

THE JOURNAL

OF THE

American Chemical Society

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

OBSERVATIONS ON COLUMBIUM.

BY CLARENCE W. BALKE AND EDGAR F. SMITH.

Received August 23, 1908.

Introduction.

The present communication contains the results obtained in a continuation of the investigation of the compounds of columbium and tantalum which is being conducted in this laboratory. It deals with the preparation of columbium oxide free from titanium and other impurities, the preparation of columbium chloride, a determination of the atomic weight of columbium through analyses of the chloride, and a study of a number of the columbates and the double fluorides of columbium. It also includes a study of certain new compounds of tantalum.

Purification of the Material.

The starting-out material used in the present investigation consisted of the double fluorides of potassium and columbium which had been obtained from the columbite of South Dakota by Roy D. Hall and Edgar F. Smith.¹ These contained as impurities traces of titanium, tin, tungsten, tantalum, silicon and iron. Of these impurities previous investigators have found titanium the most difficult to remove. After a careful investigation of the hydrogen peroxide test which has been used in this laboratory to detect traces of titanium in columbium oxide, and having failed to obtain an oxide which did not give a color reaction with hydrogen peroxide, Hall and Smith reached the following conclusion: "From these experiments it may be safely concluded that the color produced in hydrofluoric acid solutions of columbium with hydrogen peroxide is not due to the presence of titanium. Also, it is likely that columbium

¹ THIS JOURNAL, 27, 1369 (1905).

itself gives a distinctive color with hydrogen peroxide, equivalent to from 0.10 per cent. to 0.15 per cent. of its weight of titanium dioxide, yet yellow-green instead of straw-yellow, as is given by titanium in dilute solutions. Possibly there may still be present some other element. For this, careful search will be made."

Moreover, these investigators pointed out that the crystallization of potassium columbium fluoride (K_2CbF_7), which is not isomorphous with potassium titanium fluoride, might serve for the preparation of columbium compounds free from titanium. With these thoughts in mind it was determined to carry out this crystallization on a large scale.

Potassium columbium fluoride, K_2CbF_7 , is produced when the other double fluorides of columbium are recrystallized from strong hydrofluoric acid. Eighteen kilograms of the double fluorides of potassium and columbium were crystallized four times from aqueous hydrofluoric acid containing approximately 20 per cent. of the pure acid. The first crop of crystals from each crystallization served as the starting-out material for the next crystallization. The mother liquors from the more advanced crystallizations were used to further crystallize the more impure material. For the first two crystallizations commercial acid was used, but for the last two carefully purified acid was employed. The latter was obtained by distilling the commercial acid from a large lead jug provided with a platinum condenser. Previous to the distillation, potassium hydroxide was added to the acid in sufficient quantities to combine with all of the hydrofluosilicic acid present. The potassium fluosilicate formed was filtered out, large rubber funnels being employed. About one hundred kilograms of commercial acid were required to complete the crystallizations, and all of the solutions, when not perfectly clear, were filtered through large rubber funnels supplied with hot water jackets. In order to free the crystals as thoroughly as possible from adhering mother liquor, they were placed in a hard rubber funnel and swung through the air as rapidly as possible in a circle having a diameter of nearly three meters, and the drainings were allowed to collect in a tube of hard rubber. This method of draining crystals, which has been described by Richards,¹ proved very effective with this salt as the crystals were in the form of needles which did not easily retain the mother liquor between their points of contact, as would have been the case with the fluoxycolumbate of potassium, which crystallizes in thin flexible leaflets.

The first crops of crystals obtained from the various crystallizations were as follows:

From the first crystallization, 8.5 kilograms.

From the second crystallization, 3.4 kilograms.

From the third crystallization, 2.2 kilograms.

From the fourth crystallization, 1.5 kilograms (crystals A).

¹ THIS JOURNAL, 27, 110 (1905).

By a further recrystallization of the second and third crops of crystals, obtained upon concentrating the mother liquors from the third and fourth crystallizations mentioned above, four kilograms of salt (crystals *B*) were obtained, which were fully as pure as crystals *A*.

In order to test this salt for tin and tungsten 200 grams of crystals *A* were decomposed with sulphuric acid, and the oxide obtained was fused with sodium carbonate and sulphur. The soluble portion of the fusion was treated with dilute hydrochloric acid and the sulphur, which would have contained the tin and tungsten, was burned in a weighed porcelain crucible. The residue obtained amounted to 0.001 per cent. of the weight of the salt taken. It was therefore concluded that the crystallizations had removed these impurities from the material. The oxide, however, still gave a color reaction with hydrogen peroxide corresponding to about 0.15 per cent. of its weight in titanium dioxide.

The salt contained an appreciable quantity of potassium tantalum fluoride which was removed by baking the double fluoride as indicated by Hall and Smith. Crystals *A*, to the amount of 1.3 kilograms, were brought into solution in a large platinum dish and the solution was boiled for several days. Large quantities of hydrofluoric acid escaped, the potassium columbium fluoride, K_2CbF_7 , changing into fluoxycolumbate of potassium, $K_2CbOF_5 \cdot H_2O$. The latter was finally baked for several hours, then dissolved in water, and the resulting solution filtered through a rubber funnel supplied with a hot-water jacket. This operation was repeated until the insoluble residue, when dissolved in a small amount of hydrofluoric acid, showed only the solubility of potassium columbium oxyfluoride. In making this test the solution was evaporated to dryness two or three times, so that the solubility of the salt in pure water could be noted.

A possible trace of silica was removed as usual by decomposing the double fluoride with sulphuric acid. A large excess of acid was used and the heating was continued until the mass was dry and contained comparatively little free acid. The oxide obtained on treating this mass with water was washed many times in a large platinum dish by decantation. A portion of this oxide after several hours' ignition over a good burner showed a specific gravity of 4.8.

Inasmuch as this oxide, which we had reason to believe was free from titanium, still gave a color reaction with hydrogen peroxide, there seemed to be no further doubt that this reaction was due to columbium itself. The one other possible interpretation would necessitate the assumption that some other element was still present in the columbium, which had not been removed by the treatments indicated above. In order to further test this point, portions of the oxide were converted into chloride, and the latter carefully fractionated, the various fractions being examined

as to their composition, their vapor density, and the specific gravity of the oxides obtained on treating the chloride with water or ammonium hydroxide.

Preparation of Columbium Chloride.—The chloride was obtained by using the method first suggested by Smith and Hall,¹ which consisted in the ignition of columbium oxide in the vapor of sulphur monochloride and a final distillation of the product in an atmosphere of chlorine gas. The apparatus used by us is indicated in Fig. 1. The bulb A contained

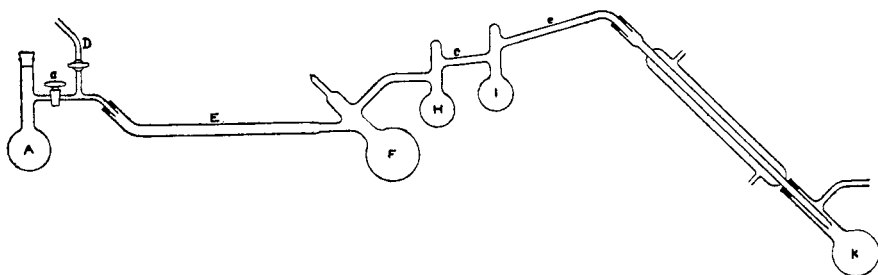


Fig. 1.—Apparatus used for the preparation of columbium chloride.

the sulphur monochloride, and the tube D served for the introduction of dry chlorine. Strongly ignited columbium oxide, in quantities of 10–20 grams, was placed in the tube E, and the latter then moderately heated with a series of four fish-tail burners. On passing the vapor of sulphur monochloride, the voluminous oxychloride of columbium was formed, but the latter was gradually converted into the chloride, which together with the excess of sulphur monochloride collected in bulb F. Great care was required to prevent the obstruction of the apparatus by the columbium oxychloride, and constant attention was required until the very completion of the experiment. The tube E was very liable to crack, due to the condensation of sulphur monochloride on the heated glass, so that it was found advisable to make the tube as short as possible, and to protect the anterior end of the tube E with asbestos paper. It was also found desirable to pass dry chlorine into the apparatus during the entire experiment. When the desired quantity of oxide had been converted into chloride, which required from ten to twenty hours, the stopcock *a* was closed and the excess of sulphur monochloride was driven through the bulbs H and I and collected in K. The columbium chloride was then distilled from F into H, and finally from H into I. It was found to be comparatively easy to remove the sulphur monochloride completely by these distillations. The bulb I was finally sealed off at *c* and *e*.

The apparatus used for the fractionation of the chloride is pictured

¹ THIS JOURNAL, 26, 1235 (1904).

in Fig. 2. The bulb I was connected with bulb L by means of the adapter N. A rubber stopper was used to make the connection, and the bulb I was adjusted as rapidly as possible after breaking off the ends of the side tubes, and a rapid stream of chlorine was immediately passed through

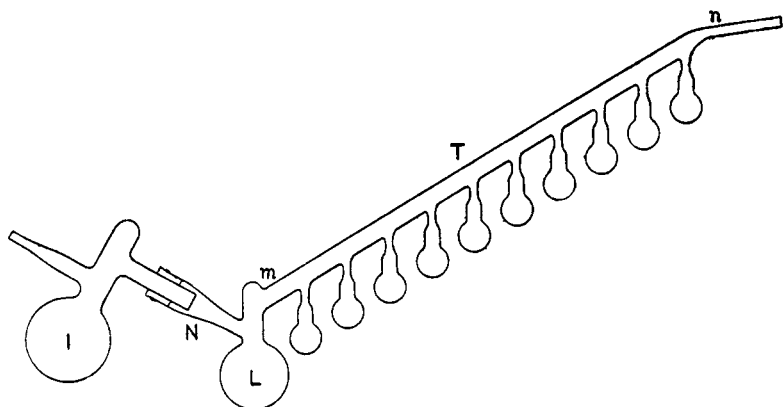


Fig. 2.—Apparatus used for the fractionation of columbium chloride.

the apparatus. The chloride was then distilled into bulb L, and from this bulb it was carefully distilled into the smaller bulbs in such a manner as to make the fractionation as effective as possible. At the conclusion of the fractionation the long tube T was sealed off at *m* and *n*, and finally the individual bulbs were sealed off at their constrictions.

The chloride thus obtained had a beautiful sulphur-yellow color when in the solid state, but when fused its color was red. On solidifying it contracted appreciably, shrinking away from the walls of the containing bulb. This was found to be a great advantage in removing the chloride for analysis, as it was an easy matter to shake it into pieces small enough to pass through the neck of the small bulbs.

Three preparations of columbium chloride were made and fractionated by this method.

Preparation.	Oxide used. Grams.	Number of bulbs in fractionating apparatus.
I.....	50	10
II.....	60	15
III.....	90	21

The bulb L of the fractionating apparatus used for the third preparation carried a thermometer which was sealed within a glass tube at the top of the bulb. The entire quantity of chloride distilled at a temperature varying but slightly from 241° . The columbium chloride had a marked tendency to volatilize at a temperature much below its boiling point, and the vapors condensed in the cooler parts of the apparatus in beautiful yellow needles. In all of the preparations the chloride collected in

the last three or four bulbs of the fractionating apparatus consisted wholly of this sublimed material, and it surely would have contained appreciable amounts of any chloride more volatile than columbium chloride had such been present in the latter at the beginning of the fractionation. It may be said here in anticipation of the results which follow that no differences could be detected between any of the fractions obtained.

A portion of the oxide obtained from this chloride has been carefully examined spectroscopically by Joel H. Hildebrand, of this laboratory. A careful measurement of the wave lengths of the lines obtained with a five-foot concave grating did not reveal the presence of any titanium or tantalum lines. Tantalum oxide, purified by the method previously described by one of us,¹ was converted into chloride and fractionated as described above, and the oxide obtained therefrom was also examined by Hildebrand, with the result that no titanium or columbium lines appeared.

Vapor Density of Columbium Chloride.—A number of determinations of the vapor density of columbium chloride were made, using the method of Dumas. The bath used consisted of a mixture of fused potassium and sodium nitrates. The side tubes of 100 cc. distilling bulbs were sealed off, and after being thoroughly cleaned and dried, an ample quantity of the chloride was introduced and the neck of the bulb was loosely stoppered. The latter was then drawn out to the form shown in Fig. 3. After the vaporization of the chloride, the bulb was sealed off at *a*. It was found impracticable to seal off the tip of the capillary tube, as is usually done, as a deposit of columbium oxide formed on the latter which produced an enamel with the glass very difficult of fusion. After the bulb had been weighed, its tip was broken off under water and the amount of residual air determined. The columbium hydroxide was dissolved out of the bulb with a hot solution of potassium binoxalate and the glass weighed. The bulb was finally filled with water and weighed as usual. In making the calculations, all necessary corrections were applied.

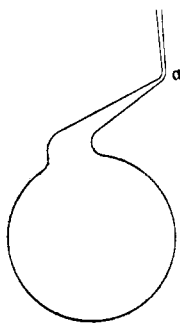


Fig. 3.

Series.	Bulb.	Temperature of bath.	Wt. CbCl_5 (vac.).	Wt. of equal vol. of air.	Density.
I	6	280°	0.8026	0.08495	9.45
I	6	300°	0.7098	0.07575	9.37
II	5	292°	0.8379	0.08989	9.32
III	1	275°	0.8333	0.08702	9.58
III	20	280°	0.7551	0.07931	9.52

Mean, 9.45

The calculated density, using 93.5 as the atomic weight of columbium,

¹ THIS JOURNAL, 27, 1140 (1905).

is 9.35. Deville and Troost¹ obtained the value 9.6. It will be observed that in Series III the chloride from the extreme fractions gave practically the same vapor density.

After the completion of the third preparation of columbium chloride, the small amount of the latter which had passed over into bulb K with the sulphur monochloride was recovered by decomposing the latter with water and burning the sulphur. The small quantity of oxide thus obtained was converted into a double fluoride with potassium.

On analysis 2.1000 grams of this salt gave 0.9368 gram of oxide and 1.2223 grams of K_2SO_4 , or 44.61 per cent. of oxide and 58.20 per cent. of K_2SO_4 . The salt was, therefore, the fluoxycolumbate of potassium which requires 44.38 per cent. of Cb_2O_3 and 57.94 per cent. of K_2SO_4 .

Density of Columbium Oxide.—The value obtained for the density of columbic oxide depended largely on its method of preparation. It is worthy of note that the density of the oxide obtained by igniting the precipitate resulting from the treatment of columbium chloride with dilute ammonium hydroxide was always about half a unit lower than that observed when the oxide was obtained by allowing the chloride to decompose in a moist atmosphere. From the results obtained it would appear that a determination of the density of columbic oxide, obtained by these methods, would be of little value as a means of detecting the presence of small quantities of an admixed oxide. The following values were obtained for the oxide prepared by the first method mentioned above: oxide made from the chloride in bulb 10, Series I, 4.51; bulb 3, Series I, 4.48. When the second method was used in the preparation of the oxide, the following results were obtained: bulb 10, Series II, 4.93; bulb 13, Series II, 4.88; bulb 1, Series I, 5.05; bulb 17, Series III, 5.02.

Density of Columbium Chloride.—The only liquids which were found to be satisfactory for use in a determination of the specific gravity of columbium chloride were sulphur monochloride and carbon tetrachloride. The others which were tried either dissolved or decomposed the chloride. While columbium chloride dissolves quite readily in hot sulphur monochloride and carbon tetrachloride, it is but slightly soluble in these compounds at the ordinary temperature. In order to obtain as great accuracy as possible, these liquids were saturated with columbium chloride at 20° C. and the solutions were used in the determinations. With sulphur monochloride the following data were obtained:

Wt. of columbium chloride	5.4442
Wt. of pycnometer	6.6145
Wt. of pycnometer + water	17.2756
Wt. of pycnometer + S_2Cl_2	24.5750
Wt. of pycnometer + S_2Cl_2 + $CbCl_3$	26.7135
$t = 20^\circ C.$	

Specific gravity of columbium chloride = 2.77.

¹ *Compt. rend.*, 56, 891 (1863).

A similar experiment in which carbon tetrachloride and 7.07 grams of columbium chloride were used gave the value 2.73.

The Atomic Weight of Columbium.

(See Clarke, "Recalculation of the Atomic Weights, Smithsonian Miscellaneous Collections," 1897.)

Of the previous determinations of the atomic weight of columbium those made by Rose, Hermann, and Blomstrand seem to be without present value, while the determinations of Marignac are far from satisfactory. Rose¹ analyzed a compound which he thought to be chloride, but which was probably oxychloride, in which case his value becomes nearly 94. The results obtained by Hermann² need not be considered, while those of Blomstrand³ are very discordant. The latter chemist analyzed columbium chloride, weighing the columbium as the pentoxide and the chlorine as silver chloride. There is a difference of nearly four units between the lowest and highest value for the atomic weight of columbium as calculated from the percentages of columbic oxide, and similar variations in the value appear when the latter is calculated from the ratios $5\text{AgCl}:\text{CbCl}_5$ and $5\text{AgCl}:\text{Cb}_2\text{O}_5$. Blomstrand also analyzed a sodium columbate, but his results in this connection are valueless in that they indicate the value of the atomic weight of columbium.

The accepted value for the atomic weight of columbium is obtained from the investigations of Marignac.⁴ This chemist made about twenty analyses of the potassium fluoxycolumbate, $2\text{KF}:\text{CbOF}_3:\text{H}_2\text{O}$. The following percentages were obtained:

Cb_2O_5	Extremes 44.15 to 44.60
K_2SO_4	Extremes 57.60 to 58.05
H_2O	Extremes 5.75 to 5.98
F	Extremes 30.62 to 32.22

Using the values $\text{O} = 16$, $\text{K} = 39.15$, $\text{F} = 19$ and $\text{H} = 1.01$, we obtain from the extreme percentages of Cb_2O_5 the values 92.27 and 94.70 for the atomic weight of columbium. In like manner, from the extreme percentages of K_2SO_4 , we obtain the values 95.38 and 93.04. In other words there is a difference of over three units between the highest and lowest values obtained by Marignac.

Pure columbium chloride having been obtained in large quantities, it was determined to use this compound in a redetermination of the atomic weight of columbium. The ratio between columbium chloride and columbium oxide was investigated. The following is an account of the analytical method employed:

¹ *Pogg. Ann.*, **104**, 439 (1858).

² *J. prakt. Chem.*, **68**, 73 (1856).

³ *Acta Univ. Lund*, 1864.

⁴ *Arch. sci. phys. nat.* [2], 23 (1865).

By carefully tapping one of the bulbs containing the columbium chloride, the latter was broken up into small pieces; the neck of the bulb was then broken off, and the chloride quickly transferred to a carefully cleaned and dry glass-stoppered weighing bottle of such size as to be nearly filled with the amount of chloride employed. After carefully weighing the bottle, the chloride was transferred to a previously tared porcelain crucible, and the bottle was again weighed. The covered crucible was placed in a desiccator containing water, and allowed to stand two or three days. The chloride was gradually converted into oxide, and when this was complete, the crucible was half filled with water and transferred to a water bath supplied with porcelain rings. In order to exclude dust a large glass funnel was suspended over the crucible. When the mass had become nearly dry, a small amount of water and several drops of pure nitric acid were added, and the evaporation continued to dryness. It was found desirable to complete the final evaporation with the lid in place, as a slight decrepitation was noticed as the oxide dried on the walls of the crucible. It was also found convenient to use a lid which was small enough to rest within the upper edge of the crucible. When the mass had become thoroughly dry, the resulting oxide was carefully ignited. Great care was necessary at this point, as the oxide had a tendency to decrepitate slightly, accompanied with a possible loss of material in the form of a fine dust. On ignition the mass became brown in color, oxides of nitrogen were expelled, and as the temperature was increased, the oxide took on the characteristic pale yellow color of ignited columbium oxide. The crucible was finally heated to constant weight with a good blast, the heat being applied for fifteen minutes between each weighing.

In the preliminary experiments nitric acid was not used and the results obtained were too low, due to a volatilization of a small amount of columbium oxide. White fumes escaped from the crucible and a sublimate formed on the under side of the crucible lid. Columbium oxide is known to form a volatile body when ignited in an atmosphere of hydrogen chloride.¹ The use of a small amount of nitric acid seemed to effectively prevent this action, the hydrochloric acid being expelled before the temperature became high enough to form a volatile body.

The exposure of columbium chloride to the air may be pointed out as a serious objection to this method of analysis. In order to test this point, a weighing bottle containing some of the chloride was carefully weighed and then allowed to remain with the stopper removed for a length of time comparable with that required to transfer the material in the determination. On reweighing the bottle its loss in weight was found to be about 0.00002 gram. It will thus be seen that the error involved, while objectionable, is not serious. When columbium chloride is exposed to

¹ Smith and Maas, *Z. anorg. Chem.*, **7**, 96 (1894), and Hall and Smith.

the air it at once becomes coated with a film of white oxide. This change can easily be detected with the eye before it would be noticed on the balance. With a little experience it was possible to transfer the chloride to the weighing bottle without the formation of such a coating.

Nearly all of the weighings were made by substitution, and the weights were standardized by the method devised by Richards.¹ In making the calculations the following atomic weights were used: O = 16 and Cl = 35.45. In making the corrections to the vacuum standard the following densities were employed: $\text{CbCl}_5 = 2.75$, $\text{Cb}_2\text{O}_5 = 5.00$ and weights = 8.4. The results obtained are contained in the following table:

Sample used.		Wt. CbCl_5 (vac.).	Wt. Cb_2O_5 (vac.).	Parts Cb_2O_5 to 100,000 parts CbCl_5 .	At. wt. of columbium.
Series.	Bulb.				
II	1	9.56379	4.71539	49.305	93.49
II	2	5.42742	2.65730	49.292	93.42
III	3	5.15992	2.54364	49.296	93.44
III	16	9.64854	4.75641	49.297	93.44
II	8	7.24572	3.57222	49.301	93.47
I	7	8.00559	3.94746	49.309	93.51
I	8	9.60763	4.73852	49.324	93.58
II	10	9.19732	4.53638	49.323	93.58
		63.85593	31.48532	49.307	93.50

An attempt was made to determine the atomic value from the ratio $\text{CbCl}_5 : 5\text{AgCl}$, by decomposing the columbium chloride with dilute ammonium hydroxide, acidifying the solution with nitric acid, filtering out the columbium hydroxide, and determining the chlorine in the filtrate as silver chloride. Several determinations were made, but the results obtained were not satisfactory. It was extremely difficult to wash out the last traces of chloride from the columbium hydroxide. In one of these determinations the columbium hydroxide was carefully collected, dried, and ignited to oxide in a weighed platinum crucible, with the following results:

Series.	Bulb.	Wt. CbCl_5 (vac.).	Wt. Cb_2O_5 (vac.).	Parts Cb_2O_5 to 100,000 parts CbCl_5 .	At. wt. of columbium.
III	13	4.27456	2.10734	49.300	93.46

These results indicate that the atomic weight of columbium as given in the International Table is probably too high. Accordingly, the value 93.5 has been used in the calculations contained in the present paper.

Columbates.

Historical.—The solubility of the fused mass obtained by heating a mixture of columbite or tantalite with sodium or potassium carbonate was recognized by the very first investigators of these minerals. Gehlen²

¹ THIS JOURNAL, 22, 144 (1900).

² Schweigger's *J. Chem. Physik.*, 6, 258 (1812).

obtained small soluble crystals from the solution of such a fusion, but the first systematic investigation of these bodies was made by H. Rose.¹

In considering Rose's work it must be borne in mind that the material which he used in the preparation of the various columbates was more or less impure, and probably always contained varying amounts of tantalum. He considered the columbates to be derivatives of "unterniobsaure," Cb_2O_3 , and after Marignac had shown that columbic acid was Cb_2O_5 , Rammelsberg² recalculated Rose's results, and the formulas obtained are given below.

$\text{Na}_2\text{O}.\text{Cb}_2\text{O}_5.6$ or $9\text{H}_2\text{O}$.—Rose described this salt as being the best crystallized and the most stable of all the salts of tantalic or columbic acids. It was prepared by fusing columbic oxide (obtained by heating columbite with acid potassium sulphate, or by decomposing columbium chloride), an acid sodium columbate or columbium hydroxide with sodium hydroxide in a silver crucible. A clear fusion did not result, and on treating the mass with water, a residue was obtained insoluble in an excess of sodium hydroxide, but soluble in water. The neutral sodium columbate was again obtained when this solution was added to a solution of sodium hydroxide. This salt was also got by heating a solution of sodium hydroxide containing columbium hydroxide in suspension. The latter did not dissolve, but after the removal of the excess of sodium hydroxide, the residue was soluble in water and on evaporating this solution the salt was obtained in a crystalline form. Finally, Rose obtained this salt by fusing columbic oxide with sodium carbonate. The fused mass was treated with water and the residue, insoluble in the excess of alkaline carbonate, was dissolved in water, the solution being allowed to stand for a long time, when on evaporating the clear liquid the neutral salt often separated in crystalline form. The following analytical results were obtained:

	Calculated.	Found (mean).			Calculated.	Found.	
Cb_2O_5	268	61.20	60.82	Cb_2O_5	268	54.47	54.05
Na_2O	62	14.16	15.86	Na_2O	62	12.60	14.40
$6\text{H}_2\text{O}$	108	24.64	$9\text{H}_2\text{O}$	162	32.93
	<hr/> 438	<hr/> 100.00	<hr/>		<hr/> 492	<hr/> 100.00	<hr/>

$3\text{Na}_2\text{O}.2\text{Cb}_2\text{O}_5.24\text{H}_2\text{O}$.—This salt was obtained but once during the preparation of the preceding salt.

$3\text{Na}_2\text{O}.\text{Cb}_2\text{O}_5$.—As calculated from the amount of carbon dioxide expelled, Rose concluded that this salt was formed when columbic oxide was fused for a long time with sodium carbonate. When treated with water it was decomposed into the neutral salt and sodium hydroxide.

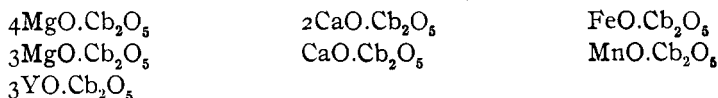
¹ *Pogg. Ann.*, 113, 105 and 292 (1861).

² *Jour. für Chem.*, 108, 77 (1869).

Wave length.	Intensity.	Wave length.	Intensity.	Wave length.	Intensity.	Wave length.	Intensity.
3341.7	3	3403.8	1	3478.1	1	3543.1	1
42.1	6	05.4	3	78.8	6	44.1	6
43.8	6	06.2	2	79.7	2	44.8	4
44.1	1	06.7	1	81.2	2	46.2	1
47.0	3	08.1	1	81.4	3	48.3	3
49.1	5	08.5	3	84.2	5	49.4	1
49.6	5	08.8	3	85.2	1	50.6	6
52.5	2	09.3	2	86.1	1	52.2	1*h
53.7	2	10.0	1	89.2	2	53.8	1*
54.8	4	13.0	4	91.2	5	54.8	9
55.5	1	14.2	2	91.6	1	56.2	1
57.1	3	16.1	3	93.6	1	58.2	1
58.5	8	18.0	2	96.2	2	59.3	1
61.0	1	20.8	4	97.9	4	60.6	1*
62.0	1	23.2	1*	98.7	8	61.3	1
63.0	1	23.9	4	3500.1	1	63.7	10
63.9	1	25.6	5	03.3	3	65.2	1*
65.7	4d, with Cu	26.0	3	05.9	2	66.2	1
67.1	7	26.7	4	07.1	1	68.2	1*
67.5	2	27.6	4	08.1	6	68.7	3
69.2	2*	29.2	5	08.6	1	69.6	3
70.0	1	31.2	1	10.4	3	71.6	1*h
71.5	2	32.1	1	11.3	2	75.3	2
72.3	1	32.7	5	12.3	1Cu	76.0	8
72.7	1	33.2	5	13.8	1*	77.9	2
74.4	1	37.1	3	15.5	5	80.4	10
75.1	4	40.1	1	16.3	1	82.5	2
76.5	1	40.8	5	17.0	2	85.1	6
76.9	3	42.8	5	17.9	3	86.9	1
80.2	2	44.4	1	19.5	1	89.2	6
80.6	6	45.8	4	20.2	4d, with Cu	91.1	1
83.0	2Ag.	48.3	1	20.8	2	92.0	1
83.9	2	50.5	4Cu	22.8	1*h	94.1	5
84.8	1Cu?	50.9	1	23.3	2	97.5	1
85.8	1	52.5	3	24.3	1Cu	98.5	1
86.4	1	55.0	1	25.4	3	99.4	2d, with Cu
87.1	1	56.7	2	26.0	1	3602.2	3Cu
87.7	3	57.9	2d, with Cu	27.2	1	02.7	5
89.1	1	58.9	2	27.6	1Cu	04.1	1
90.6	3	59.8	2	28.1	1	04.8	1
91.5	1	62.8	2	30.3	1d, with Cu	06.4	1
92.5	5	63.9	5	33.8	3d, with Cu	06.7	1
94.1	1	66.0	4	34.3	1	07.4	1
95.1	1	67.6	2	35.4	6	08.2	1
96.0	3	68.7	1	37.6	7	09.4	1*
98.4	2	69.6	3	39.8	3	10.1	1*
99.5	3	71.4	4	41.1	4	10.9	1
99.8	2	73.2	4	41.4	1	11.4	1
3401.4	1	75.7	2	42.1	1	12.8	1
03.2	1	76.1	4d, with Cu	42.7	1	15.6	2

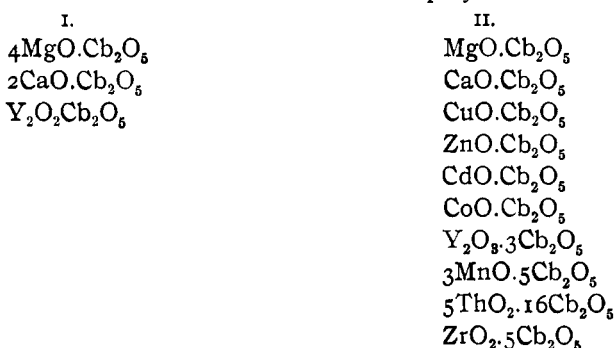
the fusion with water. The salt $\text{Na}_2\text{O} \cdot \text{Cb}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$ was soluble in water, while the salt $2\text{Na}_2\text{O} \cdot 3\text{Cb}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$, obtained by fusing the last salt mentioned with sodium hydroxide, was insoluble in water.

A. Joly¹ obtained a number of salts by heating columbic oxide with a metallic chloride at a temperature somewhat below that at which the chloride volatilized. At times the chloride was replaced by a mixture of the metallic fluoride and an alkali chloride. He obtained the following:



No analyses of these bodies are given.

Larsson² prepared a number of bodies by recrystallizing the precipitated amorphous columbates from the fused chloride of the corresponding metal, or from boron trioxide. The compounds given under I. were obtained when the fused metallic chlorides were used, and those under II. were obtained when boron trioxide was employed.



All of these salts are described as being crystalline in nature. All of the amorphous precipitates were obtained from potassium columbate. Larsson could not obtain the magnesium salt, $3\text{MgO} \cdot \text{Cb}_2\text{O}_5$, described by Joly.

P. J. Holmquist³ obtained a crystalline salt, NaCbO_3 , by fusing together columbic oxide, sodium carbonate and sodium fluoride (the last being used as a flux), which he described as being insoluble in water and acids. He also obtained a pure calcium pyrochlore to which he gave the formula $\text{NaCaCbO}_6\text{F}$.

Bedford⁴ obtained a sodium columbate to which was assigned the composition $7\text{Na}_2\text{O} \cdot 6\text{Cb}_2\text{O}_5 \cdot 32\text{H}_2\text{O}$, by recrystallizing the sodium columbate, obtained on adding sodium hydroxide to a hot solution of potassium

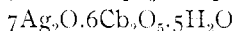
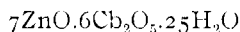
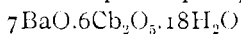
¹ *Compt. rend.*, **61**, 266 (1875).

² *Z. anorg. Chem.*, **12**, 188 (1896).

³ *Bull. geol. Instit. Upsala*, **3**, Nr. 5; *Z. anorg. Chem.*, **18**, 84 (1898).

⁴ *Thesis, Univ. of Penna.*, 1905; *THIS JOURNAL*, **27**, 1216 (1905).

fluoxycolumbate (Hermann's method). The same salt was prepared by fusing columbic oxide with sodium hydroxide and recrystallizing the product, which was insoluble in the excess of alkali, from pure water. When columbic oxide was fused with sodium carbonate, and the resulting sodium columbate was dissolved in pure water and the solution added to one of sodium carbonate, the same salt (with $36\text{H}_2\text{O}$) separated as a fine powder. From a solution of the sodium salt the following were obtained as amorphous precipitates:



Experimental.—In general, columbates of the alkali metals were obtained by fusing columbium oxide with the alkali carbonates. The products obtained depended in part upon the relative quantities of oxide and carbonate used. When too small an amount of carbonate was employed insoluble acid columbates were produced, while the use of ample quantities of potassium, rubidium, or cesium carbonates gave perfectly clear fusions which were completely soluble in small amounts of water. However, when sodium carbonate was used a clear fusion was not obtained, and the resulting columbate was not soluble in the presence of the excess of alkali carbonate, but dissolved completely in pure water.

Analysis: The water of crystallization was determined as loss on ignition. The columbic acid was precipitated from solutions of the alkali columbates by the addition of sulphuric acid, and the alkali metal was determined as sulphate in the filtrate. Exceptions to this method of analysis will be noted under the individual salts.

1:1 Columbates.—In order to obtain a sodium columbate to serve in the preparation of a sodium percolumbate, recourse was had to the method of Hermann as outlined by Bedford in his study of the 7:6 sodium columbate. A large quantity of this salt was prepared and recrystallized twice from water. A sample of this salt gave the following results on analysis:

0.6896 gram of salt lost 0.1490 gram on ignition, corresponding to 21.61 per cent. H_2O .

0.9169 gram of salt gave 0.5652 gram of Cb_2O_3 and 0.3542 gram of Na_2SO_4 , or 61.64 per cent. of Cb_2O_3 and 16.87 per cent. of Na_2O .

		Calculated.	Found.
$7\text{Na}_2\text{O}$	434	16.73	16.87
$6\text{Cb}_2\text{O}_3$	1602	61.76	61.64
$31\text{H}_2\text{O}$	558	21.51	21.51
	<hr/>	<hr/>	<hr/>
	2594	100.00	100.12

The clear mother liquors from the recrystallization of this salt were placed in a three-liter platinum dish, the latter being covered with a sheet of filter paper, and the solution was allowed to evaporate spontaneously.

On examining the dish several weeks later, a large quantity of beautiful triclinic crystals was found to have separated from the solution. On analysis they proved to have the composition $\text{Na}_2\text{O} \cdot \text{Cb}_2\text{O}_5 \cdot 7\text{H}_2\text{O}$. A second preparation, made in the same way, gave identical results. It seems very probable that Rose obtained this salt in an impure form and that it is the one to which Rammelsberg assigned the composition $\text{Na}_2\text{O} \cdot \text{Cb}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$, a conclusion reached from a comparison of Rose's results given on page 1647 with those which follow.

Analyses of powdered samples from the two preparations gave:

Calculated: Na_2O , 13.63; Cb_2O_5 , 58.68; $7\text{H}_2\text{O}$, 27.69. Found: Na_2O , 13.77, 13.86; Cb_2O_5 , 58.70, 58.73; $7\text{H}_2\text{O}$, 27.76, 27.80.

*Crystallography.*¹—The crystal habit of this salt is shown in Fig. 4. The crystals were about 2 mm. in length and fairly brilliant. Their faces, however, were more or less striated and irregular, giving multiple or indistinct images. Consequently the results obtained, although representing the means of the measurements from about twenty crystals, can only be considered as approximately correct.

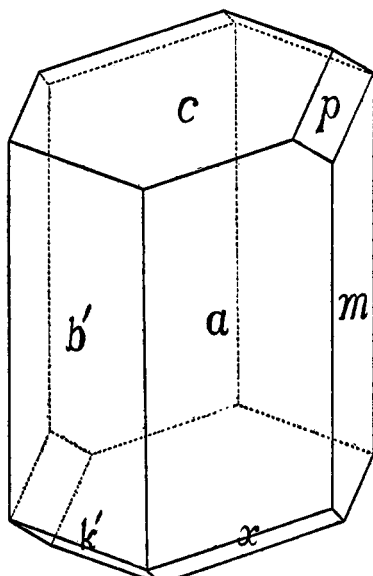


Fig. 4.

Triclinic.—Axes, $\tilde{a} : \tilde{b} : \tilde{c}$ 0.9559: 1: 0.8394. $\alpha = 71^\circ 20'$; $\beta = 105^\circ 30'$; $\gamma = 54^\circ 7'$.

Measured.	Measured.	Calculated.
ac, $100 \wedge 001 = * 53^\circ 40'$	cm', $001 \wedge 110 = 89^\circ 45'$	$89^\circ 55'$
bc, $010 \wedge 001 = * 127^\circ 38'$	cp, $001 \wedge 111 = 36^\circ 52'$	$36^\circ 25'$
ab, $100 \wedge 010 = * 137^\circ 22'$	mp, $110 \wedge 111 = 53^\circ 23'$	$53^\circ 40'$
bm, $010 \wedge 110 = * 70^\circ 45'$	ck, $001 \wedge 011 = 63^\circ 34'$	$63^\circ 43'$
cx', $001 \wedge 101 = * 64^\circ 40'$	bk, $010 \wedge 011 = 64^\circ 4'$	$63^\circ 55'$

Magnesium Columbate, $\text{MgO} \cdot \text{Cb}_2\text{O}_5 \cdot 7\text{H}_2\text{O}$.—This salt was obtained as a white, flocculent precipitate when a solution of magnesium chloride was added to a solution of the 1:1 sodium columbate. It was washed by decantation, filtered out and dried on a water bath for several hours.

Analysis: A sample was ignited in a platinum crucible, the loss in weight representing the water. The ignited material was then fused with potassium bisulphate, the melt treated with boiling water and the

¹ Sincere thanks are here given to Professor Amos P. Brown and to Dr. Charles Travis, both of this University, for invaluable suggestions and assistance in connection with the crystallographic part of the investigation.

columbium oxide filtered out. The magnesium was determined in the filtrate as usual.

Calculated: MgO , 9.32; Cb_2O_3 , 61.61; $7\text{H}_2\text{O}$, 29.07.

Found: MgO , 9.47; Cb_2O_3 , 61.51; $7\text{H}_2\text{O}$, 29.17.

Silver Salts, $\text{Ag}_2\text{O} \cdot \text{Cb}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$.—When a solution of silver nitrate was added to a solution of the 1:1 sodium columbate, a white precipitate was formed which had a slight yellow color when dry. It darkened slowly on exposure to sunlight. In the analysis of this salt the water content was determined directly.

Calculated: Ag_2O , 43.36; Cb_2O_3 , 49.91; $2\text{H}_2\text{O}$, 6.73.

Found: Ag_2O , 43.05; Cb_2O_3 , 49.53; $2\text{H}_2\text{O}$, 6.61.

Copper Salt, $\text{CuO} \cdot \text{Cb}_2\text{O}_3 \cdot 3\frac{1}{2}\text{H}_2\text{O}$.—This salt was obtained as a green precipitate on adding a solution of copper sulphate to a solution of the 1:1 sodium columbate. On ignition it became deep brown in color.

Calculated: CuO , 19.43; Cb_2O_3 , 65.19; $3.5\text{H}_2\text{O}$, 15.38.

Found: CuO , 19.37; Cb_2O_3 , 65.23; $3.5\text{H}_2\text{O}$, 14.97.

Aluminium Columbate, $\text{Al}_2\text{O}_3 \cdot 3\text{Cb}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$.—This salt appeared as a white precipitate when a solution of alum was added to a solution of sodium columbate.

Calculated: Al_2O_3 , 9.12; $3\text{Cb}_2\text{O}_3$, 71.58; $12\text{H}_2\text{O}$, 19.30.

Found: Al_2O_3 , 9.52; $3\text{Cb}_2\text{O}_3$, 71.51; $12\text{H}_2\text{O}$, 18.97.

Cadmium Salt, $\text{CdO} \cdot \text{Cb}_2\text{O}_3 \cdot 3\frac{1}{2}\text{H}_2\text{O}$.—This salt was obtained as a yellowish white precipitate when a cadmium salt solution was added to a solution of the 1:1 sodium columbate.

Calculated: CdO , 28.01; Cb_2O_3 , 58.25; $3.5\text{H}_2\text{O}$, 13.74.

Found: CdO , 28.06 (diff.); Cb_2O_3 , 58.03; $3.5\text{H}_2\text{O}$, 13.91.

4:3 Columbates.

Potassium Salt, $4\text{K}_2\text{O} \cdot 3\text{Cb}_2\text{O}_3 \cdot 16\text{H}_2\text{O}$.—Marignac prepared this salt by fusing columbic oxide with 2-3 parts of potassium carbonate. It crystallizes in large well defined monoclinic crystals, very soluble in water. This salt was made a number of times and in one instance 40 grams of columbic oxide were fused with 70 grams of potassium carbonate, and the fused mass heated with a blast lamp as long as any carbon dioxide was expelled. The melt was completely soluble in water and the solution, on standing, deposited crystals several centimeters in length. Crystals from two different preparations were analyzed with the following results:

Calculated: $4\text{K}_2\text{O}$, 25.72; $3\text{Cb}_2\text{O}_3$, 54.64; $16\text{H}_2\text{O}$, 19.64.

Found: $4\text{K}_2\text{O}$, 25.90, 26.11; $3\text{Cb}_2\text{O}_3$, 54.22, 54.49; $16\text{H}_2\text{O}$, 19.77, 19.39.

Marignac found: K_2O , 25.32; Cb_2O_3 , 53.88; H_2O , 19.12.

Crystallography.—The crystal habit of this salt is shown in Fig. 5. The pyramid faces d and d' were observed on only a few of the crystals which were examined. It was not difficult to obtain crystals of this

salt giving good reflections of the signal when measured with the goniometer.

Monoclinic.—Axes, $\bar{a} : \bar{b} : \bar{c} = 0.7120 : 1 : 0.5547$. $\beta = 84^\circ 19'$.			
	Measured.	Calculated.	Marignac found.
mm'', $110 \wedge 1\bar{1}0 =$	$70^\circ 38'$	$70^\circ 40'$
cm, $001 \wedge 110 =$	$85^\circ 22'$	$85^\circ 30'$
cn, $001 \wedge \bar{1}\bar{1}1 =$	$45^\circ 53'$
cn'', $001 \wedge 11\bar{1} =$	$134^\circ 7'$	$134^\circ 7'$	$134^\circ 6'$
cz, $001 \wedge 021 =$	$47^\circ 51'$	$47^\circ 50'$	$47^\circ 50'$
cd, $001 \wedge 111 =$	$41^\circ 20'$	$41^\circ 27\frac{1}{2}'$
nz, $\bar{1}\bar{1}1 \wedge 021 =$	$39^\circ 8'$	$39^\circ 6\frac{1}{2}'$
mz, $110 \wedge 021 =$	$68^\circ 6'$	$68^\circ 1\frac{1}{2}'$
m'z, $\bar{1}10 \wedge 021 =$	$61^\circ 8'$	$61^\circ 8\frac{1}{2}'$
nn', $\bar{1}\bar{1}1 \wedge \bar{1}\bar{1}\bar{1} =$	$49^\circ 13'$	$49^\circ 13'$
bn, $010 \wedge \bar{1}\bar{1}1 =$	$65^\circ 20'$	$65^\circ 23\frac{1}{2}'$	$65^\circ 18'$

Rubidium Salt, $4\text{Rb}_2\text{O} \cdot 3\text{Cb}_2\text{O}_5 \cdot 14\text{H}_2\text{O}$.—In the first preparation of this salt 15 grams of columbium oxide were fused with 20 grams of rubidium carbonate. On taking up the melt with water a mass of fine needles remained insoluble. These proved to be an acid rubidium columbate. On concentrating the filtrate from these needles, beautiful monoclinic crystals separated having the composition indicated above. This salt was very soluble in water and it slowly lost water on exposure to the air. On ignition in a platinum crucible the crystals lost their water content and finally fused to a transparent liquid, which solidified to a crystalline mass on cooling. On treating this mass with water a part of the rubidium oxide dissolved, leaving a mass of pearly needles which were probably identical with those mentioned above.

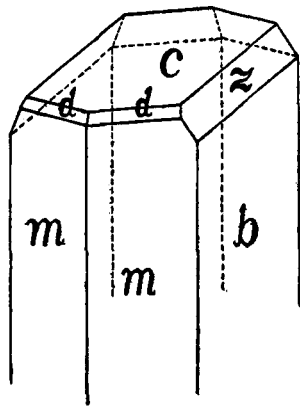


Fig. 5.

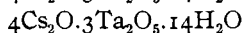
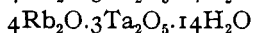
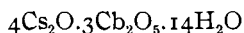
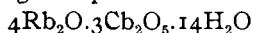
Calculated: $4\text{Rb}_2\text{O}$, 41.53; $3\text{Cb}_2\text{O}_5$, 44.48; $14\text{H}_2\text{O}$, 13.99.

Found: $4\text{Rb}_2\text{O}$, 42.20; $3\text{Cb}_2\text{O}_5$, 44.26; $14\text{H}_2\text{O}$, 14.10.

In a second preparation, 10 grams of columbium oxide were fused with 25 grams of rubidium carbonate, and in this case the melt was completely soluble in water.

Found: $4\text{Rb}_2\text{O}$, 41.66; $3\text{Cb}_2\text{O}_5$, 44.63; $14\text{H}_2\text{O}$, 13.82.

Crystallography.—This salt is one of four isomorphous salts obtained during the present investigation. They are:



The angular measurements of the crystals of these salts were identical within the limits of error made in the measurements. It was difficult

to get good measurements in the case of the cesium salts, but very good results were obtained with the rubidium salts. Many excellent crystals were obtained, some of them having a diameter of 15 mm. or more, but on exposure to the air they gradually became moist and then dull, making them unfit for further measurement with the goniometer. The crystal habit is shown in Fig. 6.

The measurements obtained from crystals of the rubidium columbate are as follows:

Monoclinic.—Axes, $a : b : c = 0.8815 : 1 : 1.0491$. $\beta = 84^\circ 7'$.		
	Measured.	Calculated.
dd' , $III \wedge I\bar{I}I =$	$65^\circ 13'$
dn , $III \wedge I\bar{I}I =$	$78^\circ 55'$
nn' , $I\bar{I}I \wedge I\bar{I}I =$	$70^\circ 36'$
dn'' , $III \wedge I\bar{I}I =$	$64^\circ 27'$	$64^\circ 30'$
cd , $00I \wedge III =$	$54^\circ 29'$	$54^\circ 35'$
ad , $100 \wedge III =$	$48^\circ 13'$	$48^\circ 7'$
ac , $100 \wedge 00I =$	$84^\circ 10'$	$84^\circ 7'$

Cesium Salt, $4Cs_2O \cdot 3Cb_2O_5 \cdot 14H_2O$.—For the preparation of this salt 10 grams of columbium oxide were fused with 30 grams of cesium carbonate.

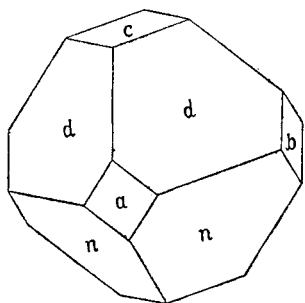


Fig. 6.

All of the cesium salts used in the present investigation were purified by recrystallizing the salt $CsCl_2I$.¹ The melt was completely soluble in water and from the solution monoclinic crystals separated which were isomorphous with the preceding salt. When ignited this salt behaved like the corresponding rubidium salt. On treating the fused salt with water a small quantity of fine pearly needles remained insoluble; they were probably an acid cesium columbate corresponding

to the acid rubidium columbate which was mentioned above. This salt was not obtained in quantities large enough to admit of analysis.

Calculated: $4Cs_2O$, 51.72; $3Cb_2O_5$, 36.73; $14H_2O$, 11.55.

Found: $4Cs_2O$, 51.42; $3Cb_2O_5$, 36.95; $14H_2O$, 11.88.

7:6 Columbates.

Potassium Salt, $7K_2O \cdot 6Cb_2O_5 \cdot 27H_2O$.—By recrystallizing the 4:3 potassium columbate from water, Marignac obtained a salt to which he assigned the composition $8K_2O \cdot 7Cb_2O_5 \cdot 32H_2O$. The result of his analyses, however, are not far from the requirements of the 7:6 ratio obtained in the present investigation, and in the light of our results, it seems quite probable that the salt which he had in hand was of the latter type.

This salt was obtained by adding alcohol to a solution of the 4:3 salt.

¹ Wells, *Amer. Jour. Sci.*, 43, 17 (1892).

It was precipitated by this treatment, dissolved in water and again precipitated by alcohol, filtered out by suction and finally washed with alcohol and ether. Analysis I.

An aqueous solution of this precipitated salt deposited crystals having the same form as those obtained by Marignac. A sample was ground to a powder and analyzed. Analysis II.

For the sake of comparison the mean of Marignac's analyses and the requirements for an 8:7 ratio are included in the following table.

Calculated for $7K_2O \cdot 6Cb_2O_5 \cdot 27H_2O$.		Found.		Marignac. Per cent.	Calculated for $8K_2O \cdot 7Cb_2O_5 \cdot 32H_2O$.
Per cent.		I. Per cent.	II. Per cent.		Per cent.
$7K_2O$	660 24.02	24.10	24.15	23.47	23.57
$6Cb_2O_5$	1602 58.30	58.21	58.31	58.35	58.42
$27H_2O$	486 17.68	17.83	17.61	17.35	18.01
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	2748 100.00	100.14	100.07	99.17	100.00

Lithium Salt, $7Li_2O \cdot 6Cb_2O_5 \cdot 26H_2O$.—A solution of lithium nitrate, containing sufficient lithium carbonate to render it slightly alkaline, was added to a strong solution of the 7:6 potassium columbate. Upon warming the solution a crystalline salt separated which was filtered out, washed with cold water and dried on a porous plate.

Calculated: $7Li_2O$, 9.21; $6Cb_2O_5$, 70.26; $26H_2O$, 20.53.

Found: $7Li_2O$, 9.22; $6Cb_2O_5$, 70.28; $26H_2O$, 20.44.

Cesium Salt, $7Cs_2O \cdot 6Cb_2O_5 \cdot 30H_2O$.—On adding alcohol to an aqueous solution of the 4:3 cesium columbate, a heavy oily-appearing liquid separated on the bottom of the beaker. On further washing with alcohol this solidified to a crystalline mass. This was filtered out, washed with alcohol and dried between folds of filter paper. On ignition it behaved like the 4:3 salt.

Calculated: $7Cs_2O$, 47.96; $6Cb_2O_5$, 38.92; $30H_2O$, 13.12.

Found: $7Cs_2O$, 47.93; $6Cb_2O_5$, 38.71; $30H_2O$, 13.14.

3:4 Rubidium Columbate, $3Rb_2O \cdot 4Cb_2O_5 \cdot 9\frac{1}{2}H_2O$.—This salt, consisting of fine silky needles, was obtained when columbium oxide was fused with a limited amount of rubidium carbonate, or when the 4:3 rubidium columbate was ignited to the point of fusion. It was very difficult to obtain a pure sample for analysis, but the results obtained agree fairly well with those required by the formula given above.

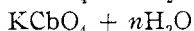
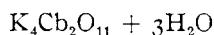
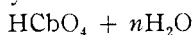
Analysis: The water was determined as loss on ignition. The ignited sample was then dissolved in hydrofluoric acid, and the analysis completed as in the case of the double fluorides.

Calculated: $3Rb_2O$, 31.17; $4Cb_2O_5$, 59.33; $9.5H_2O$, 9.50.

Found: $3Rb_2O$, 30.66; $4Cb_2O_5$, 60.33; $9.5H_2O$, 9.52.

Percolumbates.

The following percolumbates have been described by Melikoff and Pissarjewsky:¹



The free percolumbic acid was obtained by heating columbium hydroxide with a 30 per cent. solution of hydrogen peroxide, or by adding dilute sulphuric acid to a solution of the potassium percolumbate, dialyzing out the excess of sulphuric acid and potassium sulphate, and then evaporating the clear yellow solution to dryness on a water bath. It is described as being a yellow amorphous powder, insoluble in water.

Hall and Smith² obtained a yellow precipitate on adding a solution of hydrogen peroxide to a hydrochloric acid solution of columbium hydroxide. This proved to be a hydrated percolumbic acid to which they assigned the composition $\text{Cb}(\text{OH})_6$ or $\text{Cb}_2\text{O}_5\text{H}_2\text{O}_2 \cdot 5\text{H}_2\text{O}$.

During the present investigation the following percolumbates were obtained:

I.	II.	
Na_3CbO_8	$\text{MgNaCbO}_8 \cdot 8\text{H}_2\text{O}$	$\text{CaNaCbO}_8 \cdot 4\text{H}_2\text{O}$
K_3CbO_8	$\text{MgKCbO}_8 \cdot 7\text{H}_2\text{O}$	$\text{CaKCbO}_8 \cdot 4\text{H}_2\text{O}$
Rb_3CbO_8	$\text{MgRbCbO}_8 \cdot 7\frac{1}{2}\text{H}_2\text{O}$	
Cs_3CbO_8	$\text{MgCsCbO}_8 \cdot 8\text{H}_2\text{O}$	

The compounds given under I were produced by adding hydrogen peroxide in excess to solutions containing the corresponding columbates and an excess of the proper alkali carbonate or hydroxide. They were most easily obtained from such solutions by the addition of an equal volume of alcohol, the percolumbate separating as a white powder, which was filtered by suction and finally washed with alcohol and ether. They were perfectly stable in the air and dissolved in warm water without decomposition. However, oxygen escaped when their solutions were heated to the boiling temperature. On exposure to the light, the rubidium and cesium percolumbates darkened perceptibly. This was particularly true in the case of the cesium salt.

Analysis: One half of the oxygen present in the percolumbates is active and is expelled on ignition. The ignition was made in a hard glass tube containing a plug of asbestos to prevent mechanical loss of material. The loss in weight represented the active oxygen. A second sample was dissolved in water and treated with dilute sulphuric acid. No precipitate was produced at first, but on boiling the solution a part of the active oxygen was expelled and a yellow precipitate separated, probably a hydrated peroxide of columbium. This was filtered out,

¹ *Z. anorg. Chem.*, **20**, 340 (1899).

² *THIS JOURNAL*, **27**, 1369 (1905).

washed, ignited and weighed as columbic oxide, Cb_2O_5 . The filtrate was evaporated to dryness and the alkali determined as sulphate. The latter usually contained a small amount of columbium so that it was generally necessary to dissolve the ignited sulphate in a small amount of water, filter out the columbium hydroxide and finally reweigh the alkali sulphate.

Sodium Percolumbate, Na_3CbO_8 .—This salt was more difficult to prepare than the corresponding percolumbate of the other alkali metals, because of the comparative insolubility of the sodium columbate used as the starting-out material. The following procedure was finally adopted for its preparation: sodium columbate (the 7:6 salt, one part) was dissolved in as little boiling water as possible, the solution was added to a warm solution of hydrogen peroxide and sodium hydroxide (75–100 parts of a 3 per cent. solution of hydrogen peroxide and 2 parts of sodium hydroxide), the solution was filtered by suction, and an equal volume of alcohol was then added. The percolumbate, precipitated by this treatment, was filtered out by suction, dissolved in warm water and again treated with a 3 per cent. solution of hydrogen peroxide containing a small amount of sodium hydroxide. The sodium percolumbate was again precipitated from the solution by the addition of an equal volume of alcohol, filtered by suction and finally washed with alcohol and ether.

Calculated: $1.5\text{Na}_2\text{O}$, 32.01; $0.5\text{Cb}_2\text{O}_5$, 45.96; 4O , 22.03.

Found: $1.5\text{Na}_2\text{O}$, 31.88; $0.5\text{Cb}_2\text{O}_5$, 45.75; 4O , 21.85.

Potassium Percolumbate, K_3CbO_8 .—A portion of this salt, obtained by precipitation with alcohol as previously described, gave the following results on analysis:

Calculated: $1.5\text{K}_2\text{O}$, 41.74; $0.5\text{Cb}_2\text{O}_5$, 39.38; 4O , 18.88.

Found: $1.5\text{K}_2\text{O}$, 40.90; $0.5\text{Cb}_2\text{O}_5$, 39.35; 4O , 18.96.

It was found possible to prepare this salt without the use of alcohol. A warm solution of 10 grams of the 4:3 potassium columbate and 40 grams of potassium hydroxide, free from sodium, were added to an excess of a 3 per cent. hydrogen peroxide solution. A large quantity of the potassium percolumbate separated immediately in the form of small but well defined tetragonal crystals showing the faces of the prism and pyramid of reverse orders. Measured with the microscope, the angle between the intersection of the faces a and c (Fig. 7) and the intersection of the faces c and p was found to be 45° , and the upper angle between the vertical edge of aa ($100 \wedge 010$)

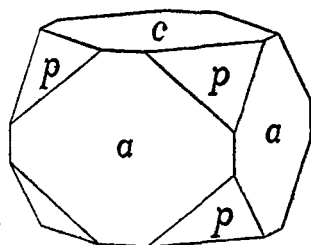


Fig. 7.

and the intersection of the faces a (100) and b (111) was found to be $49^{\circ} 50'$, giving 0.844 as the value of b .

These crystals gave the following results on analysis:

Found: $1.5\text{K}_2\text{O}$, 41.82; $0.5\text{Cb}_2\text{O}_3$, 39.45; 4O , 18.91.

This salt was prepared a number of times with identical results, and inasmuch as perfectly analogous salts were obtained with the other alkali metals, the work of Melikoff and Pissarjewsky on the potassium percolumbate, to which they assigned the composition $\text{K}_4\text{Cb}_2\text{O}_{11} \cdot 3\text{H}_2\text{O}$, was repeated following their directions as closely as possible. They made their salt as follows: Columbic oxide was fused with potassium hydroxide ($1\text{Cb}_2\text{O}_3$ to 8KOH) in a silver crucible. The fusion was dissolved in a small amount of water and after the addition of a small quantity of hydrogen peroxide, the solution was warmed for a short time on a water bath. Any black precipitate (silver) which separated was filtered out, hydrogen peroxide ($1\text{Cb}_2\text{O}_3$ to $9\text{--}10\text{H}_2\text{O}_2$) was added to the solution and this was followed by an equal volume of alcohol, whereupon a flocculent white precipitate separated, which was washed with alcohol and ether and dried on a porous plate. This precipitate was dissolved in water, hydrogen peroxide ($1\text{Cb}_2\text{O}_3$ to $3\text{--}4\text{H}_2\text{O}_2$) and potassium hydroxide ($1\text{Cb}_2\text{O}_3$ to $1/2\text{KOH}$) were added to the solution and the salt was again precipitated by the addition of alcohol ($1\text{--}1\frac{1}{2}$ vol.). The product was a white crystalline precipitate which was washed with alcohol and ether.

This procedure was carried out a number of times, but the salt described by Melikoff and Pissarjewsky was not obtained. In nearly every case the salt K_3CbO_3 appeared, and it seems very probable that the latter salt will always be formed when the solution contains a sufficient amount of hydrogen peroxide to yield the requisite quantity of oxygen. The potassium hydroxide used in the preparation of this salt must be free from sodium, for otherwise the 7:6 sodium columbate will result from the fusion of the columbic oxide with the hydroxide and remain insoluble in the alkaline solution when the melt is treated with water.

Rubidium Percolumbate, Rb_3CbO_3 .—An excess of hydrogen peroxide was added to a solution containing 4 grams of the 4:3 rubidium columbate and 10 grams of rubidium carbonate. On adding an equal volume of alcohol a white crystalline powder was precipitated from the solution. This was filtered out, washed with alcohol and ether and allowed to dry in the air.

Calculated: $1.5\text{Rb}_2\text{O}$, 58.68; $0.5\text{Cb}_2\text{O}_3$, 27.93; 4O , 13.39.

Found: $1.5\text{Rb}_2\text{O}$, 58.34; $0.5\text{Cb}_2\text{O}_3$, 27.66; 4O , 13.26.

Cesium Percolumbate, Cs_3CbO_3 .—This salt was prepared in the same manner as the rubidium salt, and gave the following analysis:

Calculated: $1.5\text{Cs}_2\text{O}$, 68.17; $0.5\text{Cb}_2\text{O}_3$, 21.52; 4O , 10.31.

Found: $1.5\text{Cs}_2\text{O}$, 67.91; $0.5\text{Cb}_2\text{O}_3$, 21.46; 4O , 10.31.

The substances, whose formulas are given under II, are all crystalline salts obtained when solutions of magnesium or calcium chlorides are added to solutions of the previously described percolumbates. The magnesium salts are soluble in water without decomposition, but they are less soluble than the corresponding percolumbates, while the calcium salts are difficultly soluble in water.

For the preparation of these salts the percolumbate was dissolved in as little warm (50°) water as possible and to this solution there was added a strong neutral or slightly alkaline solution of the alkaline-earth chloride. The double percolumbate crystallized from the solution, usually in the form of very fine silky needles, which were filtered out and washed with alcohol and ether. It was sometimes found desirable to add a small amount of alcohol to the solution to render the separation of the salt more complete. This was particularly true in the case of the rubidium and cesium salts.

Analysis: For the determination of the active oxygen and water a sample was weighed out in a short, hard glass tube closed at one end. A plug of asbestos was placed in the tube above the salt to prevent loss by decrepitation and after being weighed the tube was connected to the top of a Hempel gas burette by means of a short piece of rubber tubing. On gently heating the tube, water was expelled at first, and then at a high temperature oxygen was evolved, and from its corrected volume the amount of active oxygen in the salt was easily calculated. The tube was reweighed and its loss in weight gave the sum of the active oxygen and water, the latter being finally determined by difference.

To complete the analysis of the magnesium salts, a sample was dissolved in water and treated with a few drops of dilute sulphuric acid. No precipitate was formed at first, but a yellow color was produced. On adding a small amount of alcohol and boiling, oxygen was expelled and a yellow hydrated percolumbic acid was precipitated. This was filtered out, the filtrate was evaporated to a small bulk and heated until the vapors of sulphuric acid escaped. On taking up the residue in water, an additional quantity of columbium hydroxide was obtained. This was filtered out and the magnesium was determined in the filtrate as usual. The alkali oxide was determined by difference. In one or two cases the ignited salt was fused with potassium bisulphate, the mass was treated with water and the columbium hydroxide was filtered out and weighed as usual. The magnesium was determined in the filtrate.

In the case of the calcium salts the precipitation of the columbium hydroxide was made with nitric acid, but in other respects the method of analysis was the same as that described above.

Magnesium Sodium Percolumbate, $MgNaCbo_8.8H_2O$.—In the preparation of this salt a small amount of a flocculent precipitate was produced

when a solution of magnesium chloride was added to a solution of sodium percolumbate. This was filtered out as rapidly as possible and the above salt separated from the filtrate.

Calculated: MgO , 9.78; $0.5\text{Na}_2\text{O}$, 7.51; $0.5\text{Cb}_2\text{O}_3$, 32.33; 4O , 15.50; $8\text{H}_2\text{O}$, 34.88.
Found: MgO , 9.84; $0.5\text{Na}_2\text{O}$, 7.40 (diff.); $0.5\text{Cb}_2\text{O}_3$, 32.23; 4O , 14.89; $8\text{H}_2\text{O}$, 35.64.

Magnesium Potassium Percolumbate, $\text{MgKCbO}_8 \cdot 7\text{H}_2\text{O}$.—Analysis:

Calculated: MgO , 9.83; $0.5\text{K}_2\text{O}$, 11.46; $0.5\text{Cb}_2\text{O}_3$, 32.48; 4O , 15.57; $7\text{H}_2\text{O}$, 30.66.
Found: MgO , 9.88; $0.5\text{K}_2\text{O}$, 11.56 (diff.); $0.5\text{Cb}_2\text{O}_3$, 32.46; 4O , 15.48; $7\text{H}_2\text{O}$, 30.62.

Magnesium Rubidium Percolumbate, $\text{MgRbCbO}_8 \cdot 7\frac{1}{2}\text{H}_2\text{O}$.—This salt gave the following results on analysis:

Calculated: MgO , 8.66; $0.5\text{Rb}_2\text{O}$, 20.05; $0.5\text{Cb}_2\text{O}_3$, 28.62; 4O , 13.72; $7.5\text{H}_2\text{O}$, 28.95.
Found: MgO , 9.21; $0.5\text{Rb}_2\text{O}$, 19.26 (diff.); $0.5\text{Cb}_2\text{O}_3$, 28.81; 4O , 13.47; $7.5\text{H}_2\text{O}$, 29.25.

Magnesium Cesium Percolumbate, $\text{MgCsCbO}_8 \cdot 8\text{H}_2\text{O}$.—This salt gave the following analytical results:

Calculated: MgO , 7.73; $0.5\text{Cs}_2\text{O}$, 26.96; $0.5\text{Cb}_2\text{O}_3$, 25.53; 4O , 12.24; $8\text{H}_2\text{O}$, 27.54.
Found: MgO , 7.89; $0.5\text{Cs}_2\text{O}$, 26.81 (diff.); $0.5\text{Cb}_2\text{O}_3$, 25.77; 4O , 12.18; $8\text{H}_2\text{O}$, 27.35.

Calcium Sodium Percolumbate, $\text{CaNaCbO}_8 \cdot 4\text{H}_2\text{O}$.—Analysis:

Calculated: CaO , 15.71; $0.5\text{Na}_2\text{O}$, 8.69; $0.5\text{Cb}_2\text{O}_3$, 37.45; 4O , 17.95; $4\text{H}_2\text{O}$, 20.20.
Found: CaO , 16.50; $0.5\text{Na}_2\text{O}$, 8.16 (diff.); $0.5\text{Cb}_2\text{O}_3$, 37.31; 4O , 16.79; $4\text{H}_2\text{O}$, 21.24.

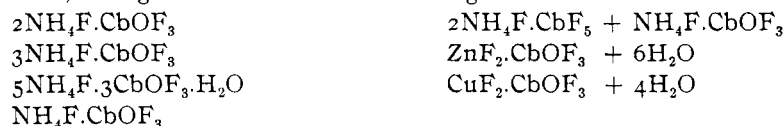
Calcium Potassium Percolumbate, $\text{CaKCbO}_8 \cdot 4\text{H}_2\text{O}$.—This salt gave the following analysis:

Calculated: CaO , 15.03; $0.5\text{K}_2\text{O}$, 12.64; $0.5\text{Cb}_2\text{O}_3$, 35.83; 4O , 17.18; $4\text{H}_2\text{O}$, 19.32.
Found: CaO , 15.49; $0.5\text{K}_2\text{O}$, 13.03 (diff.); $0.5\text{Cb}_2\text{O}_3$, 35.41; 4O , 16.74; $4\text{H}_2\text{O}$, 19.33.

Double Fluorides of Columbium.

H Rose¹ studied certain double fluorides of columbium with sodium and potassium, but his results are of little present value, due probably to the impurity of his material.

In addition to the sodium and potassium salts, which will be mentioned later, Marignac described the following double fluorides of columbium:²

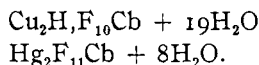
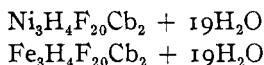


Santesson³ obtained a salt to which he assigned the composition $\text{Zn}_5\text{H}_5\text{F}_{30}\text{Cb}_3 + 28\text{H}_2\text{O}$ by evaporating a solution of zinc carbonate and columbic acid in concentrated hydrofluoric acid. It was insoluble in cold water and decomposed by hot water. Perfectly analogous salts of cadmium, manganese, cobalt and nickel were obtained. The following were also prepared and are described as crystalline substances:

¹ *Pogg. Ann.*, **104**, 581, 1858.

² *Bibl. Univ. Archives*, **23**, 249 (1865).

³ *Bull. soc. chim.* [2], **24**, 52; *J. B.*, 1875, 218.



Krüss and Nilson¹ assigned the composition $2\text{KF} \cdot 3\text{CbO}_2\text{F}$ to the white precipitate obtained on boiling a solution of the ordinary potassium fluoxycolumbate.

Piccini² obtained a potassium fluoxypercolumbate having the composition $\text{K}_2\text{CbO}_2\text{F}_5 \cdot \text{H}_2\text{O}$. This salt has been further studied by Hall and Smith.

Pennington³ described two double fluorides of columbium to which were assigned the formulas $2\text{RbF} \cdot \text{CbF}_5$ and $7\text{CsF} \cdot \text{CbF}_5$.

Sodium Salts.—In his study of the double fluorides of columbium, Marignac states that he obtained the sodium salts in the form of crystalline crusts having a more or less indefinite composition. No analyses are given, but he claims that his results point to the existence of at least two fluoxycolumbates of sodium having the composition indicated by the formulas $2\text{NaF} \cdot \text{CbOF}_3 \cdot 2\text{H}_2\text{O}$ and $\text{NaF} \cdot \text{CbOF}_3 \cdot \text{H}_2\text{O}$.

We were unable to confirm conclusively the existence of these two salts, but our results indicate the probable existence of a number of double fluorides of columbium with sodium. Inasmuch as they crystallize very poorly, we were able to obtain but one of them sufficiently pure to deduce a formula.

$3\text{NaF} \cdot \text{CbOF}_3$.—Thirty grams of columbic oxide and 24 of sodium carbonate were dissolved in hydrofluoric acid, and the solution was evaporated to dryness several times to expel the excess of acid. The salt was then dissolved in hot water and allowed to crystallize. A crystalline crust which separated from the solution was removed and crystallized from water. The salt, which again separated in crystalline crusts, had the composition indicated above, as shown by the following analyses:

Calculated: 3Na, 23.59; Cb, 31.97; 6F, 38.97.

Found: 3Na, 23.57, 23.62; Cb, 32.15, 32.14; 6F, 38.88.

$3\text{NaF} \cdot \text{CbO}_2\text{F}_3 \cdot \text{H}_2\text{O}$.—Hydrogen peroxide and a few drops of hydrofluoric acid were added to a solution of the above salt, and the yellow solution thus obtained was allowed to evaporate spontaneously. On long standing, beautiful, well defined crystals separated. They were of a pale yellow color and when removed from the solution they were perfectly transparent, but gradually became dull and opaque on continued exposure to the air.

Calculated: 3Na, 21.13; Cb, 28.64; 6F, 34.92; O (active), 4.90; H_2O , 5.51.

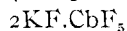
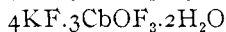
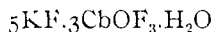
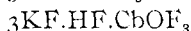
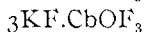
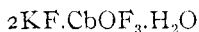
Found: 3Na, 21.05; Cb, 28.27; 6F, 35.64; O (active), 4.66; H_2O , 5.20.

¹ *Ber.*, 20, 1689 (1887).

² *Z. anorg. Chem.*, 2, 21 (1892).

³ *THIS JOURNAL*, 18, 38 (1896).

Potassium Salts.—Marignac described and analyzed the following double fluorides of potassium and columbium:



The first of these salts is the one ordinarily obtained and is formed when any of the other salts are recrystallized from water. The last salt in the series is produced when the other salts are recrystallized from strong hydrofluoric acid. Its use in the purification of columbium has already been described. Because of the large number and the complexity of some of these salts described by Marignac, it was thought worth while to prepare them again with the pure material at hand. Our results confirm the existence of all of them.

$3\text{KF} \cdot \text{CbOF}_3$.—This salt, which Marignac designated the cubic fluoxycolumbate of potassium, crystallizes from solutions containing an excess of potassium fluoride. In describing the crystalline form of this salt, Marignac said: "These crystals have exactly the appearance of cubes without any modification. But optical examination proves that they belong neither to the cubical system nor to that of the square prismatic. Besides, their angles are not exactly right angles, the determinations varying between 90° and $90^\circ 30'$, and accordingly it has been impossible for me to determine their crystalline system." However, H. Baker¹ obtained crystals of this salt which were perfectly inactive, so that they probably belong to the isometric system, and are isomorphous with the salts $3\text{NH}_4\text{F} \cdot \text{CbOF}_3$, $3\text{NH}_4\text{F} \cdot \text{ZrF}_4$ and $3\text{KF} \cdot \text{ZrF}_4$.

During the present investigation this salt was prepared by concentrating a solution containing 40 grams of the salt $2\text{KF} \cdot \text{CbOF}_3 \cdot \text{H}_2\text{O}$, and 30 grams of potassium fluoride. The salt separated from the solution in the form of small brilliant crystals, which had every appearance of being isometric cubes; however, when rotated in polarized light, the edges, but not the centers of many of these crystals possessed a very faint double refraction.

Calculated: $0.5\text{Cb}_2\text{O}_3$, 39.15; $1.5\text{K}_2\text{SO}_4$, 76.66; 6F, 33.43.

Found: $0.5\text{Cb}_2\text{O}_3$, 38.97; $1.5\text{K}_2\text{SO}_4$, 76.66; 6F, 33.14.

Marignac found (mean): $0.5\text{Cb}_2\text{O}_3$, 39.35; $1.5\text{K}_2\text{SO}_4$, 76.12; 6F, 32.49.

$3\text{KF} \cdot \text{HF} \cdot \text{CbOF}_3$.—Marignac called this salt the acicular fluoxycolumbate of potassium. It crystallizes in the form of slender needles from a solution containing an excess of potassium fluoride and hydrofluoric acid. Crystals of this and the following two salts lose their luster when exposed to the air. The solution from which we obtained the best crystals was analyzed and found to contain potassium fluoride, hydrofluoric acid,

¹ *J. Chem. Soc.*, **35**, 760 (1879).

and columbium fluoride (CbF_5) in the proportions 1.8:1.2:1. According to Marignac this salt is isomorphous with the salt $3\text{KF} \cdot \text{HF} \cdot \text{SnF}_4$.

Calculated: $0.5\text{Cb}_2\text{O}_5$, 36.89; $1.5\text{K}_2\text{SO}_4$, 72.44; 7F, 36.84; H, 0.28.

Found: $0.5\text{Cb}_2\text{O}_5$, 36.60; $1.5\text{K}_2\text{SO}_4$, 72.01; 7F, 36.91; H, 0.29.

Marignac found (mean): $0.5\text{Cb}_2\text{O}_5$, 36.90; $1.5\text{K}_2\text{SO}_4$, 72.15; 7F, 37.80.

Crystallography.—This salt crystallizes in needles which belong to the monoclinic system. The crystals were not large, but they gave fairly satisfactory reflections. The crystal habit is shown in Fig. 8. The pinacoid face (001) and an additional face, probably a clinodome, were also observed, but they were too small for measurement.

Monoclinic.—Axes, $a:b:c = 0.6304:1:0.4888$. $\beta = 86^\circ 41'$.

	Measured.	Calculated.	Marignac found.
mm''' , $110 \wedge 1\bar{1}0 = 64^\circ 22'$...	$64^\circ 10'$
dd' , $111 \wedge 1\bar{1}\bar{1} = 41^\circ 8'$...	$41^\circ 10'$
nn' , $\bar{1}11 \wedge 1\bar{1}1 = 43^\circ 12'$		$43^\circ 18'$	$43^\circ 26'$
dn , $111 \wedge 1\bar{1}1 = 69^\circ 34'$		$69^\circ 43'$	$69^\circ 30'$
md , $110 \wedge 1\bar{1}1 = 45^\circ 59'$...	$45^\circ 52'$
mn' , $110 \wedge 1\bar{1}\bar{1} = 130^\circ 53'$		$130^\circ 58'$	$130^\circ 54'$

$5\text{KF} \cdot 3\text{CbOF}_3 \cdot \text{H}_2\text{O}$.—This salt crystallizes from solutions containing columbium fluoride and an amount of potassium fluoride insufficient to form the 2:1 potassium fluoxycolumbate. Its crystals are prisms with 60° angles, but they probably belong to the monoclinic system. We did not succeed in obtaining crystals which gave satisfactory measurements.

Calculated: $1.5\text{Cb}_2\text{O}_5$, 49.55; $2.5\text{K}_2\text{SO}_4$, 53.91; 14F, 32.91; H_2O , 2.23.

Found: $1.5\text{Cb}_2\text{O}_5$, 49.04; $2.5\text{K}_2\text{SO}_4$, 53.19; 14F, 33.61; H_2O , 2.31.

Marignac found: $1.5\text{Cb}_2\text{O}_5$, 48.59; $2.5\text{K}_2\text{SO}_4$, 53.46; 14F, 31.84; H_2O , 2.00.

$4\text{KF} \cdot 3\text{CbOF}_3 \cdot 2\text{H}_2\text{O}$.—Marignac called this salt the oblique nonsymmetrical fluoxycolumbate of potassium. It separates from solutions containing potassium fluoride and columbium fluoride when the latter is present in great excess, $1\text{KF}:4\text{CbF}_5$.

Calculated: $1.5\text{Cb}_2\text{O}_5$, 52.14; $2\text{K}_2\text{SO}_4$, 45.38; 13F, 32.16; $2\text{H}_2\text{O}$, 4.69

Found: $1.5\text{Cb}_2\text{O}_5$, 52.23; $2\text{K}_2\text{SO}_4$, 45.29; 13F, 31.70; $2\text{H}_2\text{O}$, 4.66.

Marignac found: $1.5\text{Cb}_2\text{O}_5$, 52.10; $2\text{K}_2\text{SO}_4$, 45.30; 13F, 31.40; $2\text{H}_2\text{O}$, 4.70.

Rubidium Salts.—Miss Pennington states that the salt to which was assigned the formula $2\text{RbF} \cdot \text{CbF}_5$ was obtained by dissolving 0.5 gram of columbium oxide in hydrofluoric acid and adding the calculated quantity of rubidium fluoride, evaporating the solution to dryness, dissolving the residue in water, and allowing the salt to crystallize out spontaneously. From the results of the present investigation it would appear that the oxyfluoride, $2\text{RbF} \cdot \text{CbOF}_2$, is formed under these conditions. No salt having the composition $2\text{RbF} \cdot \text{CbF}_5$ was obtained.

$2\text{RbF} \cdot \text{CbOF}_3$.—This salt crystallized from a solution containing rubidium fluoride and columbium fluoride in the required proportions. A portion of the salt was recrystallized from water and analyzed.

Calculated: 2Rb, 45.54; Cb, 24.90; 5F, 25.30.

Found: 2Rb, 45.54; Cb, 24.94; 5F, 25.15.

This salt was recrystallized from an excess of rubidium fluoride, and the salt, which separated in the form of thin pearly plates, gave the following results on analysis:

Found: 2Rb, 45.66; Cb, 24.83.

RbF.CbF₅.—The preceding salt was recrystallized three times from 35 per cent. hydrofluoric acid. By this treatment it was converted into a salt consisting of small needles which gave the following results on analysis:

Calculated: RbF, 35.67; CbF₅, 64.33.

Found: RbF, 35.72; CbF₅, 64.40.

2RbF.CbO₂F₃.H₂O.—A quantity of the salt *2RbF.CbOF₃* was brought into solution in dilute hydrogen peroxide and on concentrating the yellow colored liquid which resulted, thin yellow plates separated. These were recrystallized from water containing a small amount of hydrofluoric acid and hydrogen peroxide. The salt had the same appearance as the corresponding potassium salt which has been

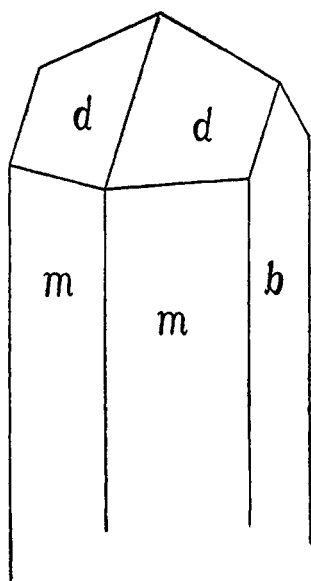


Fig. 8.

studied by Piccini and by Hall and Smith.

Calculated: 2Rb, 41.76; Cb, 22.83; 5F, 23.20; O (active), 3.91; H₂O, 4.39.

Found: 2Rb, 41.77; Cb, 23.19; 5F, 23.16; O (active), 3.95; H₂O, 4.36.

2RbF.TaO₂F₃.H₂O.—This salt was prepared from the salt *2RbF.TaF₅* by the same method as that used for the preparation of the preceding salt. It consisted of thin white leaflets which gave the following analysis:

Calculated: 2Rb, 34.27; Ta, 36.67; 5F, 19.04; O (active), 3.21; H₂O, 3.60.

Found: 2Rb, 34.17; Ta, 36.86; 5F, 19.25; O (active), 3.13; H₂O, 3.76.

Cesium Salts, 2CsF.CbOF₃.—This salt separated from solutions containing cesium fluoride and columbium fluoride in widely varying proportions (1CbF₅ to 4–10CsF). The following analyses were made of crops of crystals which separated from solutions containing cesium and columbium fluorides in different proportions. No salt richer in cesium fluoride was obtained.

Calculated: 2Cs, 56.54; Cb, 19.87; 5F, 20.19.

Found: 2Cs, 56.32, 56.24, 56.66; Cb, 20.17, 19.51, 19.82.

Crystallography.—Hexagonal; rhombohedral. Axis *c* = 0.949. Crystals of two distinct habits were observed: (1) simple crystals consisting of the prism (10 $\bar{1}$ 0) terminated by the basal pinacoid (0001), and (2) twin crystals (Fig. 9), twinning plane (10 $\bar{1}$ 1), each individual consisting

of acute plus and minus rhombohedrons (x and y), symbols undetermined, terminated by the basal pinacoid.

The axial ratio was obtained from the measured angle between the basal pinacoids of the two individuals of the twin.

$$c \wedge c' = 84^\circ 45'.$$

$$r \wedge c, (10\bar{1}1) \wedge (0001) = 47^\circ 37\frac{1}{2}'.$$

The angle $x \wedge c$ gave discordant measurements. $x \wedge c, h\bar{o}hl \wedge 0001 = 80^\circ$ to 90° .

CsF.CbF₅.—This salt was obtained in the form of fine needles when the preceding salt was recrystallized three times from 35 per cent. hydrofluoric acid. It gave the following analysis:

Calculated: CsF, 44.64; CbF₅, 55.36.

Found: CsF, 44.31; CbF₅, 55.54.

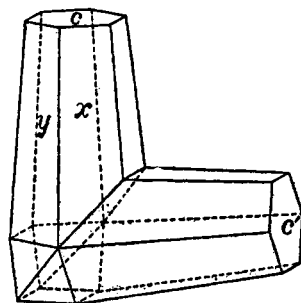


Fig. 9.

Thallium Salt, 2TlF.CbOF₃.—This salt separated from a solution containing thallium fluoride and columbium fluoride, in the required proportions, in the form of transparent, colorless crystals belonging to the orthorhombic system. It is easily soluble in water and may be recrystallized, in which case it separates in thin plates resembling very closely the ordinary potassium fluoxycolumbate.

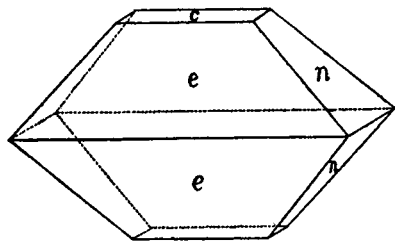


Fig. 10.

Analysis: A sample was decomposed with sulphuric acid, and the

residue was treated with water. It was found to be impossible to wash the columbic oxide free from thallos sulphate, so that it was fused with potassium bisulphate and again digested with water. The thallium was determined in the combined filtrates as thallos iodide. A recrystallized sample of the salt consisting of thin leaflets gave the following results:

Calculated: 2Tl, 66.62; Cb, 15.26; 5F, 15.51.

Found: 2Tl, 66.58; Cb, 15.21; 5F, 15.62.

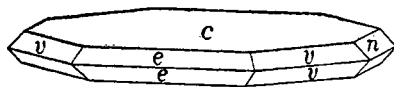


Fig. 11.

A sample of the original plates which had not been recrystallized gave the following analysis:

Found: 2Tl, 66.07; Cb, 15.36.

Crystallography.—The crystal habit of this salt is shown in Figs. 10 and 11. The measurements obtained were fairly satisfactory.

Orthorhombic.—Axes, $a : b : c = 0.4261 : 1 : 1.0129$.

	Measured.	Calculated.
cn, $001 \wedge 011 = 45^\circ 22'$	
ce, $001 \wedge 101 = 67^\circ 11'$	
en, $101 \wedge 011 = 74^\circ 10'$		$74^\circ 11\frac{1}{2}'$
ev, $001 \wedge 122 = 72^\circ 13'\frac{1}{2}$		$72^\circ 14\frac{1}{2}'$
ev, $101 \wedge 122 = 38^\circ 4'$		$38^\circ 8\frac{1}{2}'$
nv, $011 \wedge 122 = 49^\circ 6'$		$49^\circ 10'$

Tantalates, $4Rb_2O \cdot 3Ta_2O_5 \cdot 14H_2O$.—For the preparation of this salt 15 grams of tantalum oxide were fused with 25 grams of rubidium carbonate. The melt was completely soluble in a small quantity of warm water, and on cooling the solution there separated beautiful transparent colorless crystals which were isomorphous with the corresponding rubidium salt.

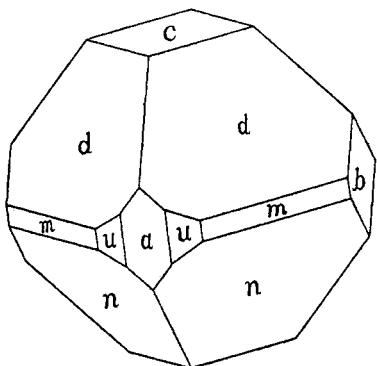


Fig. 12

Calculated: $4Rb_2O$, 31.99; $3Ta_2O_5$, 57.23; $14H_2O$, 10.78.

Found: $4Rb_2O$, 31.38; $3Ta_2O_5$, 57.50; $14H_2O$, 10.88.

Crystallography.—As previously stated this is one of four isomorphous salts obtained during the present investigation.

Nearly all of the crystals had the form shown in Fig. 12, but several of the crystals which had a diameter of 10–12 mm. showed the additional faces of the two prisms m and u shown in Fig. 12.

Monoclinic.—Axes, $a : b : c = 0.8822 : 1 : 1.0510$. $\beta = 84^\circ 2'$.

	Measured.	Calculated.
dd', $111 \wedge 1\bar{1}\bar{1} = 65^\circ 15'$	
dn, $111 \wedge 1\bar{1}\bar{1} = 78^\circ 55'$	
nn', $111 \wedge 1\bar{1}\bar{1} = 70^\circ 42'$	
dn''', $111 \wedge 1\bar{1}\bar{1} = 64^\circ 23'$		$64^\circ 26'$
dm, $111 \wedge 110 = 30^\circ 57'$		$30^\circ 56\frac{1}{2}'$
cd, $001 \wedge 111 = 54^\circ 28'$		$54^\circ 34\frac{1}{2}'$
ad, $100 \wedge 111 = 48^\circ 10'$		$48^\circ 5\frac{1}{2}'$
am, $100 \wedge 110 = 41^\circ 13'$		$41^\circ 16'$
au, $100 \vee 210 = 23^\circ 30'$		$23^\circ 41'$

$4Cs_2O \cdot 3Ta_2O_5 \cdot 14H_2O$.—For the preparation of this salt one part of tantalum oxide was fused with two parts of cesium carbonate. The melt was completely soluble in a small amount of hot water, and the solution on cooling deposited monoclinic crystals isomorphous with the corresponding columbium salt. The crystals of this salt showed only the faces of the pyramids; the pinacoid faces were not observed. Within the limits of error the angles were the same as those of the rubidium salt.

Calculated: $4\text{Cs}_2\text{O}$, 41.50; $3\text{Ta}_2\text{O}_5$, 49.23; $14\text{H}_2\text{O}$, 9.27.

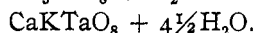
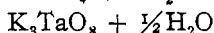
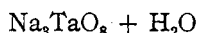
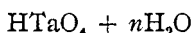
Found: $4\text{Cs}_2\text{O}$, 41.11; $3\text{Ta}_2\text{O}_5$, 49.16; $14\text{H}_2\text{O}$, 9.57.

$7\text{Cs}_2\text{O} \cdot 6\text{Ta}_2\text{O}_5 \cdot 38\text{H}_2\text{O}$.—A portion of the above salt was precipitated from its aqueous solution by means of alcohol. The salt which separated gave the following analysis:

Calculated: $7\text{Cs}_2\text{O}$, 37.01; $6\text{Ta}_2\text{O}_5$, 50.17; $38\text{H}_2\text{O}$, 12.82.

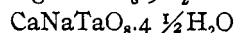
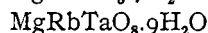
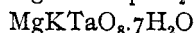
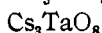
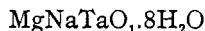
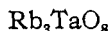
Found: $7\text{Cs}_2\text{O}$, 36.97; $6\text{Ta}_2\text{O}_5$, 50.20; $38\text{H}_2\text{O}$, 12.81.

Pertantalates.—Melikoff and Pissarjewsky have described the following pertantalates:



Two salts, K_3TaO_8 and $\text{Na}_3\text{TaO}_8 + 14\text{H}_2\text{O}$, have been reported from this laboratory.¹

The following additional salts have been obtained:



These salts were made and analyzed in the same manner as the corresponding columbium salts. They were not as soluble in water as the latter salts.

Rubidium Pertantalate, Rb_3TaO_8 .—This salt was only prepared in small amounts and was not of a high degree of purity, but the analytical results obtained are sufficiently accurate to establish its composition.

Calculated: $15\text{Rb}_2\text{O}$, 49.43; $0.5\text{Ta}_2\text{O}_5$, 39.29; 4O , 11.28.

Found: $15\text{Rb}_2\text{O}$, 50.38 (diff.); $0.5\text{Ta}_2\text{O}_5$, 38.01; 4O , 11.61.

Cesium Pertantalate, Cs_3TaO_8 .—A sample of this salt gave the following analysis:

Calculated: $1.5\text{Cs}_2\text{O}$, 59.58; $0.5\text{Ta}_2\text{O}_5$, 31.41; 4O , 9.01.

Found: $1.5\text{Cs}_2\text{O}$, 59.18; $0.5\text{Ta}_2\text{O}_5$, 32.27; 4O , 9.09.

Magnesium Sodium Pertantalate, $\text{MgNaTaO}_8 \cdot 8\text{H}_2\text{O}$.—Analysis:

Calculated: MgO , 8.04; $0.5\text{Na}_2\text{O}$, 6.17; $0.5\text{Ta}_2\text{O}_5$, 44.39; 4O , 12.74; $8\text{H}_2\text{O}$, 28.66.

Found: MgO , 8.87; $0.5\text{Na}_2\text{O}$, 6.69 (diff.); $0.5\text{Ta}_2\text{O}_5$, 43.98; 4O , 12.52; $8\text{H}_2\text{O}$, 28.74.

Magnesium Potassium Pertantalate, $\text{MgKTaO}_8 \cdot 7\text{H}_2\text{O}$.—This salt gave the following analysis:

Calculated: MgO , 8.07; $0.5\text{K}_2\text{O}$, 9.41; $0.5\text{Ta}_2\text{O}_5$, 44.56; 4O , 12.79; $7\text{H}_2\text{O}$, 25.17.

Found: MgO , 8.06; $0.5\text{K}_2\text{O}$, 9.76 (diff.); $0.5\text{Ta}_2\text{O}_5$, 44.17; 4O , 12.67; $7\text{H}_2\text{O}$, 25.32.

Magnesium Rubidium Pertantalate, $\text{MgRbTaO}_8 \cdot 9\text{H}_2\text{O}$.—Analysis:

Calculated: MgO , 6.93; $0.5\text{Rb}_2\text{O}$, 16.04; $0.5\text{Ta}_2\text{O}_5$, 38.26; 4O , 10.98; $9\text{H}_2\text{O}$, 27.79.

Found: MgO , 7.10; $0.5\text{Rb}_2\text{O}$, 15.89 (diff.); $0.5\text{Ta}_2\text{O}_5$, 38.37; 4O , 11.00; $9\text{H}_2\text{O}$, 27.64.

¹ THIS JOURNAL, 27, 1140 (1905).

Calcium Sodium Pertantalate, $\text{CaNaTaO}_8 \cdot 4\frac{1}{2}\text{H}_2\text{O}$.—The composition of this salt was perfectly analogous with the corresponding potassium salt described by Melikoff and Pissarjewsky. It gave the following analytical results:

Calculated: CaO , 12.31; $0.5\text{Na}_2\text{O}$, 6.81; $0.5\text{Ta}_2\text{O}_5$, 49.01; 4O , 14.07; $4.5\text{H}_2\text{O}$, 17.80.
 Found: CaO , 12.81; $0.5\text{Na}_2\text{O}$, 6.69 (diff.); $0.5\text{Ta}_2\text{O}_5$, 48.85; 4O , 14.03; $4.5\text{H}_2\text{O}$, 17.62.

UNIVERSITY OF PENNSYLVANIA,
 PHILADELPHIA, PA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

A STUDY OF THE SPECTRUM AND THE BROMIDES OF COLUMBIUM.¹

BY WILLIAM M. BARR.

Received August 21, 1908.

The results presented in this communication constitute a short chapter in the larger research upon columbium and tantalum begun years ago in this laboratory and still in progress.

Hall and Smith² proved that the hydrogen peroxide test for titanium in a hydrofluoric acid solution of columbium was not reliable, so that it seemed as if the only means remaining for the identification of titanium in the presence of columbium was the spectroscopic examination.

Balke and Smith³ obtained large quantities of potassium oxyfluocolumbate, K_2CbOF_3 , from American columbites. This was freed from all other metals usually accompanying it. From titanium it was separated by recrystallizing the salt five times from concentrated hydrofluoric acid. The oxide from this salt was submitted to a spectroscopic examination by Hildebrand⁴ who found by comparing the spectrum with that published by Exner and Haschek that nearly all the titanium lines given by these investigators were absent from the oxide of Balke and Smith. However, there were some lines common to both spectra and to the spectrum of titanium.

As the pure oxide of Balke and Smith had been prepared from columbite from Lawrence County, South Dakota, it seemed desirable to obtain columbium oxide from minerals of widely different character and locality. The thought was of course to purify such an oxide by the methods used with the Dakota material and then examine it spectroscopically, comparing the results with those previously obtained by Hildebrand. It was further hoped to determine whether the lines that appeared to be common to the spectra of titanium and columbium were really coincident lines or whether they belonged to some other element.

¹ From author's thesis for the Ph.D. degree.

² *Proc. Am. Phil. Soc.*, **44**, 209 (1905).

³ *THIS JOURNAL*, preceding article.

⁴ *THIS JOURNAL*, following article.