

progress, and it is hoped that it may ultimately be possible to employ this process to determine the ratio in which potassium and chlorine are combined in potassium chloride.

UNIVERSITY OF PENNSYLVANIA.

---

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

## THE ELECTROLYTIC DEPOSITION OF ANTIMONY.

By NEWCOMB K. CHANEY.

Received August 4, 1913.

The rapid electrolytic deposition of antimony from an alkaline electrolyte of sodium sulfide, potassium cyanide and sodium hydroxide as carried out in this laboratory, affords a method for the estimation of antimony which has no superior for ease, rapidity and accuracy.

Tin may also be very satisfactorily deposited as metal from the solution of its sulfide in ammonium polysulfide.

When both antimony and tin are present together, however, neither of these methods is available, as tin is incompletely deposited from a sodium sulfide electrolyte, and metallic antimony is appreciably soluble in ammonium sulfide. These facts have seriously limited the usefulness of the electrolytic methods mentioned above for practical analytical purposes.

With a view, therefore, of finding an electrolytic process readily applicable in the determination of antimony or tin, when both are present, the following work was undertaken.

The behavior of a large number of electrolytes with respect to antimony and tin has been studied. Those electrolytes which gave indications of availability have been more carefully tested over a wide range of conditions, *e. g.*, voltage, current density, addition of various salts, temperature range, form and size of electrodes and rates of rotation of anode or cathode.

The description of the experimental work is arranged under the headings of the various electrolytes studied.

### I. Ammonium Lactate Electrolyte.

About fifteen determinations were made using antimony chloride. The voltage, current density, rate of rotation of anode, concentration of ammonia and of lactic acid were systematically varied. The deposits were spongy and non-adherent.

### II. Ammonium Polysulfide Electrolyte.

The fact that the deposition of antimony was incomplete from an ammonium sulfide bath, and complete from a sodium sulfide bath, suggested that the cause was in the different concentration of hydroxyl ions. Therefore the addition was made to the ammonium polysulfide bath of sodium carbonate, barium hydroxide and calcium hydroxide, respectively.

Ten cc. of antimony chloride were precipitated and redissolved in the least possible quantity of ammonium polysulfide. This was diluted to

110 cc. with water and 20 cc. of saturated barium hydroxide were added. The anode was rotated with moderate speed. The voltage was 3.5 and amperage 0.5 N. D.<sub>100</sub>. The deposits were brilliant and metallic in character, like polished platinum, very unlike the usual dark electro-deposits of antimony. The greater part of 0.2 gram of antimony was deposited in 30 minutes. Similar brilliant metallic deposits were obtained by the addition of 20 cc. of saturated calcium hydroxide solution or 1 gram of sodium carbonate to the ammonium sulfide bath.

The deposits, however, were not quantitative by several milligrams. Slight differences in the concentration of ammonia and ammonium polysulfide were found to have very disturbing influences upon the course of the electrolysis. Particularly was this true of the amount of sulfur dissolved in the ammonium polysulfide. As sodium carbonate was preferable to barium or calcium hydroxide as an addition reagent, a careful investigation was made of the effect upon the deposition of antimony of the three substances: sodium carbonate, ammonium polysulfide and ammonia, respectively.

First, the addition of increasing amounts of sodium carbonate to the ammonium sulfide electrolyte was tried, and a steady decrease in the rate of deposit was noticed for increasing concentration of sodium carbonate. This may be due to the increased amount of free ammonia.

It would seem that the sodium carbonate in small concentration does not exert any retarding influence in the deposition of antimony, while in larger amounts there is a slight effect.

Upon the addition of 10 cc. of ammonia to the sodium sulfide-potassium cyanide bath, a distinct loss was apparent.

Metallic antimony is appreciably soluble in colorless ammonium sulfide. This, and not the lower hydroxyl concentration, explains the incomplete deposition from ammonium sulfide solution. It seemed, therefore, that while the greater part of the antimony could be deposited as a brilliant white metal from an ammonium polysulfide electrolyte, quantitative results would not be possible unless at the end of the electrolysis the concentration of ammonia and ammonium sulfide could be made negligible.

To effect this result, the electrolysis of antimony chloride was carried out with ammonium sulfide at boiling temperature. The ammonia and ammonium sulfide were thus removed or oxidized to ammonium sulfate as the antimony was deposited. The deposits were of polished white metal. The results were quantitative. In the early part of the electrolysis much sulfur separated upon the anode. This was subsequently oxidized and the free ammonia volatilized, leaving a clear, colorless bath, free from antimony. A highly essential condition to the satisfactory progress of the electrolysis is the proper initial concentration of the ammonium polysulfide.

This must have enough sulfur in it so that not more than 5 cc. of the solution are required for the solution of 0.2 gram of antimony in the form of the chloride solution.

A standard solution of ammonium polysulfide which could be easily duplicated was prepared.

*Solution A.*—Saturate concentrated aqueous ammonia with hydrogen sulfide in the presence of excess of powdered sulfur. Filter off excess of sulfur after long shaking.

*Solution B.*—Saturate a concentrated ammonia solution with hydrogen sulfide.

One part of solution A is added to six parts of solution B for final use.

The ammonium polysulfide so prepared is added dropwise to the antimony chloride solution in a small covered beaker until there is formed a clear solution.

This is then washed into the platinum dish, diluted to 125 cc. and electrolyzed at the boiling point, with an initial voltage of 3.5 and  $N. D_{100} = 1$  ampere. As soon as the amperage falls by exhaustion of the bath, the voltage is raised to 4 volts. Time, 1 hour. Rotation of anode, 400 revolutions per minute.

Wt. Sb found by $Na_2S$ -KCN method.....	0.2385 gram
Wt. Sb found by $(NH_4)_2Sx$ method.....	0.2386 gram
Wt. Sb found by $(NH_4)_2Sx$ method.....	0.2384 gram

The deposition of antimony from an ammonium sulfide electrolyte has two points of interest. One is the metallic appearance and character of the deposit, while the second is the fact that it makes it possible to determine total tin and antimony in the form of their sulfides quantitatively in the same electrolyte. It remains to separate and determine one of these two metals in the presence of the other to provide a complete analytical method.

Because of the metallic character of the deposit, an attempt was made to determine antimony in the mercury cup with the ammonium sulfide electrolyte. It was found that antimony up to 0.1 gram in weight could be amalgamated with mercury and weighed, when a rotating anode was used and the E. M. F. was kept below 3.5 volts. Time required, one hour. The surface of the mercury seemed eventually to become saturated and then a loose, powdery deposit was formed which did not amalgamate. It is possible that with larger quantities of mercury and a means of agitating the same, a successful method could be developed.

### III. Tartrates and Tartaric Acid Electrolytes.

It was found that tin in the stannic condition was not deposited from sodium or ammonium tartrate solutions, while antimony could be (under certain conditions) deposited in an adherent and weighable form. Weak and concentrated solutions of sodium and potassium and ammonium

tartrates were carefully investigated, but it was found, that as in the case of the lactate solutions, the last traces of antimony could never be quantitatively removed.

Saturated solutions of tartaric acid were found to give firm graphite-like deposits of antimony with less than two volts, but they were not quantitative.

To determine whether interfering decomposition products were produced in a course of electrolysis, 20 cc. of saturated tartaric acid solution were diluted to 50 cc. with water and electrolyzed for one hour, at 5 volts and 1 ampere. To this and to a similar unelectrolyzed bath, antimony chloride solution was added drop by drop till deposition occurred. No difference was observed. More than 15 milligrams of antimony were added before any deposition occurred in either case. Since the bath seems to remain constant an attempt was made to "saturate" a tartaric acid bath with antimony by adding a small amount of antimony sulfide and electrolyzing till no more antimony was deposited. This bath was then to be used for the determination of a regular sample of antimony and tin. It seemed from the preliminary work that conditions might be standardized rapidly enough to permit of a determination of antimony in the presence of tin in this manner. The difficulties and obvious objections to such a procedure, however, led to the search for more promising electrolytes.

#### IV. The Alkaline Earth Sulfides as Electrolytes for Antimony.

Solutions of the hydrosulfides of magnesium calcium and barium were formed by passing hydrogen sulfide through saturated solutions of the hydroxides in the presence of excess of the solid hydroxide or oxide and the relative solubilities of the sulfides, arsenic, antimony and tin were roughly determined. Barium hydrosulfide alone dissolved a sufficient amount of antimony sulfide to appear practicable as an electrolyte, the others required too bulky a solution for work in platinum vessels. With the use of barium hydrosulfide, the formation of solid barium carbonate in the vessels during electrolysis proved troublesome.

It was found that a simple qualitative separation of antimony and tin sulfides consisted in adding to them cold saturated barium hydroxide in large excess. The antimony sulfide readily dissolved upon stirring, leaving the bulk of the tin sulfide to be filtered out. Upon boiling the filtrate, the slight amount of tin present was quantitatively precipitated as stannic hydroxide. This has some advantages over the more usual separation of these sulfides by calcium hydroxide. The antimony sulfide is more soluble, the tin sulfide is more insoluble and is more promptly precipitated upon boiling. Where large amounts of both tin and antimony are present, a rough qualitative separation can be obtained with cold solutions.

Since it is desired to avoid the removal of tin from antimony by a tedious

process of filtration and washing, it seemed that to remove the antimony, by electrolysis, from the precipitated hydroxide would afford the best prospect of a convenient and simple separation. Satisfactory deposits of antimony were not obtained with magnesium hydrosulfide. Barium salts were objectionable because of the formation of solid carbonate. The remainder of the work was, therefore, devoted to the problem of securing quantitative deposits of antimony from electrolytes of calcium hydroxide and sulfide, in the presence of and free from tin.

The initial objection to calcium hydrosulfide as an electrolyte had been the large bulk of solution required to dissolve a small amount of antimony sulfide. It appeared, however, that the solution of antimony sulfide is largely due to the presence of calcium sulfide ( $\text{CaS}$ ) in the solution, which seems to form a weak complex salt with antimony sulfide ( $\text{Sb}_2\text{S}_3$ ). This double salt is so weak that it is broken down by excess of hydrogen sulfide with the partial reprecipitation of antimony sulfide. This is indicated as follows:

To a saturated solution of calcium hydroxide add antimony trisulfide in excess. Heat the solution and pass in hydrogen sulfide. The excess of solid antimony sulfide will go into solution, clear and colorless. Cool the solution and again saturate with hydrogen sulfide and antimony sulfide will be precipitated. Again boiling off the excess of hydrogen sulfide will give a clear solution. The most probable explanation of this behavior is that given above. In a solution of calcium hydroxide, saturated at boiling temperature with hydrogen sulfide, antimony sulfide is sufficiently soluble so that the difficulties of too bulky an electrolytic bath are removed. An attempt was made to determine the best conditions depositing antimony from a calcium sulfide electrolyte. The apparatus consisted of a platinum dish as cathode, a rotating spiral anode and about 125 cc. of electrolyte covering 100 square cm. of cathode. A standard antimony chloride solution in hydrochloric acid was prepared. Merck's calcium oxide was powdered and the desired amounts added in dry form to the bath. The presence of a small amount of ammonium polysulfide seemed to favor the formation of a brilliant white deposit. Therefore the following procedure was tried:

Ten cc. of antimony chloride solution were neutralized in a beaker with powdered lime. Ammonium polysulfide was added in sufficient amount to get the antimony in solution. A slight excess of powdered lime was then added, the whole diluted to 100 cc. and boiled until the excess of ammonia was removed. The solution was then put in the platinum dish and electrolyzed over a low flame at the boiling point. The most successful results were obtained with an initial E. M. F. of 3.0 to 3.25 volts and a current of  $N. D._{100} = 0.3$  ampere for the first ten minutes, then 3.5 volts and 0.4 amperes. In thirty minutes the current would drop

to 3.0 volts and 0.4 amperes and in forty-five minutes it would rise to 3.5 volts and 2.5 amperes. After seventy-five minutes, the current was raised for fifteen minutes to 4 volts and 0.4 amperes. Total time, one and a half hours. The rotation of the anode was as rapid as possible without spilling the electrolyte. The deposit was washed with water and then with a solution of 4 cc. of concentrated hydrochloric acid in 400 cc. of water and dried at 100°. The deposits were brilliant and adherent and no sulfur remained upon the anode at the end of the electrolysis. The results, however, were high unless extreme care was taken, as a white deposit of calcium hydroxide or carbonate tended to form in a small spot in the center of the dish and the removal of this with acidulated water sometimes caused bits of antimony to break off. After practice, fairly concordant results were obtained, *e. g.*:

	Gram.
Wt. Sb by KCN and Na <sub>2</sub> S method.....	0.2146
Wt. Sb by KCN and Na <sub>2</sub> S method.....	0.2148
Wt. Sb by KCN and Na <sub>2</sub> S method.....	0.2151
Wt. Sb by CaS and (NH <sub>4</sub> ) <sub>2</sub> Sx.....	0.2149
Wt. Sb by CaS and (NH <sub>4</sub> ) <sub>2</sub> Sx.....	0.2150

To avoid the difficulty of solid particles lying upon the bottom of the dish and becoming embedded, a beaker was used in which a double gauze platinum disc was rotated as cathode, a platinum wire being introduced and coiled above the disc as anode.

The electrolytic solution of antimony was prepared as before in the beaker and the electrodes then introduced. The electrodes were separated so that a current of 3.0 volts and 0.2 ampere could be maintained during the first ten minutes. As the amperage tended to fall the voltage was increased, being 3.5 volts and 0.25 ampere at the close. Rotation of cathode, moderate. Time, two hours.

The gauze disc was then washed in acidulated water, and dried carefully over a heated asbestos mat:

	Gram.
Wt. Sb-KCN-Ba <sub>2</sub> S method.....	0.2149
Wt. Sb rotating gauze cathode in CaS + (NH <sub>4</sub> ) <sub>2</sub> Sx electrolyte.....	} 0.2147
	} 0.2148

If conditions were not perfectly satisfactory the antimony showed a tendency to peel off from the edges of the discs, or solid particles would become embedded in the meshes of the gauze, and were removed with difficulty.

Moreover, when solid stannic hydroxide was present, particles of this seemed to catch in the gauze and become reduced to metal. The tendency for tin to be deposited was also apparently greatly increased by the presence of ammonia or ammonium salts. Not all of the tin is precipitated as stannic hydroxide, even by long boiling with excess of lime if (NH<sub>4</sub>)<sub>2</sub>Sx

is present and some tin may be deposited in the presence of excess of  $\text{Ca}(\text{OH})_2$  and at boiling temperatures. Therefore a solution of calcium sulfide free from ammonium salts is required as the electrolyte, and a cathode presenting a surface upon which solid particles will not easily become attached.

An apparatus was made by the Bishop Platinum Company. A platinum cylinder 12.5 cm. in circumference and 4 cm. in height with a strong platinum stem 7 cm. in length attached to the top of the cylinder by a cross bar, formed a rotating cathode. The anode was a heavy platinum iridium wire extending in a spiral coil (6 cm. in diameter) outside the cylinder to the bottom of the beaker and then upwards in a smaller spiral (1 cm. in diameter) inside of the cylinder. These electrodes were used in a No. 5 beaker, the cylinder being attached by its stem to the motor and slipped down between the anode spirals. It was found upon using the cylinder that on boiling the antimony scaled off from the bottom of the cylinder; also that the rotation should be fairly slow.

For antimony alone the following procedure proved successful:

To 10 cc. of antimony chloride in hydrochloric acid an excess of powdered lime was added. The solution was heated and hydrogen sulfide passed in at boiling. The solution was cooled and electrolyzed at 2.5 volts and 0.2 ampere = N. D.<sub>100</sub>. The voltage was raised gradually during the electrolysis till 3.5 volts were reached, the amperage being kept constant. The rotation of the cylinder was moderately slow. After two hours the cylinder was removed, washed in water acidulated with hydrochloric acid, dried over a hot plate and weighed.

	Gram.
Wt. Sb. present.....	0.2149
Wt. Sb. found.....	0.2146

When the work was repeated with the addition of tin sulfides, a great many contradictory results were at first obtained. Sometimes tin was deposited and again under apparently identical conditions none would appear. The order in which the lime and hydrogen sulfide were added, the temperature and amount of boiling previous to electrolysis were found to introduce uncertain variations.

A solution of stannic chloride was precipitated with hydrogen sulfide and then boiled with excess of lime and divided into two portions. The unfiltered portion was electrolyzed at successive voltages. Above three volts a slight deposit of tin could be obtained. The filtered solution gave no deposit, even with 4.5 volts.

Again lime was added to a stannic chloride solution and well-boiled, hydrogen sulfide passed in and the solution again boiled. This solution was cooled and electrolyzed with the platinum cylinder for thirty minutes at 3.0 volts. No tin was deposited. The E. M. F. was raised to 4 volts

without any deposit occurring. These results are typical of a large number of apparently contradictory results.

In no case, however, was tin obtained from a filtered solution after boiling with excess of lime. The deposit of tin seems to be due to the reduction of solid particles of stannic hydroxide which adhere to the surface of the cathode. If the stannic hydroxide is in a soft colloidal form there is a great deal of this reduction, on the other hand, if it is well coagulated and granular there is little tendency for it to stick or become reduced. The precipitation of the stannic hydroxide in a compact form and in a solution under conditions which are unfavorable to a gelatinous, sticky form would enable such a separation to be made successfully.

Such conditions are possible and the separation has been made successfully in several instances, but more precise experience is needed to make it a reliable separation. The best conditions so far obtained are as follows:

To a mixture of antimony and tin chlorides or sulfides add hydrogen sulfide and boil, then introduce an excess of powdered lime and boil. Add an excess of powdered lime to water, boil, pass in hydrogen sulfide and filter. Add this solution to the beaker containing antimony and tin sulfides as above. Boil ten minutes, let cool to  $70^{\circ}$  and electrolyze at 2.5 volts and  $N. D_{.100} = 0.2$  ampere. After one hour remove the cylinder containing the antimony deposit, wash in acidulated water and dry over a hot plate, weigh and clean the cylinder. If any antimony remains in the solution, re-insert the cylinder, add one-half gram of lime, boil, cool to  $80^{\circ}$  and electrolyze one-half hour. In this manner all the antimony may be removed from solution, in successive instalments, if necessary. If the cylinder is returned to the bath without cleaning or re-weighing, the original coating may peel in spots. With an E. M. F. not above 2.75 volts the tin is never deposited from such an electrolyte. The addition of certain salts may be found particularly useful in coagulating the stannic hydroxide.

#### Summary.

The electrolytic deposition of antimony was carefully examined in the following electrolytes with the results noted.

1. *Ammonium, Sodium and Barium Lactates.*—Tin is not deposited from these electrolytes. Antimony may be deposited but not quantitatively.

2. *Ammonium Polysulfide.*—The conditions for the successful deposition of antimony from this electrolyte were satisfactorily worked out. The method is novel in that it depends upon the removal or chemical change of the electrolyte during the process of electrolysis by heating. The character of the deposit of antimony is very different from the dark slate-colored deposits of antimony previously obtained, being like polished platinum in appearance. Since tin may be deposited from the same elec-



trolyte a method of determining total tin and antimony from their sulfides or chlorides is provided.

3. *Ammonium, Sodium and Potassium Tartrates and Tartaric Acid.*—The results for a completely quantitative deposition of antimony were negative. A certain amount of antimony always remains in solution.

4. *Calcium Sulfide.*—Of the alkaline earth sulfides, that of calcium was shown to be best suited for the deposition of antimony. The deposits were made most successfully with rotating anodes and were of a brilliant platinum-like appearance under suitable conditions. The possibility of the separation of antimony from tin by the precipitation of the tin as stannic hydroxide and the electrolysis of the antimony from the latter in a solution of calcium sulfide was demonstrated.

UNIVERSITY OF PENNSYLVANIA.

## SOME COLLOIDAL SOLUTIONS DERIVED FROM HYDRATED ALUMINA.

By WILLIAM B. BENTLEY AND R. PHILLIPS ROSE.

Received August 15, 1915.

It has long been a matter of experience in this laboratory that, in complex solutions used for qualitative analysis, barium is often missed. It has been suspected that the missing barium was precipitated with some of the preceding elements, possibly aluminum. The present research was therefore undertaken for the purpose of ascertaining if barium was brought down from a solution containing aluminum when the latter was precipitated with ammonium hydroxide. Our results indicated an affirmative answer to this question but in attempting to discover the proportion in which these elements were precipitated together, an observation was made which led us to postpone the original problem and take up what appeared to be a more interesting question.

A precipitate of aluminum hydroxide containing some barium was in process of analysis for barium when it was dissolved in acetic acid and acidified with hydrochloric acid previous to the precipitation of barium with sulfuric acid. To our surprise hydrochloric acid gave a gelatinous precipitate resembling somewhat aluminum hydroxide. We at first supposed that this precipitate contained barium but on repeating the experiment with aluminum hydroxide which contained no barium, the same result was obtained. We were unable to find in the literature available anything which threw light on this phenomenon and therefore determined to investigate the reaction and find, if possible, the identity of the precipitated substance. In this object we were only partially successful for our work revealed difficulties which seemed insurmountable.

Naturally our first attempt was to get the substance out of the solution and analyze it. We tried all ordinary filtering media including the densest