Summary.

The radical difference between the theory of the molecular mechanism of protein swelling presented by Tolman and Stearn and that evolved by Procter and Wilson is pointed out.

It is shown that if a colloid jelly combines chemically with a given electrolyte forming a highly ionizable colloid salt, the jelly must swell to a maximum and then contract indefinitely as the concentration of ionized electrolyte in the solution is increased.

It is shown further that the addition to the system of any electrolyte which does not combine with the colloid will produce contraction of the swollen jelly to an extent depending upon the resulting increase in ionic concentration.

A suggestion is given as to the origin of microscopic pores observed in certain hardened jellies.

Upon the assumption that a colloid combines chemically with ions of one sign of a dissolved electrolyte, both the concentration of chemically combined electrolyte and the total quantity of electrolyte either combined with or present in the solution in contact with the colloid are represented as functions of the concentration of electrolyte in the solution. The curves for these functions are approximately the same as those obtained by use of the empirical adsorption formula. It is believed that further development of the reasoning given in this paper will result in a more satisfactory formula for adsorption than the one now so generally used.

The authors wish to express their thanks to the Editors of THIS JOURNAL for their helpful criticism of the manuscript before publication.

THE USE OF HYDROFLUORIC ACID IN ANALYSIS.

BY N. HOWELL FURMAN.

Received February 15, 1918.

Introduction.

In recent years a number of new analytical procedures have been developed which are based upon the behavior of certain fluorides in neutral and acid solution. The main chemical facts of which use is made in these procedures are:

First, by choosing the proper solvent true solutions of the metals of the copper-tin group, or of the metals chromium, tungsten, and molybdenum, may be obtained. Indeed, nearly all of the metals, especially those most frequently found in alloys, are readily soluble in a mixture of nitric and hydrofluoric acids.

Second, having obtained such solutions, a number of separations which are difficult, or impracticable by any other known method, may be effected quickly and completely by the use of reagents commonly employed in analysis.

The qualitative behavior of certain fluoride solutions has been investigated by A. A. Noyes, and the results of his experiments are to be found in "A System of Qualitative Analysis Including Nearly All of the Metallic Elements."[1] In this work some separations were mentioned as affording promise from a quantitative standpoint, although no effort was made to establish the fact that such separations were quantitative, and the hope was expressed that others would find opportunity to develop this field.

A study of the quantitative separations possible in such solutions was undertaken by L. W. McCay,[2] and the results thus far obtained show clearly that several types of alloys whose analysis was previously a difficult and tedious task can now be analyzed rapidly[3] and accurately by the aid of these new methods.

A list of the separations which can be effected in acid fluoride solution is given in Table I. An examination of this list will give some idea of the wide variety of alloys and ores to which the methods of separation can be applied. In this table a plus sign indicates that the element can

TABLE I.—ANALYTICAL SEPARATIONS POSSIBLE IN ACID FLUORIDE SOLUTION.

(*a*) Electro-Analytical Separations.

Element remaining in solution.	Element precipitated.			
	Copper.	Lead.	Silver.	Mercury.
Stannic tin	+	+	*V*	+
Antimony (ic)	+	+	*V*	+
Arsenic (-ic)	*V*			
Tungsten	+	+	*V*	+
Molybdenum	+	+	*V*	*V*
Chromium	+	+	*V*	+
Vanadium	+			

(*b*) Using Hydrogen Sulfide as Precipitating Agent.

Element remaining in solution.	Element precipitated.					
	Copper.	Lead.	Silver.	Mercury.	Antimony(-ous).	Arsenic(-ous).
Stannic tin	+	+	*N*	*N*	+	+
Tungsten	*N*	*N*	*N*	*N*		

All of the separations indicated above are known to be quantitative except those marked *N*, which are mentioned in the work of Noyes to which reference has been given, and which are in all probability quantitative.

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[1] *Tech. Quart.*, **16**, 93(1903); **17**, 214 (1904).

[2] L. W. McCay, "The Separation of Tin and Antimony," THIS JOURNAL, **31**, 373 (1909); "The Analysis of the Tin-Antimony Alloys," *Ibid.*, **32**, 1241 (1910); "The Use of Hydrofluoric Acid in the Separation of Copper and Lead from Tin and Antimony by Means of the Electric Current," *Ibid.*, **36**, 2375 (1914); L. W. McCay and N. Howell Furman, "The Use of Hydrofluoric Acid in the Separation of Some Heavy Metals from Tin, Antimony, Tungsten, and Molybdenum by Means of the Electric Current," *Ibid.*, **38**, 640 (1916).

[3] Preliminary experiments indicate that Babbitts and other tin-antimony alloys may be analyzed in less than 8 hours' working time by these methods.

be precipitated quantitatively from a solution containing all of the elements listed; *V* indicates a separation in which the voltage cannot exceed a definite maximum value.

An illustration will perhaps make the use of the above table more clear. The table shows that it is possible, for example, to separate quantitatively, copper, or lead, copper, silver, and mercury simultaneously from *one* or *all* of the elements—tin(-ic), antimony(-ic), tungsten, molybdenum, and chromium—by means of the electric current in hydrofluoric acid solution. If hydrogen sulfide be used as the precipitating agent, copper, lead, silver, mercury, antimony (-ous), and arsenic (-ous), can be separated individually, or collectively, from tin(-ic), and undoubtedly from tungsten as well.

The references which are cited in footnote 1 should be consulted for the precise conditions which are necessary in effecting a given separation.

Work is being continued by the writer and others upon several of the separations mentioned, and incidental observations upon the behavior of some metals not mentioned in the list are being made, with the idea of making the hydrofluoric acid method as comprehensive as possible.

The Separation of Copper and Vanadium.—The experimental data proving that copper can be separated quantitatively from vanadium by means of the electric current in acid fluoride solution are given in Table II. Weighed amounts of sodium vanadate were dissolved in water, 2.5 cc. of nitric acid, sp. gr. 1.4, and suitable amounts of hydrofluoric acid were added, and a definite amount of a standard copper nitrate solution was run in. The total volume of the solution was 100 to 110 cc. The current was maintained at 0.2 amp. $N. D._{100}$ and 2.5 to 4.5 volts for 8 to 10 hours, or overnight.

TABLE II.—THE SEPARATION OF COPPER AND VANADIUM.

Vanadium. G.	Hydrofluoric acid, 48% cc.	Copper taken. G.	Platinum found. Mg.	Copper found.[1] G.
0.1694	0.0	0.2506	0.1	0.2500
0.1479	5.0	0.2506	0.4	0.2508
0.1645	0.0	0.2506	0.2	0.2504
0.1773	5.0	0.2506	1.8	0.2505
0.1938	5.0	0.5012	1.3	0.5017
0.1941	2.5	0.5012	0.4	0.5008

It is evident that vanadium behaves just as do tin, tungsten, etc., in

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[1] These copper values are corrected for the amounts of platinum indicated in the fourth column of the table. In the first 3 and the last determinations an anode of platinum-iridium was used. In such cases the amount of platinum deposited with the copper is almost invariably less than 0.5 mg. When an anode of pure platinum is used the amount deposited with the copper is much greater as shown in the fourth and fifth determinations in Table II. See McCay, THIS JOURNAL, **36**, 2376 (1914).

similar solutions. A few preliminary observations upon uranium and titanium seem to indicate that they too may be separated from copper, and without doubt from other elements by the same method.

A preliminary note has appeared indicating that cobalt and nickel[1] can be separated in ammoniacal fluoride solution, and there may be other separations possible in neutral or alkaline fluoride solutions. Little work has been reported in this field.

The Behavior of Stannic Tin in Acid Fluoride Solution.

Several elements when in the higher state of oxidation, in a solution containing free hydrofluoric acid, show a chemical deportment utterly different from that which they exhibit in a similar acid solution, which, however, contains no hydrofluoric acid. This behavior is the basis of the separations given in Table I. It may be illustrated in the most striking manner by the facts relating to stannic tin.

STANNIC TIN IN ACID SOLUTION.

	With a moderate amount of free hydrofluoric acid.	Without hydrofluoric acid.
1 Action on dilution....	No hydrolysis on great dilution, or after long standing.	Hydrolysis on moderate dilution, or on standing.
2 Electric current......	No reduction with electromotive forces as great as 9 volts, and current densities as high as 5 amperes $N.D._{100}$ on a mercury cathode.	Reduction to the metal.
3 Action on boiling with zinc or aluminium....	No reduction to the stannous condition or metallic state after prolonged boiling.	Reduction to the stannous condition and metal.
4 Effect of hydrogen sulfide............	Not a trace of precipitation on long-continued passage of the gas even when the solution is boiled.	Complete precipitation as stannic sulfide.
5 Effect of neutralization..............	The tin in such solutions cannot be estimated by neutralizing, and "salting out" the stannic hydroxide, for considerable amounts of tin remain in soluble form.	A satisfactory determination of the tin may be made by neutralizing, and "salting out" the stannic hydroxide.

It is evident that acid solutions of stannic fluoride containing free hydrofluoric acid in sufficient amount give none of the characteristic reactions of the stannic ion. Similar facts about the behavior of antimony, tungsten, and molybdenum, in their highest states of oxidation, are given in a previous paper.[2]

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[1] E. F. Smith and H. S. Lukens, *Trans. Am. Electrochem. Soc.*, 27, 30 (1915).

[2] McCay and Furman, *Loc. cit.*

It is likewise obvious that this behavior of stannic tin, which is of value in its separation from other metals, makes its subsequent estimation a matter of difficulty. The estimation of the tin is the largest time-consuming factor in the analysis of tin-antimony alloys by the hydrofluoric acid method,[1] of which a brief schematic representation is given below.

The Analysis of Tin-Antimony Alloys by the Hydrofluoric Acid Method.—The alloy is dissolved in hot conc. sulfuric acid and the cold solution poured into water containing hydrofluoric acid.[2]

PRECIPITATE: Lead sulfate.	FILTRATE: Copper, antimony, in the trivalent condition, tin in the stannic form, and a trace of lead.

When the filtrate is treated with hydrogen sulfide the copper, lead and antimony are completely precipitated as sulfides, which, after filtration, are digested with colorless potassium sulfide solution.

PRECIPITATE: Consisting of copper and lead sulfides is ignited; the residue is dissolved in nitric acid and the copper and lead determined electrolytically.	FILTRATE: Is heated with conc. sulfuric acid until the antimony sulfide is dissolved. The metal is then estimated volumetrically with standard potassium permanganate or bromate solution.

The filtrate containing the tin is evaporated in a platinum dish until the hydrogen fluoride is removed and the sulfuric acid has commenced to fume copiously. The tin may then be determined as stannic oxide, after the sulfuric acid solution has been poured into a large volume of water, the stannic hydroxide salted out and collected by filtration.

If the tin filtrate could be made to exhibit the properties of stannic ions, and if the use of platinum could be avoided, the value of the method would be greatly enhanced. In a recent article by O. L. Barneby[3] it is stated that in determining ferrous iron with potassium permanganate in solutions of rock powders in hydrofluoric and sulfuric acids, satisfactory results are obtained by adding boric acid to the solutions prior to titration. Ordinarily the manganous fluoride generated in such solutions is oxidized by the permanganate used in the titration, and the red-brown tint of the undissociated manganic fluoride formed obscures the end-point. The addition of a moderate excess of boric acid removes the fluorine from the sphere of action, possibly by the formation of the complex acid, HBF_4, thus making it possible to obtain a satisfactory end-point in the titration. After the addition of the boric acid the ferrous iron solutions are as stable in air as are sulfuric acid solutions of ferrous sulfate. Titanic, molybdic, and silicic acids act in a manner similar to boric acid.

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[1] THIS JOURNAL, 32, 1241 (1910).

[2] The water and hydrofluoric acid are contained in a ceresin beaker. A funnel which has been paraffined is used in the filtration.

[3] *Ibid.*, 37, 1481 (1915).

These facts at once suggested the possibility of causing a hydrofluoric acid solution of stannic tin to behave like an ordinary acid solution of the metal, by the addition of a moderate amount of boric acid. A thorough test of this possibility was made with complete success, not only from a qualitative standpoint, but from a quantitative one as well, as the following experiments show.

The Precipitation of Tin as Sulfide in the Presence of Hydrofluoric and Boric Acids.—Weighed portions of metallic tin of tested purity were dissolved in 5 cc. hot conc. sulfuric acid, and the resulting solutions poured into a platinum dish containing water and 2 cc. of 48% hydrofluoric acid. A slight excess of solid boric acid was added, and, after dilution to 200–250 cc., the solution was warmed and a rapid stream of hydrogen sulfide gas run in for at least half an hour. After standing until the precipitate had settled the sulfide was filtered off, washed thoroughly with 0.5% ammonium chloride solution and then with alcohol. The sulfide was transformed into the oxide by roasting, observing the usual analytical precautions. The results are given in Table III.

TABLE III.—DETERMINATION OF TIN AS SULFIDE IN SOLUTIONS CONTAINING HYDROFLUORIC AND BORIC ACIDS.

Tin taken. G.	Boric acid. G.	Residue from filtrate. Mg.	Tin found. G.
0.1014	5.0	1.0	0.1013
0.1000	5.0	0.3	0.0990
0.2013	3.0	0.2	0.2019
0.2029	3.0	0.3	0.2020
0.2009	4.0	0.2	0.2003

In the third column are given the weights of material recovered from the filtrate after filtering off the stannic sulfide precipitates. These filtrates were in each case evaporated in platinum until the hydrogen fluoride was completely removed. Sufficient water was then added to dissolve the boric acid which had separated out, and hydrogen sulfide was passed through the solution for 15 to 20 minutes. A slight yellow color appeared, and after standing 12 to 18 hours, a small amount of a light brown precipitate had settled out. This precipitate was collected, ignited, and the residue weighed. In only one case was the residue as great as one mg.; in this case the bulk of the residue was found later to be platinum, which had been dissolved from the dish by the action of the sulfuric acid.[1] The other residues also consisted mainly of platinum.

Electrolytic Precipitation of Tin from Solutions Containing Hydrofluoric and Boric Acids.—Solutions of tin were prepared exactly as described above. To each solution, after the addition of boric acid, 5 g. of ammonium oxalate and 5 g. of oxalic acid were added, the final volume

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[1] See L. W. McCay, "The Action of Boiling Sulfuric Acid on Platinum," *Reports 8th Internat. Cong. Applied Chem.*, 1, 351 (1912).

of the solution being brought to 300 cc. The deposition of the tin was effected under the conditions of current recommended by Classen.[1] The cathodes used were coated with copper to prevent the alloying of the platinum with tin, which otherwise takes place. The tin was deposited completely from this solution, but the time required was excessive (48 hours). The results are given in Table IV.

TABLE IV.—ELECTROLYTIC DEPOSITION OF TIN FROM SOLUTIONS CONTAINING HYDROFLUORIC AND BORIC ACIDS.

Tin taken. G.	Boric acid. G.	Hydrofluoric acid, 48% cc.	Platinum found. Mg.	Tin found.[2] G.
0.1076	2.0	1.0	0.5	0.1065
0.1020	3.0	2.0	1.5	0.1022
0.2003	3.0	2.0	1.6	0.2009
0.2074	4.0	2.0	1.1	0.2071
0.2072	3.0	1.0	0.7	0.2062

The solutions from which the tin had been deposited were tested for the presence of tin in the following manner: After being made ammoniacal, the solution was saturated with hydrogen sulfide gas, then made faintly acid with acetic acid; the precipitate formed was filtered off, ignited, and weighed. In no case was the weight of the residue greater than 0.3 mg., nor could tin be detected therein.

Reduction of Stannic Tin by Metals in Solutions Containing Hydrofluoric and Boric Acids.—Acid fluoride solutions of stannic tin to which an excess of boric acid had been added were found to be reduced by metallic zinc or aluminium, the tin of course being reduced to the metallic state.

The Hydrolysis of Stannic Tin Salts in the Presence of Hydrofluoric and Boric Acids.—When a solution of stannic tin, prepared as above, is rendered ammoniacal, then very slightly acid with sulfuric acid, it undergoes partial hydrolysis on standing or on being diluted to a sufficient degree. The precipitated stannic hydroxide settles well and may readily be filtered off. The hydrolysis is never complete, however, for if hydrogen sulfide be run into the filtrate, a yellow coloration appears almost immediately, and a considerable amount of stannic sulfide is precipitated.

The Use of Silica Instead of Boric Acid.—Since silicon has a very great affinity for fluorine, it seemed reasonable to suppose that its presence would cause tin to behave as if fluorine were absent, in much the same manner as boric acid does. Experiments of a purely qualitative nature proved that this was the case. If, for example, an excess of sodium silicate is added to an acid solution of stannic fluoride, the tin may be completely precipitated by hydrogen sulfide.

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[1] "Quant. Analysis by Electrolysis," 1915, p. 135.

[2] The tin values are corrected for the weights of platinum given in the fourth column of the table.

Experiments showed that silica itself is not very effective in counteracting the effect of the fluorine, owing to the difficulty with which *dilute* solutions of hydrofluoric acid attack it. It was found that silica prepared by purifying a sample of kieselguhr with hydrochloric acid and subsequent water extractions, when placed in large excess in one of the tin solutions, did not combine with the fluorine to an extent sufficient to permit even a trace of tin to be precipitated by hydrogen sulfide, although the solution was boiled for half an hour and allowed to stand overnight in an atmosphere of hydrogen sulfide, after saturation with the gas.

Silica prepared by the dehydration of silicic acid precipitated from water glass was found to be fairly reactive, and with its use a complete precipitation of the tin as sulfide could be made after sufficient boiling.

The Action of Solutions Containing Hydrofluoric and Boric Acids upon Glass.—The above experiments suggested the possibility that fluoride solutions to which boric acid had been added in excess would have little action on glass vessels. A beaker of good American glass, weighing at the outset 97.16 g., was subjected to the action of a solution containing 2 cc. of 48% hydrofluoric acid, 0.5 cc. of 5 N sulfuric acid, and 4 g. of boric acid per 300 cc. The average loss in weight was found to be 0.00049 g. per 24 hours, per 100 cm^2. of exposed surface, at room temperature. Omitting the boric acid, the average loss was 0.088 g. per 24 hours per 100 cm^2. of exposed surface.

When one of the solutions containing boric acid was boiled for half an hour, the loss which the beaker suffered was about equal to that occasioned by 2 days' action of the solution at room temperature.

Solutions which contained no hydrofluoric acid attacked the beaker to the extent of 0.5 mg. at most, under the conditions which prevailed in the above experiments.

It is apparent that boric acid exerts a very marked protective action. These results show that glass vessels may be used in qualitative and quantitative work with such solutions, since the material removed from the glass is moderate in amount, and remains in a soluble form. As a matter of fact, the last 2 electrolytic determinations given in Table IV were made in glass beakers.

The scheme for the analysis of tin-antimony alloys, which is outlined on page 899, is modified to avoid the use of platinum vessels as follows:

The filtrate containing the tin is collected in a glass beaker in which a solution containing the requisite amount of boric acid has been placed. The acidity of the solution is adjusted by the addition of ammonium hydroxide until 0.5 cc. or less of 0.5 N acid remains. The tin is then precipitated by hydrogen sulfide and estimated in the form of tin dioxide.

The Qualitative Analysis of the Tin Group.—The facts above presented, together with others previously known about the behavior of certain fluorides in solution, lend themselves readily to a method for the qualitative examination of the tin group of elements, which is outlined below.

Dissolve the tin group precipitate in 10 cc. of hot conc. sulfuric acid.[1] Pour the resulting solution into water containing hydrofluoric acid and run in hydrogen sulfide until the precipitation is complete.

PRECIPITATE: Arsenious and antimonious sulfides.	FILTRATE: Stannic fluoride in solution.
Treat with hydrochloric acid and potassium chlorate.	Add an excess of solid boric acid and heat until solution is complete. Precipitate the tin with hydrogen sulfide, dissolve the precipitate in conc. hydrochloric acid, and make the usual confirmatory test.
One portion of the resulting solution is diluted considerably. A red precipitate formed when hydrogen sulfide is introduced indicates antimony. The presence of antimony is confirmed by a suitable test.	
The other portion of the solution is divided into two equal parts.	
To the first is added two or three times its volume of conc. hydrochloric acid. A yellow precipitate formed when hydrogen sulfide is run in indicates arsenic.	
The second part of the solution is made ammoniacal, filtered, and the formation of a white crystalline precipitate on the addition of magnesia mixture to the filtrate indicates arsenic.	

As a test of this procedure, a number of unknowns were examined, which Mr. L. B. Dobie, Assistant in Quantitative Analysis, kindly prepared. These solutions were made from stock solutions of copper, arsenic, antimony, and tin, each solution containing 0.50 g. of metal per 50 cc., so that the amount of metal present was known quantitatively in each case. The procedure used was as follows:

The copper-tin group precipitate was treated with colorless potassium sulfide[2] in a porcelain dish at water bath temperature for 10 to 15 minutes, and the solution of sulfo-salts formed filtered directly into a tall narrow beaker, or Erlenmeyer flask of 200 to 300 cc. capacity, all unnecessary dilution being avoided. From 5 to 15 cc. of

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[1] A small piece of sulfur is added so that the sulfur dioxide formed may reduce all arsenic and antimony to the lower state of oxidation.

[2] Colorless, freshly-made potassium sulfide is usually preferable for this separation, in alloy analysis. A separation of the copper and tin groups described by M. Cannon Sneed, THIS JOURNAL, 40, 187 (1918), involves the use of colorless sodium sulfide. The method of analysis of the tin group described above could be applied to the filtrate obtained in Sneed's method, after the removal of the mercury as carbonate. The use of yellow or colorless ammonium sulfide in the separation of the copper and tin groups does not alter the subsequent procedure for the analysis of the tin group by the hydrofluoric acid method.

conc. sulfuric acid were added cautiously, a little at a time, after which heat was applied until the sulfides were completely dissolved.[1] By this treatment any antimony and arsenic in the higher states of oxidation were completely reduced to the lower state, while the tin remained entirely in the stannic condition.[2] When cool the solution was diluted somewhat and after cooling poured into 100 cc. of water containing 1 to 3 cc. of 48% hydrofluoric acid.[3] After a thorough mixing, a rapid stream of hydrogen sulfide gas was introduced until the precipitation of the arsenic and antimony was completed.

A portion of the well-washed precipitate was treated as follows: Solution and complete oxidation of both antimony and arsenic were effected by treatment with 10 to 20 cc. of conc. hydrochloric acid with the addition of small portions of potassium chlorate; the solution was boiled down to half of its volume, made up to the original volume with conc. hydrochloric acid, and again evaporated to half its volume.[4] Any free sulfur present was removed by filtration at this point.

One-half of this solution was diluted to a volume of about 600 cc., and a rapid stream of hydrogen sulfide run in for 5 minutes or so.[5] A yellow coloration, or reddish precipitate indicated antimony. After all excess of hydrogen sulfide had been expelled by a rapid current of filtered air, some of the well washed precipitate was subjected to one of the usual confirmatory tests for antimony.

Some of the remaining portion of the original solution was made ammoniacal, any precipitated antimony hydroxide removed by filtration and the filtrate tested with magnesia mixture. The formation of a white crystalline precipitate indicated, of course, the presence of arsenic.

As an alternative or confirmatory test for arsenic, some of the original solution was mixed with twice its volume of conc. hydrochloric acid, and a rapid stream of hydrogen sulfide gas then led in, the solution being well-cooled during the process. Under these conditions only arsenic in the form of the yellow pentasulfide[6] is precipitated.

A portion of the filtrate which may contain tin is poured into a glass beaker in which 2 to 4 g. of solid boric acid has been placed. Most of the free acid is neutralized by the addition of ammonium hydroxide, after which a rapid stream of hydrogen sul-

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[1] This process can be completed in 40 to 60 minutes.

[2] Free sulfur is necessary for this reduction. This may be furnished by the decomposition of the sulfides, but it is safest to add a small piece of sulfur.

[3] The hydrofluoric acid solution is placed in a beaker made of paraffin or ceresin. An empty hydrofluoric acid bottle can be made into a beaker admirably suited for this sort of work. A paraffined funnel is used in the filtrations. Some sulfur separates when the solution of the sulfides is made, but this may be removed by filtration, most conveniently at this point.

[4] A. A. Noyes, "Qual. Analysis," 1915, p. 61; also Treadwell "Quant. Analysis," 1914, p. 241.

[5] This is an adaptation of Bunsen's quantitative method for the separation of antimony and arsenic (*Ann.*, **192**, 305 (1878)). The arsenic remains in solution because of the formation of sulfoxyarsenic acids, especially monosulfoxyarsenic acid, H_3AsO_3S. For an account of the preparation, properties, and deportment with reagents, of these acids, see L. W. McCay, *Am. Chem. J.*, 10, 459 (1888); *Z. anorg. Chem.*, **29**, 36 (1901); L. W. McCay and Wm. Foster, *Ibid.*, 41, 452 (1904); L. W. McCay, THIS JOURNAL, 24, 661 (1902); see also Wm. Foster, *Ibid.*, **38**, 52 (1916).

[6] The procedure given follows the quantitative method devised by F. Neher, *Z. anal. Chem.*, **32**, 45 (1893).

fide gas is led in until precipitation is complete. A yellow precipitate indicates tin, whose presence is confirmed by the usual test with mercuric chloride solution.[1]

The procedure given for the separation and detection of arsenic and antimony is preferable to the treatment of the sulfides with conc. hydrochloric acid, in as much as arsenious sulfide is appreciably soluble in this acid, whereas the pentasulfide usually obtained in most procedures for the examination of the tin group, is practically insoluble in this acid. Good results were obtained by using hydrochloric acid of a concentration obtained by mixing 2 parts of the concentrated acid with one part of water. The sulfides were digested with this acid at water-bath temperature. Following the procedure outlined above there is no difficulty in detecting arsenic and tin in a solution containing 2 mg. of the former and 500 mg. of the latter per 200 cc., either in the presence of large or small quantities of antimony.

In Table V are summarized the results of the examination of the unknown solutions previously mentioned, together with the actual amounts of the metals present in each case; this latter information was supplied by Mr. Dobie after all the analyses had been completed.

TABLE V.—RESULTS OF EXAMINATION OF UNKNOWN SOLUTIONS.

	Copper.		Tin.		Antimony.		Arsenic.	
	Amount present. Mg.	Reported.	Amount present. Mg.	Reported.	Amount present. Mg.	Reported.	Amount present. Mg.	Reported.
1.	500	Abundant	0	Absent	0	Absent	0	Absent
2.	500	Abundant	100	Abundant	250	Abundant	500	Abundant
3.	500	Abundant	0	Absent	500	Large amount	2	Extremely small amount
4.	500	Abundant	500	Large amount	5	Very small amount	200	Large amount
5.	500	Abundant	2	Quite small amount	0	Doubtful	500	Large amount
6.	500	Abundant	200	Considerable amount	0	Absent	10	Small amount
7.	500	Abundant	2	Small amount	500	Abundant	0	Absent
8.	500	Abundant	5	Fair amount	5	Small amount	200	Abundant
9.	500	Abundant	10	Fairly small amount	200	Abundant	5	Small amount

Comments on Examination of Unknown Solutions.—In each case the original volume of the unknown solution was 200 cc. Not more than 50 cc. of each solution was taken for examination.

It will be noticed that in the fifth unknown the presence of antimony is reported as doubtful. No antimony was placed in this solution. Aside from this error, there is in every case at least qualitative agreement. The quantities of metals reported agree to a fair extent with the amounts actually present. The amount of tin reported in the ninth unknown was

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[1] In the examination of some of the unknowns a positive indication of the presence of tin was obtained, both by the mercuric chloride test and the formation of a yellow precipitate, when the amount of tin actually present was later calculated to be less than 0.3 mg. in 30 cc. of the solution tested. This fact is an indication of the completeness with which the tin is precipitated, and the fluorine held in combination, through the agency of the boric acid.

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).