and concentrated. The same large, thin plates crystallized out. These crystals were very beautiful, being frequently over an inch in length and one-half inch in width. They were so transparent that often their presence in the dish was altogether unnoticed.

ANALYSIS.

Substance taken. gram.	K_2SO_4 found. gram.	Cb_2O_5 found. gram.
0.5000	0.5268	0.0059

This analysis would indicate that the salt is probably acid potassium fluoride with a small quantity of the double fluoride of columbium, yet it must not be forgotten that the reactions given above cannot be regarded as conclusive evidence of the presence of columbium.

Because of the brown color with zinc and hydrochloric acid these crystals were also tested for titanium. Its presence could not be detected.

QUALITATIVE REACTIONS.

Throughout this investigation the following questions constantly arose: How shall the purity of the columbium and tantalum compounds be determined? When is columbium free from tantalum? When is it free from titanium?

In the earlier work upon columbium we find Hermann describing a new element which he obtained from the mother liquors of the columbium potassium fluoride. This element, he states, gave a dark brown solution when reduced with zinc and hydrochloric acid, while the pure columbium compound gave a blue color. Both these solutions on standing in the air reverted to the white hydrate. Marignac replied that the brown color was not due to ilmenium but to titanium, a view which is now generally accepted.

He also declares that a brown color is produced when the potassium columbium oxyfluoride is treated with zinc and hydrochloric acid, the acid being in considerable excess. Then by titrating with permanganate he found that an intermediate oxide had been formed, to which he gave the formula Cb_3O_5.

Crystals of the columbium salt, prepared as described above, continued to give this brown solution even after they had been subjected to five or six recrystallizations. Following the plan of Krüss and Nilson[1] the atomic value of the oxide contained in such crystals was determined by decomposing with sulphuric acid, weighing the pentoxide and the potassium sulphate, then

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[1] *Ber. d. chem. Ges.*, **20**, 1676.

by the ratio $2\ K_2SO_4 : Cb_2O_5$ determining the value for Cb^V. This was found to be 85.7. Iron and manganese had been eliminated, titanium, therefore, was the probable cause of this low atomic value. The salt used was perfectly white, yielding a pure white oxide. This oxide was tested for titanium by the most delicate reactions known for the metal, but its presence could not be proved by any of them.

1. Color and Reduction Reactions. It has been found that the qualitative tests given in the various text-books for these three elements do not always hold good when the solution used is a double fluoride. As it is in this form that the separations are usually made, it has been thought advisable to note the action of some of the common reagents on these salts.

Gallotannic acid, which is considered the most characteristic test for columbium salts, behaves differently with different double fluorides. An acid solution of the laminated salt gives almost instantly, a deep, brick-red precipitate. The salt crystallizing in long needles gives a lighter red precipitate which does not separate so rapidly. The large, thin, transparent plates previously mentioned, give only a slight precipitate, and this is yellow in color. These reactions are most delicate if the salt be dissolved in water, a drop of hydrochloric acid added, then a little gallotannic acid dissolved in alcohol. After standing several hours all the precipitates assume the same color—a dark, brick red.

Tantalum double fluoride gives a sulphur yellow color with gallotannic acid. This, however, on standing becomes brick red, as the columbium does.

Titanium compounds are said to give a brownish color with gallotannic acid which changes quickly to an orange red. The potassium titanium fluoride gave a straw yellow color with this reagent; in time a flaky precipitate forms, but the color does not materially alter.

The following color reaction serves for the detection of very small quantities of columbium, and is applicable to any soluble columbium compound. An excess of potassium thiocyanate is added to a small quantity of the dissolved substance; then some pieces of zinc followed by strong hydrochloric acid. At once the solution becomes a bright golden brown, which if much columbium be present may be almost red. A brisk and continued evolution of the gas does not alter this tint which is also stable for more than twenty-four hours in the acid solution. Neither titanium nor tantalum give any reaction with potassium thiocyanate under the above conditions.

Hyposulphurous acid, H_2SO_2, gives noteworthy color reactions with these salts. The tests were conducted in the following manner: A few cubic centimeters of a concentrated solution of sulphur dioxide were placed in a test tube provided with a cork, and granulated zinc was added. The liquid changed to a greenish color, and hydrogen was liberated. As soon as the evolution of the gas had ceased the solution containing the hyposulphurous acid was poured into the salt solution to be tested.

A solution of titanium double fluoride gave an orange yellow color at once. The oxide when treated in like manner became yellow.

Columbium double fluoride gave no color, but a white hydrate was soon precipitated. Columbic oxide gave a slight yellow tinge.

Tantalum double fluoride gave no color, but after standing a white precipitate separated. Tantalic oxide remained colorless when treated with hyposulphurous acid.

The white precipitates from the tantalum and columbium salts were probably hydrates due to the oxidation of the acid and its consequent action upon these salts.

Zinc and hydrochloric acid gave no reaction with the double fluoride of tantalum. With titanium a clear, delicate green was obtained. The columbium salts always gave a color with these reagents. The solution is at first dark blue, then a greenish brown, and finally a dark brown. Frequently a brown precipitate separates which on standing becomes white.

The hydrochloric acid solution of columbic oxide, and also the potassium columbium fluoride, were tested with hydrogen peroxide, this being accepted as one of the most delicate reagents for titanium. No yellow color in either case was obtained.

2. *Reactions with Wet Reagents.* A number of the ordinary reagents have been tried with these salts, the results being given in the following table. The reactions for the greater number are very different when the metal tested is as double fluoride. The ferrocyanides, in particular, have quite abandoned their ordinary colors with these compounds.

	2 KF. $CbOF_3.H_2O$.	2 KF. $Ta F_5$.	2 KF. $Ti F_4$.
Lead acetate.	White precipitate.	White precipitate.	White precipitate.
Mercuric chloride.	Slight precipitate in 24 hours.		
Mercurous nitrate	Yellow precipitate	Yellowish green precipitate.	Yellowish green precipitate.
Potassium chromate.	White precipitate, soluble in H_2O. Partly soluble in $K_2 CrO_4$ solution		Precipitate soluble in water.
Potassium bichromate.		Precipitate after standing.	
Potassium cyanide	White precipitate on boiling.	White precipitate.	White precipitate.
Potassium ferrocyanide.	Green blue precipitate on boiling.	Yellow precipitate on boiling.	Precipitate on boiling.
Potassium thiocyanate.	White precipitate.	White precipitate, soluble in the cold. Comes down by boiling.	
Potassium iodide.	White, granular precipitate. Iodine is liberated.	White granular precipitate.	No precipitate, but iodine is liberated.
Disodium hydrogen phosphate.		White precipitate after standing.	White precipitate.
Silver nitrate.		White precipitate after standing.	
Sodium bisulphite	White precipitate.	White precipitate.	White precipitate.
Sodium pyrophosphate.		Slight cloudiness.	Precipitate.
Hypophosphorous acid.			Precipitate.
Sodium metaphosphate.		Slight cloudiness.	
Potassium bromide.	White precipitate.		

Disodium hydrogen phosphate, when added to titanium double fluoride, precipitates the titanium completely. The filtrate tested with ammonium hydroxide gave no precipitate. Columbium double fluoride, on the contrary, is not affected by this reagent.

After boiling a long time in a platinum dish a few white flocks were observed in the solution, but in such small quantity that they were disregarded. Whether this behavior may or may not be made the basis of a separation of these two elements is not yet determined, because of the difficulty in getting rid of the phosphoric acid. Fusion with sodium carbonate, extraction with water, and subsequent precipitation by sulphuric acid gives a mixture of sodium salt and columbic oxide. Some columbium remains in solution. Fusion with potassium acid sulphate is more satisfactory, yet is not complete.

DEPORTMENT OF TANTALUM, COLUMBIUM AND TITANIUM DOUBLE FLUORIDES TOWARD THE ELECTRIC CURRENT.

1. A solution of potassium columbium double fluoride, $2\,KF.\,CbOF_3.\,H_2O$, in water, was treated with a small amount of sodium acetate. The precipitate formed was dissolved in acetic acid, and through this solution a current of one ampere, obtained from a thermopile, was conducted for five hours. A white precipitate, seemingly a hydrate, was formed. On breaking the current this rapidly went into solution.

2. (*a*) A solution of the salt in water was subjected to the same current for eight hours. Almost immediately the bottom of the platinum dish was covered with a blue deposit. This gradually spread over the whole surface exposed to the action of the current, and became in a short time iridescent. As the deposit increased, the deep blue tint changed to more of a gray, and remained so until the current was broken. It was washed quickly with water, then with alcohol, and it was dried on the hand.

0.1315 gram of the salt was taken; the deposit weighed 0.0282 gram. This metallic looking substance did not alter in the air, but on subjecting it to a red heat, a white, shining, apparently crystalline compound resulted. It was readily soluble in hydrofluoric acid.

(*b*) A second experiment, with 0.2195 gram of the substance, gave under the same conditions, a deposit weighing 0.0388 gram. This when ignited in the air burned to a white oxide weighing 0.0312 gram. The blue compound is in all probability, a lower hydrated oxide of columbium.

3. The electrolysis of an aqueous solution of a sodium columbate gave a white, flucculent hydrate, not adherent to the dish. The precipitation was not complete. A current of one ampere was employed for a period of seven hours.

4. With a much stronger current (two amperes), a solution of the double salt $2\,KF.\,CbOF_3.\,H_2O$, gave first a white hydrate, then beneath the outer edge of the anode appeared a dark brown ring which gradually grew in toward the centre of the dish, never reaching it however, but stopping when about half an inch in width.

This brown substance was slightly adherent to the dish, but just as soon as the current was broken, and the liquid poured off, it reverted to the white hydrate. This change was so rapid that it was impossible to separate the brown from the white substance.

Thinking that this brown compound might be a contaminating element, about one gram of the double salt was dissolved in water and electrolyzed until the brown ring had appeared. Then the liquid was poured into another dish as quickly as possible, and the current run through again. The brown ring appeared as before, and was treated in the same manner. After changing the dish four times only a trace of brown could be seen. When the remaining solution was evaporated it was found that almost the entire quantity of the columbium had been precipitated. The brown substance here formed resembles in its behavior that produced in a like solution by zinc and hydrochloric acid.

The resistance of this solution is very high.

5. Potassium tantalum fluoride in aqueous solution was subjected to the action of a current of two amperes for six hours. A small quantity of hydrate was found in the liquid and on the dish a very slight iridescent deposit mixed with some white hydrate.

6. Potassium titanium fluoride was treated in the same manner as the previous salt. A small quantity of hydrate was found here, some of which adhered to the dish. The iridescent deposit, however, was wanting.

ACTION OF HYDROFLUORIC ACID UPON THE OXIDES OF TANTALUM, COLUMBIUM, TITANIUM, AND SILICON.

The well known volatility of the oxides of tantalum and columbium when heated with hydrofluoric acid led to the hope that in this behavior might lie a separation from titanium and also from silica.

Rose states that a very appreciable loss occurs when the first two oxides are treated as suggested, but he makes no attempt to separate them from the latter two. To this end one gram of the mixed oxides of tantalum and columbium was evaporated to dryness with hydrofluoric acid, the residue being heated over the free flame for a few minutes. By this treatment dense white vapors were driven off. Upon weighing the residual oxides they were found to equal 0.5464 gram. A second evaporation gave further loss, but as both columbium and tantalum continued to remain, the method is without value.

The separation of silica from these oxides can be accomplished by the heat of an iron plate after evaporating to dryness on a water bath. The final heating must be carefully done, and the acid should not be in too great excess.

I have never found it impossible to dissolve either the mixed or the pure oxide in hydrofluoric acid, even though strongly ignited. It is true, concentrated acid is necessary, and a little time is often required, but a perfect solution does take place.

Tantalic oxide, containing columbic oxide, is far more soluble in hydrofluoric acid than the pure oxide. The same behavior has been observed with pure columbic oxide, though it is not so pronounced as with tantalic oxide. Titanium dioxide, ignited, is very difficultly soluble in this reagent, though columbic oxide, containing titanic oxide, went quickly into solution.

DOUBLE FLUORIDES OF TANTALUM, COLUMBIUM, AND TITANIUM, WITH RUBIDIUM AND CESIUM.

The potassium double fluorides of tantalum and columbium have been found of great service in separating these two metals. Marignac first showed that a separation could be effected through these salts, and he also demonstrated that the sodium and ammonium salts were inapplicable.

Of the potassium double fluorides of tantalum and columbium we possess considerable information. A number have been isolated and studied. The sodium salts crystallize so poorly that their history is not so well known. It seemed probable that rubidium and cesium would form double fluorides of definite crystalline character with these three metals. At least, a study of their behavior might be found instructive. Before taking up their preparation, however, the simple fluorides of rubidium and cesium may be discussed.

Rubidium Fluoride (RbF). An examination of the literature on rubidium showed that its fluoride had not been prepared. In order to procure this, rubidium iodide was dissolved in water and moist silver oxide added to precipitate the iodine. The solution of rubidium hydrate resulting, was filtered off and evaporated in porcelain dishes. A very appreciable quantity of silver oxide was held in solution by the rubidium hydroxide, so that it was necessary to evaporate it almost to dryness, then to take it up in the smallest possible quantity of water and filter. This treatment may have to be repeated two or three times before the solution is perfectly colorless. When quite free from silver, the concentrated solution was made slightly acid with hydrofluoric acid, and evaporated. If hydrofluoric acid be present it is almost impossible to obtain crystals, a thick syrup being formed which defies all attempts in this direction. The solution is therefore evaporated with water several times until the excess of acid is expelled. The rubidium fluoride then crystallizes in long, transparent plates. These were drained, and dried between filter paper. The salt was anhydrous. Conversion into sulphate by evaporating with sulphuric acid gave, from 0.5 gram of the salt, 0.5236 gram rubidium sulphate. This corresponds, therefore, to the formula RbF.

Cesium Fluoride.—Cesium chloride was dissolved in water, and the chlorine precipitated by moist silver oxide. The solubility of the oxide of silver in cesium hydrate is even greater than in rubidium hydrate, therefore some difficulty was experienced in obtaining a hydrate free from silver. It was finally accomplished by evaporating to dryness repeatedly, taking up the cesium hydrate in a very small quantity of water and filtering it. The pure hydrate was then neutralized with hydrofluoric acid and evaporated. A thick syrup was obtained, which refused to crystallize. Upon heating in an air bath to 130° C., a crystalline mass formed, but it was always in such a sticky condition, and absorbed moisture so rapidly, that it could not be analyzed satisfactorily. This mass was dissolved in water and added to the solutions of the metals in hyrofluoric acid.

Double Fluoride of Columbium and Rubidium.—One-half gram of columbic oxide was dissolved in hydrofluoric acid and the calculated quantity of rubidium fluoride added. The solution was evaporated on a water bath to expel the excess of acid. The residue was taken up in hot water and allowed to crystallize spontaneously. White microscopic plates separated. These were filtered off, dried between filter paper, and analyzed. Two-tenths gram of the dry salt gave

	Found.	Calculated for $2RbF.CbF_5$.	Difference.
Cb_2O_5	0.0670	0.0673	—0.0003
RbF	0.1048	0.1049	—0.0001

The formula of the salt is therefore, $2RbF.CbF_5$, corresponding to the tantalum salt usually obtained with potassium fluoride.

The filtrate from this first crop of crystals was slightly concentrated, when small, shining, or even iridescent crystals, apparently plates, separated. Upon standing a short time these changed over into crystals like those first mentioned. This salt is very soluble in water containing hydrofluoric acid, and also in pure water. It is insoluble in alcohol.

Double Fluoride of Rubidium and Tantalum. — Rubidium fluoride in slight excess was added to tantalic oxide dissolved in hydrofluoric acid. Small white needles crystallized out. An excess of acid must be present, otherwise heat decomposes the double salt, giving a fine, white, insoluble compound, as is the case with the potassium salt.

Analysis of two-tenths gram gave

	Found.	Calculated for $2RbF.TaF_5$.	Difference.
Ta_2O_5	0.0915	0.0913	+0.0002
RbF	0.0861	0.0859	+0.0002

Double Fluoride of Titanium and Rubidium.—The preparation of this salt was conducted as described with preceding salts. The crystals here were also microscopic needles. Some difficulty was at first experienced in completely drying the salt, but this was overcome by several recrystallizations from pure water, when an anhydrous product was obtained. One-tenth gram of the salt gave on analysis

	Found. Gram.	Calculated for $2RbF.TiF_4$. Gram.	Difference.
TiO_2	0.0238	0.0240	—0.0002
RbF	0.0622	0.0626	—0.0004

Double Fluoride of Tantalum and Cesium[1].—This double salt was formed by the addition of a solution of the cesium hydrate in hydrofluoric acid to a solution of tantalic oxide in hydrofluoric acid. Very beautiful white needles separated, which were not easily soluble in water, and were not decomposed by recrystallization from pure water. The aqueous solution may be evaporated on a water-bath with perfect safety, this salt being apparently much more stable than either the potassium or rubidium salt.

The crystals were dried in the air, then heated to 125° C. in an air-bath. No loss in weight was observed. 0.25 gram gave on analysis

	Found.	Calculated for $15CsF.TaF_5$.	Difference.
Ta_2O_5	0.0212	0.0217	—0.0005
CsF	0.2232	0.2228	—0.0004

The formula deduced from the analytical data varies widely from that generally followed by tantalum double fluorides. Neither is it in accordance with Remsen's law for the double halides[2] though it will be observed that its fluorine content bears a simple ratio to the fluorine in combination with the tantalum.

Double Fluoride of Columbium and Cesium.—This double salt was formed in the manner described for the preparation of the cesium tantalum fluoride. It is very soluble in water containing hydrofluoric acid, and in pure water, from which it crystallizes in needles. These when pure are anhydrous. Boiling

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[1] This and all the other cesium double fluorides are being subjected, at this writing, to further study in this laboratory. EDGAR F. SMITH.

[2] *Am. Chem. J.*, **2**, 291.

with pure water does not decompose the salt. Analysis of two-tenths gram gave the following result :

	Found.	Calculated for $7CsF.CbF_5$.	Difference.
Cb_2O_5	0.0216	0.0213	+0.0003
CsF	0.1694	0.1698	—0.0004

This salt, which appears to be $7CsF.CbF_5$, is even more erratic in its constitution than the tantalum cesium compound. There is apparently no relation here between the fluorine in combination with the columbium and the number of molecules of cesium fluoride present.

Double Fluoride of Titanium and Cesium.—This salt separates in very small shining crystals when cesium fluoride is added to a rather concentrated solution of titanic oxide in hydrofluoric acid. It is more readily soluble in water than the tantalum cesium compound, and is not decomposed by pure water. The air dried crystals showed no loss in weight after heating for some time at 125° C. An analysis of 0.25 gram gave the following amounts of titanic oxide and cesium fluoride :

	Found.	Calculated for $4CsF.TiF_4$.	Difference.
TiO_2	0.0269	0.0271	+0.0002
CsF	0.2071	0.2076	—0.0005

The figures point to the formula $4CsF.TiF_4$. This is a departure from the usual titanium double fluorides, and agrees with the law laid down by Remsen for these salts.

When we consider the atomic masses of tantalum, columbium, and titanium, the first 182, the second 94, and the third 48, and also consider the quantities of cesium fluoride which unite with a molecule of each of the metallic fluorides, we find that with tantalum the quantity (fifteen) is nearly twice that with columbium (seven) and the latter almost double that (four) uniting with titanium, just as 182 is about twice 94, and 94 nearly twice 48.

These new cesium compounds tend to confirm the conclusions drawn by Wells and others[1] from their work on the cesium double halides. The compounds investigated by these chemists show that the cesium double halides are not wholly conformable to Remsen's law.

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[1] *Am. J. Sci.*, 47.

The method of analysis pursued for the determination of these double salts is, briefly, as follows :

The dry substance was decomposed in a platinum crucible by a few drops of concentrated sulphuric acid. The hydrofluoric acid was driven off, and the excess of sulphuric acid was then expelled on a sand-bath. The temperature must be just sufficient to drive off the acid. The metallic oxide was obtained from the sulphate by long boiling with a large quantity of water. It was then filtered, washed about twenty times with boiling water, ignited, and weighed. The filtrate, containing the alkaline sulphate, was evaporated, the excess of acid neutralized with ammonium carbonate, and the solution then evaporated to dryness on a water-bath. A saturated solution of ammonium carbonate was added, and the mixture evaporated again to dryness. The ammonium salts were expelled by careful heating. Constant weight can generally be obtained after two or three evaporations with ammonium carbonate. The rubidium sulphate decrepitates on heating, which necessitated great care while expelling ammonium salts, and also rendered the method proposed by Krüss (heating in a stream of ammonia gas), untrustworthy. The alkalies were then weighed as normal sulphate, and the cesium or rubidium content calculated. This method, while slow, has been found very satisfactory for these rare alkalies.

PRODUCTS OBTAINED ON HEATING THE OXIDES OF TANTALUM AND COLUMBIUM WITH PHOSPHORUS PENTACHLORIDE.

One-half gram of columbic oxide was heated with phosphorus pentachloride, the quantity being calculated from the following equation :

$$Cb_2O_5 + 5PCl_5 = 2CbCl_5 + 5POCl_3.$$

The experiment was conducted in a sealed tube from which all air had been expelled, the temperature being maintained at 180°–200° C., for seven hours. The resulting mass was moist, and a dirty green. The tube was opened, connected quickly with a small test tube, and then heated in an air-bath. A small quantity of liquid distilled into the front part of the tube. This was a yellowish green, and gave with water a white precipitate, apparently a hydrated columbic oxide.

At a higher temperature, about 200° C., yellow vapors collected in the cool portion of the tube. These settled on the glass as yellow, oily drops, and on cooling solidified, long yellow needles being detected here and there. Nearly all of the substance in the tube, however, remained as the greenish mass, which had become dry. No change was observed on heating above 360° C. The tube was then wrapped in copper gauze and heated with a Bunsen lamp. The green substance swelled up, became white, iridescent, and almost filled the tube. No green color remained. Analysis of this compound showed it to be columbium oxychloride, $CbOCl_3$. The long yellow needles which had been observed in the front part of the tube changed gradually on heating, and became white and iridescent like the remainder of the substance.

This behavior indicated the formation of a pentachloride, which was then changed to oxychloride by the small quantity of air which entered the tube when it was connected with the receiver.

A second tube, heated for eight hours at 230°–235° C., gave a dark yellow, semi-fluid mass. Great care was taken in this experiment to exclude all traces of moisture, and the distillation was conducted under reduced pressure. Phosphorus oxychloride in considerable quantity distilled over, leaving in the tube a yellow crystalline substance, which, on treating with water, decomposed with hissing and an evolution of hydrochloric acid gas. This compound was analyzed according to the method of Marignac.[1] The ignited oxide weighed 0.5642 gram. As only one-half gram of columbic oxide was used in the experiment, the contaminating substance was sought, and was found to be phosphorus. Two fusions with bisulphate were necessary for the extraction of this element. Phosphoric acid was also found in the filtrate from the pentoxide.

The question now arose regarding the position of this phosphorus: Is there a compound formed containing columbium, phosphorus, and chlorine, or is the phosphorus content due to an incomplete expulsion of the excess of phosphorus pentachloride?

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[1] *Ann. chim. phys.*, 8, 5.

Another experiment was therefore tried under the following conditions: One-half gram columbium pentoxide was heated with the calculated quantity of phosphorus pentachloride at a temperature not exceeding 210° C. for eight hours. The tube contained a yellow mass as before. It was placed in an air-bath and connected with a chlorine generator, the receiver having been previously filled with chlorine. At 190° C. a very volatile substance collected in the front part of the receiver. This was a lemon yellow, and when analyzed gave 15.85 per cent. columbium and 6.095 per cent. phosphorus.

At 190°–200° C., long yellow needles collected; some of these were nearly half an inch in length. Analysis gave 27.37 per cent. columbium and 32.19 per cent. phosphorus.

The substance which did not volatilize at 200° C. was brownish-yellow, and apparently crystalline. Analysis gave 28.11 per cent. columbium, and 1.34 per cent. phosphorus.

In none of these analyses could the chlorine content be determined, because of the violence with which water acts upon the compounds, resulting invariably in the loss of some hydrochloric acid.

It seemed probable that the brownish-yellow residue in the tube was columbium pentachloride, enclosing a small quantity of phosphorus pentachloride. To determine all three elements, the following method was used:

The more volatile compounds having been removed by distillation in a stream of chlorine gas the residual substance was quickly weighed and thrown into a dilute solution of silver nitrate. The precipitate of silver chloride, silver phosphate, and hydrated columbic oxide was then filtered, and washed on the filter with dilute nitric acid. The phosphoric acid obtained was determined by a magnesium mixture. Dilute ammonium hydroxide was then poured over the mixture of silver chloride and columbic oxide. It was found that all the silver salt could not be removed by this means. The mixture was therefore transferred to a porcelain crucible and reduced in a stream of hydrogen gas, the metallic silver being dissolved out with dilute nitric acid, then precipitated as chloride. The columbium remained in the form of a violet compound, which on ignition in the air went over to pentoxide.

A small quantity of phosphorus was obtained, which was calculated into pentachloride and deducted from the material taken.

Rose states that a columbate of silver, $Cb_2O_5.Ag_2O$, is formed on the addition of silver nitrate to a solution of sodium columbate. As, upon the addition of water to columbium pentachloride, an almost perfect solution is produced for a few moments, the columbium in solution may combine with the silver. In such a case the silver chloride finally weighed would represent both the silver in combination with chlorine and that with columbium.

The analytical results are as follows:

Substance taken = 0.8917 gram.
Phosphorus found = 0.02596 gram.

This, as phosphorus pentachloride, requires 0.14829 gram of chlorine.

Substance taken minus PCl_5 = 0.7175 gram.
Columbium found = 0.2485 gram.
Columbium required = 0.2484 gram.
Chlorine found = 0.66509 gram.

Taking from this 0.14829 gram of chlorine, which is in combination with phosphorus, we have chlorine = 0.5168 gram; columbium pentachloride requires 0.4691 gram. Calculating the quantity of silver which, according to Rose's formula, would combine with the amount of columbium oxide found, and deducting the chlorine corresponding to it, 0.4699 gram of chlorine is found to be in combination with the columbium.

The volatile compounds mentioned above were recalculated into phosphorus pentachloride and columbium pentachloride. It was found that by removing the phosphorus as pentachloride satisfactory analyses for columbium pentachloride were obtained from the residues.

Tantalic oxide was also heated with phosphorus pentachloride, the same conditions being maintained as in the columbium experiments. A yellow mass was formed lighter in color than the columbium compound, and only slightly moist. The tube was placed in an air-bath and distilled at a temperature not exceeding 245° C. This distillation was conducted under reduced pressure. A small quantity of phosphorus oxychloride distilled over, and in the front part of the tube a little phosphorus pentachloride collected. The tantalum compound remaining was light yellow, dry, and powdery—apparently amorphous. It combined with water with hissing, liberating tantalic oxide, which contained no phosphorus. A small quantity of this element was found in the filtrate from the oxide. It was calculated into phosphorus pentachloride, and deducted from the total quantity.

Weight of substance taken = 0.6700 gram.
Weight of tantalum found = 0.3389 gram.
Required tantalum = 0.3391 gram.

Tantalum pentachloride is, therefore, formed when tantalic oxide is heated with phosphorus as pentachloride.

REDUCTION OF THE COMPOUNDS OF COLUMBIUM AND TANTALUM TO METAL.

Two experiments aiming at the preparation of columbium and tantalum in the metallic state have been tried during this research, and I regret exceedingly that lack of time has prevented a more careful study of the reactions obtained. It is my intention to go more deeply into the subject than I have been able to do.

Experiment 1. An iron cylinder, three inches in diameter, having an inch bore, was charged in the following manner: First, a layer of dry salt, then a layer of metallic sodium, above which were placed about seven grams of potassium tantalum fluoride, this being followed by another layer of sodium. The cylinder was then tightly packed with dry salt, and a heavy lid screwed on. It was then placed in a wind furnace, the temperature of which was comparatively low. In less than one-half hour it was found that the cylinder had melted down, and no trace of the charge could be found.

Experiment 2. Marignac obtained an alloy of columbium and aluminum by heating the potassium double fluoride with aluminum scales in a carbon crucible. In the experiment to be described columbic oxide was used, salt and cryolite being employed as a flux. The following layers were placed in a graphite crucible:

1. Salt.
2. Cryolite.
3. Aluminum clippings.
4. Columbic oxide.
5. Aluminum clippings.
6. Cryolite.
7. Salt.

The proportion of these substances used were:

2 parts Cb_2O_5.
10 parts cryolite.
15 parts aluminum.
x parts sodium chloride.

The graphite lid was firmly luted on with fire-clay, the crucible was buried in a wind furnace which was kept at a white heat for eight hours. At the end of this time it was found that the graphite crucible had been severely attacked. It was reduced to a shapeless mass, but on breaking, a powdery substance was found, in which were contained many little metallic buttons varying in size from a large pea to those of microscopic proportions. These were carefully picked out, and various reagents tried upon them.

Single acids do not attack them. Aqua regia makes a slight impression on long heating. Fusion with bisulphate affords only a partial decomposition. The substance is exceedingly light, it is dark gray, and does not alter in the air. A partial oxidation occurs after prolonged heating in the air. The substance is not brittle.

SUMMARY.

1. The decomposition of columbite is more readily and satisfactorily accomplished by the Gibbs than by the bisulphate method. This method is also more valuable for the preparation of large quantities of pure oxides.

2. The qualitative reactions of columbium, tantalum and titanium when existing as double fluorides are not the same as when the metals exist as tantalates, columbates and titanates.

3. The action of the electric current upon tantalum and columbium double fluorides gives a lower hydrated oxide. The precipitation is not complete.

4. It was hoped that in preparing the double fluorides of

columbium, tantalum and titanium with rubidium and cesium a difference in solubility of the salts would be found which would afford a better separation of these metallic oxides under discussion. This hope has not been realized.

5. Heating the oxides of columbium and tantalum in sealed and vacuous tubes with phosphorus pentachloride yields the pentachlorides of these metals and phosphorus oxychloride.

I take pleasure in acknowledging the kindness shown, and the interest taken in the preceding work by Dr. Edgar F. Smith, of this University, in whose laboratory it was carried out.

UNIVERSITY OF PENNSYLVANIA,
JUNE, 1895.

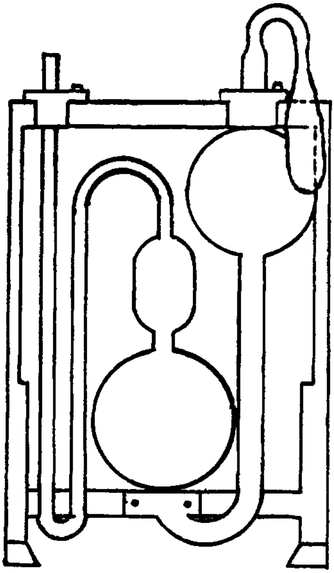
AN IMPROVED GAS PIPETTE FOR THE ABSORPTION OF ILLUMINANTS.

BY AUGUSTUS H. GILL.

Received October 12, 1895.

IN the use of the apparatus for this purpose ordinarily furnished by the dealers, difficulty has always been experienced in sucking the gas back from the pipette, owing to the moist beads and the glass wool entrapping some bubbles.

To obviate this, the writer has, for the past two years, made use of the modification shown at one-fourth size in the sketch. The round bulb filled with beads and glass wool in the usual form, is replaced by a cylindrical one about two inches long and an inch and a quarter in diameter, filled with tubes standing vertically, after the manner of the Orsat pipettes. The surface presented is nearly the same and no trapping of the gas can take place.



The stand is the one already described,[1] and the whole apparatus may be obtained of the Ziegeler Electric Co., of Boston.

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[1] Gill: *Am. Chem. J.*, 14, 231.