This research was undertaken at the suggestion of Professor Nernst, and it is a pleasure to express my gratefulness for his help and constant interest in the work. I am also indebted to Dr. von Wartenberg for the results on the diffusion of hydrogen through iridium.

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COLUMBATES.[1]

BY M. HUME BEDFORD.

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AN EXAMINATION of the literature relating to the columbates of the alkali metals shows decided variations in the ratios existing between the base and the acid. For example, the following sodium columbates have been recorded:

(1) $Na_2O.Cb_2O_5.6H_2O$ or $9H_2O$ (Rose);
(2) $3Na_2O.2Cb_2O_5.24H_2O$ (Rose);
(3) $3Na_2O.Cb_2O_5$ (Rose);
(4) $4Na_2O.5Cb_2O_5$ (Rose);
(5) $3Na_2O.4Cb_2O_5.21H_2O$ (Hermann).

The first salt was obtained by fusing columbic oxide with sodium hydroxide in a silver crucible. Rose pronounced it the best crystallized and most stable of the columbates. The second salt was obtained simultaneously.

When columbic oxide was fused for some time with sodium carbonate the third salt was formed. The fourth salt was described as the only acid salt of exact ratio, while Hermann obtained the fifth salt upon the addition of an excess of sodium hydroxide to a solution of potassium columbium oxyfluoride.

It was resolved, having an abundance of the latter compound, to repeat Hermann's experiment. Accordingly, 50 grams of potassium columbium oxyfluoride were dissolved in a liter of hot water and to this solution a concentrated solution of 150 grams of sodium hydroxide was added. A white, finely divided precipitate separated. It was filtered out and washed with cold water until the filtrate became milky. It was then dried as far as possible by suction and was recrystallized three times from dis-

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

tilled water. It was then allowed to dry in the air. It was very stable. It dissolved in water without leaving any residue. Beautiful crystals were obtained when its solution was allowed to cool slowly, but it was found advisable to cool rapidly and stir well because the salt readily formed supersaturated solutions.

On proceeding to the analysis of this compound its water content was obtained by the ignition of a weighed portion of the salt. The ignited sample was then fused with from four to five parts of potassium acid sulphate. The cold melt was boiled with water until it had completely disintegrated, when the columbic oxide was filtered out, thoroughly washed, ignited and weighed. The determination of the sodium content was made by dissolving a portion of the salt in 100 cc. of water, adding from five to ten drops of dilute sulphuric acid and boiling for several minutes, whereupon the columbic hydroxide separated completely, was filtered, washed with boiling water, dried, ignited and weighed as oxide. The filtrate from the columbic hydroxide was evaporated to dryness and the residual sodium sulphate weighed after ignition. A trace of the columbic oxide sometimes remained with the sodium sulphate, which was removed by dissolving the sulphate in water and again filtering. The percentages found for the several constituents were: Na_2O, 16.59 and 16.57; Cb_2O_5, 61.54 and 61.64; H_2O, 21.96 and 22.08, which would lead to the formula $7Na_2O.6Cb_2O_5.32H_2O$, the requirements for which would be Na_2O 16.58, Cb_2O_5 61.42 and H_2O 21.96. These results are far more concordant than those which led Hermann to write the formula as indicated under the fifth salt.

Thinking that possibly the above salt might contain an extra molecule of sodium oxide, its aqueous solution was precipitated by alcohol. The product, after drying, was analyzed and showed the same composition as before, with the exception of the water content, which was now 31 instead of 32 molecules. Hence it may be concluded that the ratio given above correctly represents the composition of the salt.

On adding a dilute solution of barium chloride to a hot solution of the sodium salt, a heavy white precipitate was produced and settled very quickly. It was washed by decantation with boiling water and was then collected on a filter and dried at a water-bath temperature for one and one-half hours, after which it was reduced to a fine powder and analyzed. In its analysis the water content was obtained by the loss on ignition of a weighed sample. The ignited residue was then fused with a mixture consisting of equal parts of sodium and potassium carbonates. The cold fusion was treated with dilute oxalic acid and hydrochloric acid. Everything dissolved. The liquid was brought to boiling and the barium precipitated in the form of sulphate. The columbium hydroxide was obtained in the filtrate from the barium sulphate. The found percentages of the constituents present were as follows: BaO, 35.83 and 36.08; Cb_2O_5, 53.37 and 53.06; H_2O, 10.80 and 10.75, which led to the formula $7BaO.6Cb_2O_5.18H_2O$, the requirements of which would be BaO 35.66, Cb_2O_5 53.55 and H_2O 10.79. In other words, in this salt again the ratio of the basic oxide and acid oxide remained 7 : 6.

The silver salt was also prepared by treating a solution of the sodium salt with a dilute solution of silver nitrate. It was a white, insoluble precipitate. It was washed by decantation with boiling water, and when dry it was analyzed.

In determining the water a sample of the salt was ignited in a current of dry air and the water collected in a weighed calcium chloride tube. For the estimation of the silver and columbium a second portion of the salt was fused with acid potassium sulphate. The melt was dissolved in boiling water and the columbium determined in the usual way. The silver, contained in the filtrate from the columbium hydroxide, was titrated with potassium sulphocyanate. The percentages of the constituents present were found to be as follows: Ag_2O, 48.72; Cb_2O_5, 48.72; H_2O, 2.52, from which was deduced the formula $7Ag_2O.6Cb_2O_5.5H_2O$, which would require Ag_2O 48.89, Cb_2O_5 48.40 and H_2O 2.71.

Rose described a silver columbate which, according to Rammelsberg, contained Cb_2O_5 50.45, Ag_2O 47.31 and H_2O 1.98.

It was thought that it would be well to prepare a zinc salt, which was done by transposing sodium columbate with zinc sulphate. This salt was white in color and insoluble in water. It was washed by decantation with boiling water and after drying was analyzed. It showed the presence of ZnO 21.86, Cb_2O_5 60.87, H_2O 17.27, from which was deduced the formula $7ZnO.6Cb_2O_5.25H_2O$, requiring ZnO 21.69, Cb_2O_5 61.18 and H_2O 17.13.

The analyses of the four salts described in the preceding paragraphs demonstrate very conclusively that the latter are not derivatives of a metacolumbic acid. On turning to the first paragraph in this communication it will be observed that the first salt described by Rose shows a ratio favoring the existence of metacolumbates, but the very excellent concordance of the experimental results, as exhibited above, would argue for the ratios which have been deduced. Zinc metacolumbate would require ZnO 19.32 and Cb_2O_5 63.59, or if we were to adopt another ratio, which has been suggested by the study of the potassium salts, namely, that of 8 : 7, the percentage of zinc oxide required would be 21.23, while that of columbic oxide would be 61.16. It may be added further that the results obtained in the analysis of the barium salt do not harmonize with the requirements of the ratio 8 : 7.

Having obtained the preceding results from a sodium salt prepared after the manner of Hermann, it was concluded to make the same salt by the methods employed by Rose. To that end 10 grams of ignited columbic oxide were fused with 40 grams of sodium hydroxide in a silver crucible. The excess of sodium hydroxide was washed out, the sodium columbate filtered by suction, and then crystallized twice from water and analyzed after drying in the air. Exceedingly beautiful crystals of the salt were obtained. They were readily soluble in water. Upon analysis they showed the presence of Na_2O 16.65, Cb_2O_5 61.43, and H_2O 21.98, which was in perfect harmony with the requirements of the formula $7Na_2O.6Cb_2O_5.32H_2O$, while Rose himself found in the salt made in this way Na_2O 15.68 and Cb_2O_5 60.82. If his formula for the metacolumbate in this instance were granted it would require Na_2O 14.16 and Cb_2O_5 61.20.

The second method proposed by Rose consisted in fusing columbic oxide for a long period with sodium carbonate. This gave him the salt $3Na_2O.Cb_2O_5$. In imitation of this experiment 8 grams of columbic oxide were fused in a platinum crucible with 25 grams of sodium carbonate. The cold melt was treated with water, the excess of sodium carbonate washed out and the sodium columbate filtered by suction and then recrystallized from water, in which it dissolved completely. Upon analysis it showed Na_2O 15.84, Cb_2O_5 60.20; and H_2O, 24.16, from which percentages was deduced the formula $7Na_2O.6Cb_2O_5.36H_2O$. The only difference, therefore, between this salt and the sodium salts prepared by the other two methods was a slightly higher percentage of water. There was a great tendency on the part of the salt to form supersaturated solutions, and in order to obtain it from the same it was necessary to add sodium carbonate. It then separated as an extremely fine powder.

It may be concluded from what has been recorded in the preceding paragraphs that but one sodium columbate is definitely known, and that the three methods which have been employed in the past for its preparation lead to one and the same salt, in which the ratio of basic oxide and acid oxide is 7 : 6, which ratio has been preserved in the barium, silver and zinc salts.

It is altogether probable that when the potassium columbates are subjected to a similar study, the many ratios shown by them will be reduced to one simple ratio. This, however, is a matter for further investigation.

SEPARATION OF COLUMBIC AND TUNGSTIC ACIDS.

This study arose from the great difficulty experienced in trying to separate columbic and tungstic oxides in salts obtained by dissolving moist tungstic oxide in a boiling solution of sodium columbate. The purpose was to form columbotungstates analogous to the phosphotungstates and vanadotungstates. A salt was obtained that crystallized in the same form as the sodium columbate and contained about 22.50 per cent. of tungstic oxide and 43.30 per cent. of columbic oxide. It was crystallized without undergoing any decomposition.

In the separation of the columbic and tungstic acids in this salt, concordant results were not obtained by the usual methods. The first method tried consisted in fusing the sample with a mixture of sodium carbonate and sulphur. It will be sufficient to state here that the results varied within wide limits. Digestion of the ignited sample with a strong solution of sodium hydroxide was next tried but did not prove satisfactory.

One of the thoughts that suggested itself was the precipitation of the columbic oxide with magnesia mixture in an alkaline solution, the usual method of separating phosphoric and tungstic acids. It was soon found that the magnesium columbate could not be weighed as such.

PROCEDURE.

Weighed quantities of the two oxides were fused with potassium carbonate (because the potassium salts are more soluble than the sodium salts). The melt was taken up in 150 cc. of water. To the potassium carbonate solution an excess of magnesia mixture was added. The precipitate formed was allowed to stand several hours and then filtered. It was washed on the filter five or six times with the precipitant, dried and ignited. After all of the carbon had burned off, the residue was fused with acid potassium sulphate, boiled with water, filtered, washed, ignited and the columbic oxide weighed. The tungstic oxide was obtained by difference.

No. of sample.	Cb_2O_5 taken. Gram.	WO_3 taken. Gram.	Cb_2O_5 found. Gram.	WO_3 by difference. Gram.
1	0.2086	0.0986	0.2078	0.0994
2	0.3218	0.1500	0.3208	0.1510
3	0.5004	0.1000	0.4951	0.1053
4	0.2026	0.1000	0.2032	0.0994
5	0.1503	0.1200	0.1506	0.1197

When this method was applied to a solution containing unknown quantities of columbic and tungstic acids, a solution of mercurous nitrate was added, and then a slight excess of nitric acid. Freshly precipitated mercuric oxide was next introduced and the solution boiled five minutes. As soon as the precipitate had settled it was filtered out and washed with boiling water. It was dried, ignited and the columbic and tungstic oxides weighed together. The two oxides were then separated by the method described above. Very fair results were obtained. They varied 0.3 to 0.5 per cent. from the mean.

From a study of the preceding data it will be seen that this method gives very good results. They were superior to those obtained from a sodium carbonate and sulphur fusion. The method can be carried out in a short time and is very easy to manipulate. It was not tried on a mixture of a trace of tungstic oxide and a large quantity of columbic oxide, but under such conditions very good results might be expected.

This method is probably applicable also in the separation of tantalic and tungstic acids.

UNIVERSITY OF PENNSYLVANIA.