Wt. of $TaBr_5$. (vac.).	Wt. of Ta_2O_5. (vac.).	Ratio $TaBr_5 : Ta_2O_5$.	At. wt. of Ta.
0.86837	0.33117	2.6221	181.68
1.50903	0.57570	2.6212	181.80
1.56554	0.59718	2.6216	181.75
1.23239	0.47030	2.6204	181.91
1.31815	0.50295	2.6208	181.85
1.31702	0.50244	2.6212	181.80
1.20090	0.45830	2.6204	181.91
1.04050	0.39688	2.6217	181.74
		Mean,	181.80

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

THE ACTION OF HYDROFLUORIC ACID GAS UPON CERTAIN OXIDES.

BY WALTER K. VAN HAAGEN AND EDGAR F. SMITH.

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From time to time in this laboratory various metallic oxides have been exposed at varying temperatures to the influence of gaseous halogen acids. In the past summer we have taken occasion to ascertain the volatility or non-volatility of certain oxides when heated in hydrofluoric acid gas. The latter was generated from well dried calcium fluoride and concentrated sulfuric acid contained in a platinum retort which was connected with a platinum combustion tube, in which there was also a platinum boat carrying the material to be acted upon. The constricted portion of the combustion tube was cooled by means of a moist wad of filter paper, while its extreme end was allowed to dip into distilled water. The retort and its contents were gradually heated in a glycerol bath, by which means a constant and even flow of hydrofluoric acid gas was obtained.

On treating strongly ignited and powdered aluminium oxide as above indicated, the boat and its contents became exceedingly hot to the touch but there was no volatilization of the material. At a white heat a small portion of fluoride of aluminium could be detected in the receiver. The conversion of oxide into fluoride was perfectly quantitative after heating in the bath for twenty minutes.

Yttrium oxide suffered a complete change at a red heat to fluoride or oxyfluoride. There was no volatilization and, therefore, no yttrium was found in the receiver.

The conversion of lanthanum oxide to fluoride was also quantitative and there was no volatilization of lanthanum salt. Finely divided quartz volatilized easily and completely without the application of external heat. The heat of the reaction was intense.

In the action of titanium oxide volatilization took place below a red heat and was complete at this temperature.

Zirconium oxide was fully converted at a red heat into fluoride, a portion of it passing into the receiver but the greater part remaining in the constricted portion of the water-cooled part of the combustion tube in crystallized form. The boat was empty.

Finely powdered zircon mineral when heated to a dull red heat sustained complete decomposition. Zirconium was found in the receiver liquid. Nothing was left in the boat. The major portion of the zirconium lodged in the constricted part of the tube in large crystals, which dissolved almost wholly in water, but complete solution required the addition of a few drops of hydrochloric acid.

Cerium dioxide quantitatively changed to fluoride without any volatilization.

Thorium dioxide suffered a slight alteration without any volatilization.

Tin stone was converted only slightly into a fluoride or oxyfluoride, which was volatilized with extreme difficulty at a white heat.

Columbium and tantalum pentoxides were completely expelled from the boat in which they were present at a low red heat.

The volatilization of tantalum fluoride proceeded with more difficulty than in the case of columbium fluoride.

On exposing one-half gram of powdered columbite to the action of hydrofluoric acid gas, the mineral was completely decomposed. The columbic and tantalic oxides which were expelled and caught in the receiver amounted to 78 per cent. A careful analysis of the mineral previously made showed 80 per cent. of these mixed oxides. The boat contained a fused residue consisting of iron and manganese. This dissolved in water, although a few drops of dilute hydrochloric acid were added to produce a clear solution.

The mineral fergusonite was similarly decomposed with a complete volatilization of the metallic acids, while the contents in the boat consisted of fluorides of rare earths, *e. g.*, yttrium, lanthanum, etc.

The following salts were treated in a similar manner: (*a*) Potassium dichromate lost nearly all of its chromic acid by this treatment. (*b*) Sodium tungstate was attacked with difficulty and the tungstic acid was not completely expelled. (*c*) Sodium pyrophosphate in a finely divided state was attacked at the ordinary temperature with evolution of a great amount of heat. The phosphoric acid was completely driven into the receiver. The residue in the boat was soluble in water and gave no precipitation when its solution was treated with silver nitrate. An example will show how complete this change was: 0.4794 gram of sodium pyrophosphate left a residue weighing 0.3026 gram instead of the calculated 0.3028 gram. Indeed, the change was effected with so much ease and was of such a truly quantitative character that it was thought that the atomic weight of phosphorus might readily be determined in this way. This investigation is now in progress. It will give the ratio of P : NaF. As sodium fluoride is readily converted into sodium chloride the ratio of P : NaCl is the one that is being determined. Incidentally, this will also give the ratio of F : Cl.

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THE ACTION OF SALICYLIC ACID UPON THE METALLIC ACIDS.[1]

BY JOHN HUGHES MULLER.

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On exposing the hydrates of columbium, tantalum and titanium to the action of a number of organic acids salicylic acid alone showed a marked difference in its behavior with them. An excess of salicylic acid was slowly added to a solution of sodium columbate and a precipitate, gelatinous in form and orange-yellow in color resulted. Continued digestion of this precipitate at boiling temperature caused it to become bright yellow in color and to lose much of its gelatinous form. After washing with water containing some salicylic acid to prevent hydrolysis, the precipitate was dried and the percentage of columbium present determined by the ignition of weighed quantities, thus converting them to columbic oxide. The precipitation of the columbium was complete.

On precipitating an alkaline tantalate solution with salicylic acid the precipitate, while gelatinous, was colorless. This reaction was also quantitative.

Warm solutions of ammonium hydroxide and potassium hydroxide decompose these salicylates of columbium and tantalum. They are insoluble in ether, methyl alcohol, ethyl acetate, chloroform, carbon tetrachloride, carbon bisulfide, and petroleum ether.

The presence of an alkali fluoride prevents the precipitation of columbium or tantalum by salicylic acid. Orthotitanic acid dissolves in salicylic acid in the presence of fluorides to an almost colorless solution and in their absence to an intensely yellow colored salicylate. Zirconium and thorium hydroxides are difficultly soluble in aqueous salicylic acid while after ignition the corresponding oxides are practically insoluble.

Known amounts of each of the oxides of columbium, tantalum, zirconium and thorium were mixed with weighed amounts of titanic oxide and these mixtures then fused with 5 grams of potassium carbonate, the fusions being taken up in from 350–400 cc. of water at 60° and treated with 14–15 grams of salicylic acid, the solution being heated for three to

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