taken to be about the same as that in the eighth, while that in the seventh was thought to be slightly greater than that in the fifth, but there was no doubt in any of these cases as to the actual presence of tin.

In no case was any tin found with the arsenic, or antimony, nor could a trace of these elements be detected in the tin filtrates.

Summary.

A review of the established quantitative separations of metals in hydrofluoric acid solution, which have been described in various separate papers, was made in order to call attention to the possibilities of their use in the analysis of various types of ores and alloys. Some new quantitative separations have been described.

A further study of the effect of adding boric acid to hydrofluoric acid solutions of various substances has shown that the virtual removal of the fluorine from the field of action, which has been previously described by others, may be applied in making the analysis of the tin-antimony and other types of alloys more rapid and economical. This principle was also found useful in a modified scheme for the qualitative examination of the tin group of elements.

The effect obtained by adding boric acid to hydrofluoric acid solutions of various substances suggests further applications than those described, some of which are being investigated.

In conclusion, the writer wishes to express his thanks to Dr. L. W. McCay for the inspiration and guidance which made this work possible. He wishes also to acknowledge the valuable advice and assistance given to him by Dr. E. C. Franklin in the revision of this paper.

PRINCETON, N. J.

THE BEHAVIOR OF SOLUTIONS OF STANNIC FLUORIDE.

BY N. HOWELL FURMAN.

Received February 15, 1918.

Introduction.

In the preceding paper the analytical deportment of acid solutions of a variety of metals, with free hydrofluoric acid present, and the absence under these conditions of some or all of the characteristic reactions of the ions of the metals, tin, tungsten, molybdenum, antimony, chromium and vanadium, in their highest states of oxidation, has been described. The following investigation of some of the properties of stannic fluoride solutions was made in the hope that it would explain, or at least throw some light on, the reasons for the observed facts.

Stannic fluoride cannot be prepared by the evaporation of its aqueous solutions, for oxyfluorides, and eventually stannic oxide itself are formed;[1]

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[1] Berzelius, *Traité de Chimie*, 4, 124 (1847).

nor has the compound been prepared by heating any of its dry double salts.[1] Thus far the only successful method for its preparation is that of Ruff and Plato,[2] based on the reaction

$$SnCl_4 + 4HF = SnF_4 + 4HCl\uparrow$$

with the use of strictly anhydrous materials, platinum apparatus, and with the rigid exclusion of moisture.

The product obtained by these investigators, and subsequently by Wolter,[3] using the same apparatus, has the following properties:

It is a snow-white, crystalline solid, extremely hygroscopic, which sublimes at 705°, and has a density of 4.780 at 19°. It dissolves in water with a hissing sound, liberating heat, and yielding a clear solution which becomes turbid on standing, or on boiling, eventually undergoing complete hydrolysis. When such a solution is made acid with hydrochloric or sulfuric acid, the tin is precipitated very slowly, though completely, by hydrogen sulfide. In addition to the double salts described by Marignac,[4] it forms the following double compounds: SnF_4SnCl_4,[5] SnF_4NH_3, $SnF_4.2NH_3$.[6]

Dry hydrogen sulfide gas has little or no action on dry stannic fluoride, but with liquid hydrogen sulfide a violent double decomposition takes place according to the equation

$$SnF_4 + 2H_2S = SnS_4 + 4HF.$$

(This is a difference in chemical deportment from that of the chloride, for the latter substance forms an addition compound under similar conditions.)

Stannic fluoride is reduced with violence by metallic zinc or aluminium, but the formation of the intermediate bifluoride was not observed in Wolter's experiments.[6] The chlorides and oxychlorides of phosphorus enter into simple double decomposition reactions with stannic fluoride.

Experimental.

Preparation of Pure Hydrofluoric Acid.—The method of Ruff and Plato was used for the preparation of stannic fluoride. The apparatus will be readily understood from Fig. 1. Anhydrous hydrofluoric acid was prepared by heating dry potassium-hydogen fluoride in the platinum vessel *A*.[7] The hydrofluoric acid vapor passed into the copper condenser *B*, and was collected in the copper flask *C*, both of these portions of the

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[1] O. Ruff, *Z. angew. Chem.*, **20**, 1217 (1907).

[2] *Ber.*, [1] **37**, 673 (1904).

[3] *Chem. Ztg.*, **36**, 165 (1912).

[4] *Ann. mines*, [5] **15**, 221 (1859).

[5] Ruff and Plato, *Loc. cit.*

[6] Wolter, *Ibid.*

[7] Fremy, *Ann. phys.*, [3] **47**, 5 (1856); Gore, *Phil. Trans.*, **1869**, p. 173. See also *Monatsh.*, **28**, 297 (1907), for the use of copper vessels in preparing the anhydrous acid.

apparatus being of course surrounded with a freezing mixture. The copper vessel *C*, which was designed by Dr. G. A. Hulett, was found to be particularly useful in collecting and storing the anhydrous acid. It is a seamless copper cylinder with the ends and delivery tubes, also of copper, brazed in. The working portions of the valves are of copper, the remainder of brass. The entire interior of the vessel was given a heavy coat of electrolytic copper to prevent contact of the acid with the brazed portions. A copper tube *D* containing calcium chloride served as a guard against moisture; at *C* a current of dry air could be introduced. The joints *a*, *a*, *a*, were made tight by a wrapping of thin copper foil which was covered by several turns of rubber dam; these joints were found quite serviceable, and only very slight leakage took place.

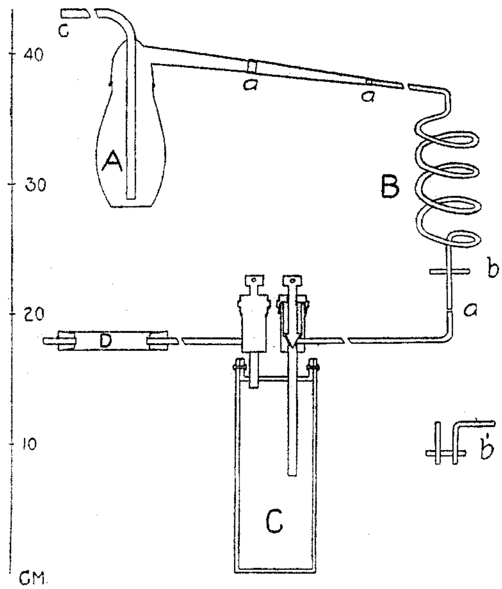

Fig. 1.

When sufficient acid (80 to 100 g.) had been collected, the copper vessel was put in the place of the retort, the lower pear-shaped part of the retort then being connected with the condenser by means of the brass stopper *b'*, which carried two copper tubes. The brass stopper *b'* was heavily coated with platinum black, and further protected from acid fumes by a piece of platinum foil. The acid was distilled by surrounding the copper vessel with water at 20° to 25°.

Preparation of Stannic Fluoride.—Sufficient hydrofluoric acid having been distilled into the retort, one-half of the theoretical quantity of anhydrous stannic chloride required was added,[1] and the retort quickly connected to the condenser by means of the straight tube of the stopper *b'*. This stopper fitted very tightly into the neck of the retort, but slight leakage occurred, which was reduced to a minimum by a seal of paraffin placed above the stopper. The reaction was allowed to continue at room temperature for 2 or 3 days, or at all events until hydrochloric acid ceased to be evolved, the condenser being continually surrounded with a freezing mixture. The platinum top of the retort was then fitted on, after

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[1] The stannic chloride, prepared in the usual manner, was freshly distilled before using.

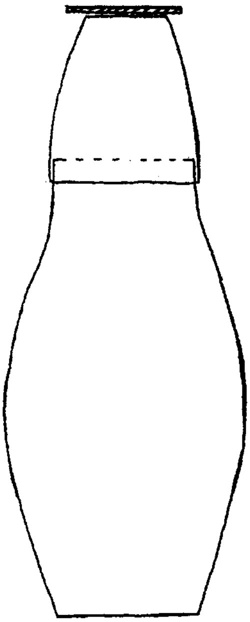

Fig. 2.

which the excess of hydrofluoric acid was distilled off by careful heating, the temperature being gradually raised to 130°, at which temperature the decomposition of the compound SnF_4SnCl_4 commences. The heating was continued in a cautious manner until all stannic chloride had been removed. The temperature was then raised to about 700°, the stannic fluoride being sublimed and collected on the inner surface of a platinum crucible as shown in Fig. 2. The outside of this crucible was cooled with moist asbestos. The product condensed in beautiful white gleaming crystals. A Smith alkali-fusion crucible was found convenient as a container for the stannic fluoride until it was used, the crucible being placed in a desiccator over conc. sulfuric acid.

Weighed portions of the stannic fluoride were placed in a platinum crucible and the fluorine was expelled in the form of hydrofluoric acid by repeated evaporations with nitric acid, the tin being weighed as dioxide.

Sample taken. G.	% of tin found.	Calc. % of tin in stannic fluoride.
0.0956	61.6	61.03
0.1000	61.4	...
0.1107	60.8	...
0.7341	61.17	...

The Hydrolysis of Stannic Fluoride.

The hydrolysis of stannic chloride has been studied very successfully by the conductance method,[1] and it seemed reasonable to suppose that stannic fluoride could be studied in a similar manner. Weighed quantities of stannic fluoride were dissolved in conductivity water of specific conductivity 1.2×10^{-6} mhos, and weighed amounts of these solutions were placed immediately in a platinum conductivity bottle, Fig. 3. The electrodes were of the usual Ostwald type and the supporting wires, as well as the glass cross-piece, were coated with paraffin. The cell

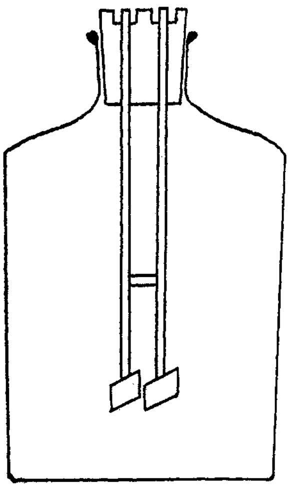

Fig. 3.

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[1] Wm. Foster, "The Hydrolysis of Stannic Chloride," *Phys. Rev.*, 9, 41 (1899); Kohlrausch, "Uber die durch die Zeit und durch das Licht bewirkte Hydrolyse einiger Chlorverbindungen von Platin, Gold und Zinn," *Z. phys. Chem.*, 33, 257 (1900).

constant was frequently determined by means of 0.02 *N* potassium chloride solution, and remained the same, within the experimental error, during the course of the measurements. The conductivity apparatus was of ordinary precision. The cell was placed in a thermostat, which was maintained at a temperature of 25° ± 0.02°.

The conductivity changed rapidly at first, later becoming practically constant. The manner of the change may be understood from the following table, and the accompanying graphic representations of these results, which are plotted in Fig. 4:

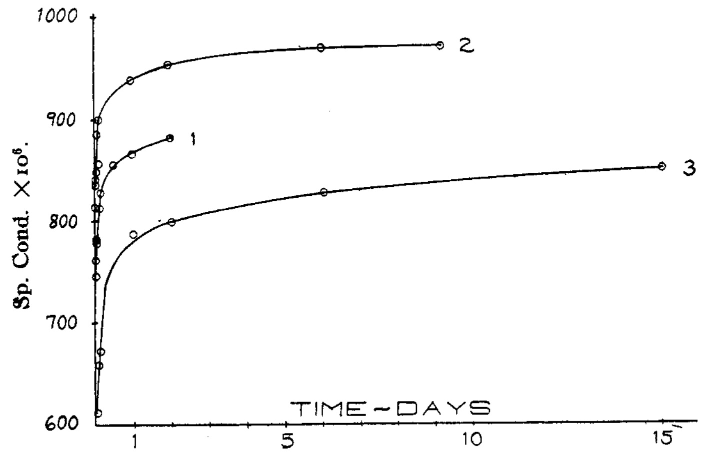
Table I.—The Hydrolysis of Stannic Fluoride Solutions.

Time from start of experiment.	Specific conductivity × 10^6 mhos.		
	Normality 0.0125.	Normality 0.013.	Normality 0.0155.
3 mins	748	...	...
5 mins	...	609	815
12 mins	765	...	...
20 mins	...	659	838
25 mins	773	...	...
30 mins	...	670	844
45 mins	...	...	849
50 mins	781	...	...
1 hr	...	695	858
3 hrs	...	...	888
4 hrs	816	...	...
6 hrs	833	...	899
12 hrs	859	...	...
24 hrs	867	793	941
48 hrs	880	798	959
144 hrs	...	834	974
216 hrs	...	...	974
480 hrs	...	880	...
600 hrs	...	890	...
624 hrs	...	890	...

In the case of stannic chloride, Foster found that it was not possible to follow the hydrolysis of solutions more dilute than 0.1 *N* by the conductance method, for equilibrium was established before the first conductivity reading could be made. Stannic fluoride plainly hydrolyses at a very much slower rate, for the change in conductivity of approximately 0.01 *N* solutions can be followed very easily by this method. The conductivity values obtained would seem to indicate a very slight initial dissociation of stannic fluoride into its ions.

The hydrolysis in these solutions is practically complete, and the final conductivity value is very closely that of a solution of hydrofluoric acid of the normality furnished by the decomposition of the stannic fluoride present in the sense of the equation

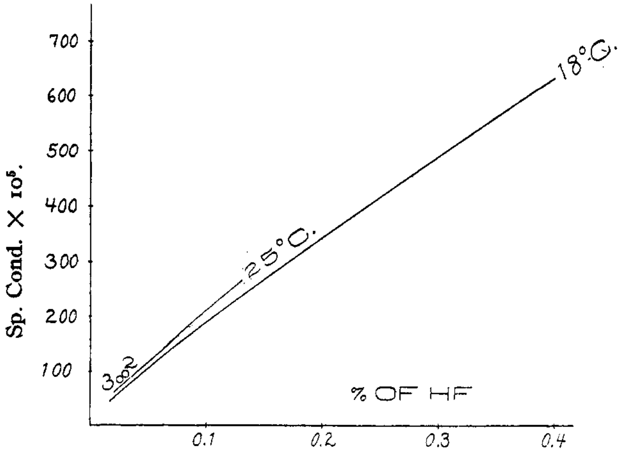
$$SnF_4 + 4HOH = Sn(OH)_4 + 4HF.$$



Hydrolysis of SnF_4.

Fig. 4.

The conductivity curve of hydrofluoric acid at 25°[1] is given in Fig. 5, together with the limiting conductivity values of Solutions 1 and 2.



Sp. Cond. of HF.

Fig. 5.

Prevention of Hydrolysis.—It seemed of interest to determine the minimum amount of hydrofluoric acid which would be needed to prevent tin from being precipitated by the hydrogen sulfide. For a solution containing 0.207 g. of tin per 100 cc., it was found that when hydrofluoric acid was present in the ratio

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[1] Hill and Sirkar, "The Density and Conductivity of Solutions of Hydrogen Fluoride," *Trans. Roy. Soc. London*, **83**, 130 (1910).

9 mols HF : 1 gram atom of tin.	Precipitation began after 5 minutes' passage of hydrogen sulfide.
10 mols HF : 1 gram atom of tin.	Precipitation began after 20 minutes.
11.5 mols HF : 1 gram atom of tin.	The solution remained perfectly clear for 35 minutes.
13 mols HF : 1 gram atom of tin.	The solution remained clear for 70 minutes, the passage of the gas being then discontinued.

It is necessary to have a sufficient concentration of hydrogen ions to prevent hydrolysis, as well as a suitable concentration of fluorine ions. The truth of the above statement is made evident by a consideration of the results of the following experiments:

The Effect of Hydrogen Sulfide on Solutions of Stannic Fluoride Containing Alkali Fluorides.—(1) A solution of crystallized stannic chloride, which contained 0.1 g. of tin per 100 cc. was treated with a solution of 4 g. of sodium fluoride made by neutralizing 48% hydrofluoric acid with sodium hydroxide. Hydrogen sulfide was passed through the solution for a long time. A whitish precipitate was formed, which gradually became yellow. The precipitate, after a thorough washing with water, alcohol, and finally carbon disulfide, was found to consist mainly of stannic oxide and sulfide.

A solution precisely similar to the above was made fairly acid with hydrochloric acid. Long passage of hydrogen sulfide gas through this solution did not occasion the slightest precipitation.

(2) Experiments similar to those described under (1) were made, using ammonium and also potassium fluoride. The results were in all respects similar to those described. In all cases the formation of the precipitate was sluggish, and in no case did the color of the precipitate reach that of pure precipitated stannic sulfide after a treatment of the solution with hydrogen sulfide lasting for 2 or 3 hours.

In his method for the separation of tin from antimony, McCay[1] recommends the use of sodium acetate to repress the dissociation of the hydrofluoric acid and thus make the precipitation of the antimonious sulfide more complete. Although the use of sodium acetate was later found to be unnecessary for the quantitative precipitation of the antimony,[2] it seems well to call attention to the fact that the conditions there recommended, namely, 0.2 to 0.5 g. of tin and antimony, 5 cc. of 48% hydrofluoric acid, in a volume of 300 cc., with the addition of 10 g. of crystallized sodium acetate, do not lead to the complete interaction of all of the hydrofluoric acid present with the sodium acetate to form sodium fluoride and acetic acid. If sufficient sodium acetate be added to react completely, stannic sulfide is precipitated when hydrogen sulfide is introduced, the

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[1] This Journal, **31**, 375 (1909).

[2] *Ibid.*, **31**, 381 (1909); **32**, 1241 (1910).

precipitation in all respects resembling that described under (1) and (2) above.

Discussion of Results.—It seems clear that the function of the hydrofluoric acid in the quantitative separations described is a double one—that it represses the dissociation of certain fluorides to such an extent that in several cases, as for example that of stannic tin, or tungsten, it is difficult or impossible to observe any of the reactions of the ions of these metals; further, that the acid supplies a sufficient concentration of hydrogen ions to prevent hydrolysis of the metal fluorides. There are at least two ways in which we might explain the apparent absence of the ions of these metals, when a suitable quantity of hydrofluoric acid is present. These different view-points may be illustrated by the facts relating to stannic fluoride, as follows:

(*a*) Stannic fluoride undergoes a slight initial dissociation into its ions, as indicated by its very slight conductivity. A suitable excess of hydrofluoric acid represses this dissociation to such an extent that none of the characteristic reactions of the stannic ion can be observed.

(*b*) Stannic fluoride may form a complex with the excess of hydrofluoric acid, of the general type H_nSnF_{4+n}. Any tendency of the complex to dissociate and give rise to the formation of ions of stannic tin, would be diminished or completely prevented by a sufficient excess of hydrofluoric acid.

The first explanation is simple and seems capable of accounting for all of the facts observed in working with hydrofluoric acid solutions of various metals.

The following are some objections which might be raised against the second explanation:

(1) An acid of the type mentioned, for example, H_2SnF_6, is certainly not stable in water solution, for solutions of stannic fluoride hydrolyze completely, in marked contrast to solutions of silicon tetrafluoride, which hydrolyzes partially to form silicic and hydrofluosilicic acids in the sense of the equation

$$3SiF_4 + 3H_2O = 2H_2SiF_6 + H_2SiO_3.$$

(2) Hydrofluoric acid solutions containing a known amount of stannic tin were neutralized with standard alkalies. The voltage change of a combination of the hydrogen electrode and 0.1 *N* calomel electrode was observed during this process. The containing vessel, and all glass tubes entering the solutions were protected from the action of the hydrofluoric acid by a coating of paraffin. The voltage readings were plotted against the cc. of standard alkali used. The curves obtained showed inflections only at the point where stannic hydroxide began to be precipitated, and that at which the precipitation was complete. These results would seem

to indicate the absence of a complex acid, for Hildebrand and Bowers[1] were able to show the existence of halogen acids of zinc, of the type $HZnCl_3$, by this method, which they devised.

(3) The action of hydrogen sulfide on solutions of stannic tin containing large quantities of alkali fluorides seems to indicate that in this case, where we have ideal conditions for the formation of a complex, we are able to precipitate the tin practically completely, although slowly.

Summary.

Stannic fluoride has been prepared with a minimum use of platinum ware. Experiments have established the facts that this compound has a slight initial dissociation, as indicated by conductivity measurements, and that the compound hydrolyzes much less rapidly than does stannic chloride in solutions of the same normality.

Reasoning from the results of the experiments on the hydrolysis of stannic fluoride, and from facts encountered in other experiments with solutions of stannic fluoride containing alkali fluorides, or free hydrofluoric acid, there has been advanced a possible explanation of the mechanism whereby tin, and a number of elements which act in similar manner, in hydrofluoric acid solution, are prevented from being precipitated by various reagents.

The writer wishes to thank Dr. L. W. McCay for interest and guidance and to thank other members of the Chemical Department of Princeton University for valuable advice, during the progress of this work.

PRINCETON, N. J.

[CONTRIBUTION FROM THE LABORATORY OF QUALITATIVE ANALYSIS, COLLEGE OF THE CITY OF NEW YORK.]

THE DETECTION OF IODIDES IN THE PRESENCE OF CYANIDES.

BY L. J. CURTMAN AND C. KAUFMAN.

Received March 14, 1918.

The object of this investigation was twofold: first, to determine the extent of the interfering influence of cyanides in the test for iodides by the use of oxidizing agents; second, to provide a rapid and reliable method whereby one mg. of iodide could be detected in the presence of 500 mg. of cyanide.

Determination of the Amount of Interference.—In the presence of limited amounts of cyanide, iodine is visibly liberated by potassium nitrite as well as by other oxidizing agents. The reddish brown coloration which the liberated iodine imparts to the solution disappears, how-

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[1] "A Study of the Action of Alkali on Certain Zinc Salts by Means of the Hydrogen Electrode," THIS JOURNAL, 38, 785 (1916).