To determin the purity of the material finally obtained, a photograph of the spark spectrum was made. No lines other than those characteristic of scandium were found.

As a still further test of the purity of the material, about 1 gram of the oxide was tested by means of a very delicate electrometer. It gave no evidence of radioactivity. The instrument was then tested quantitatively and it was found possible to have detected easily as little as 0.05% of thorium in the sample used.

The tests of radioactivity of the oxide were very kindly performed by Dr. Dicran Hadjy Kabakjian, of the Department of Physics.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

THE ELECTROLYSIS OF POTASSIUM CHLORIDE.

BY HIRAM STANHOPE LUKENS.

Received August 4, 1913.

A number of papers[1] have appeared from this laboratory treating of the determination of anions by the electrolysis of salts in the so-called "double cup." For the most part, small quantities of salt have been the subject of investigation. The simplicity of the process and the accuracy of the results obtained make it appear an attractive method for the analysis of larger quantities of material. The purpose of this investigation has been to determin the accuracy of the results that might be expected from the electrolysis of solutions of potassium chloride containing from 1 to 2 grams of the salt.

Preparation of Pure Materials.

The water, nitric acid, ammonia water, ammonium oxalate, silver nitrate and mercury, used in this study were prepared and purified with the utmost care. The potassium chloride was obtained by the method of Richards and Staehler[2] with halides.

The purest potassium nitrate prepared by a German factory was dissolved in pure water and recrystallized six times in platinum, using a hand-power centrifuge of high velocity to free the crystals from the mother liquor. The spark spectrum of this material was quite free of lines other than those of potassium. A portion of the salt so purified was dissolved in water in a platinum dish and transposed to chloride by exposing the liquid to the action of pure hydrochloric acid gas. The gas was prepared by the well-known method devised by Robert Hare, and used so often in this laboratory for the preparation of hydrochloric acid. Purest commercial sulfuric acid was allowed to drop from a tap-funnel into pure concentrated hydro-

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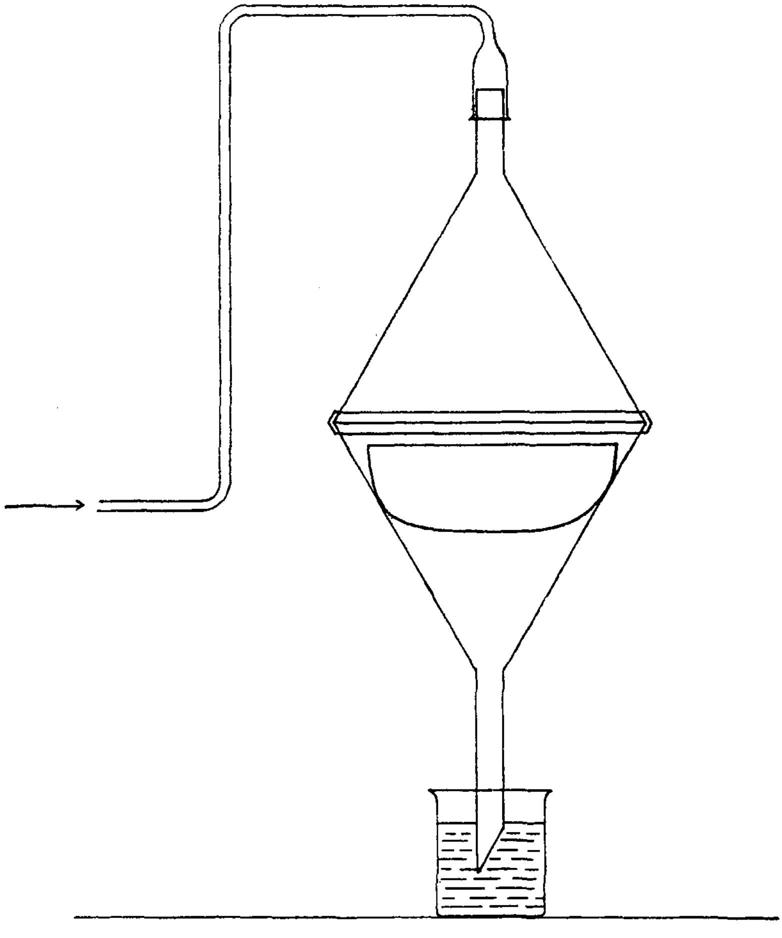
[1] THIS JOURNAL, 29, 447; 29, 1445; 29, 1455; 29, 1460; *Proc. Am. Philos. Soc.*, 46, 341; THIS JOURNAL, 30, 1705; 31, 900; 32, 1468; 33, 35.

[2] THIS JOURNAL, 29, 623.

chloric acid contained in a vessel constructed entirely of glass. The gas was thoroughly washed by passing through three wash bottles containing saturated water solutions of the gas. A platinum funnel or other suitable platinum apparatus not being at hand, it was necessary to devise some means of saturating the liquid with hydrochloric acid gas. This was accomplished by means of the apparatus illustrated in the drawing.



This was constructed by grinding the edges of two seven-inch glass funnels on a plane surface so that their edges would fit closely when one was inverted on the other. A five-inch rubber band one-half inch in width served to keep them in place. The hydrochloric acid gas entered the upper funnel and passed over the liquid contained in the dish resting in the lower funnel, the excess being absorbed in water in the beaker below.

The use of a platinum dish to contain the solution was abandoned after one trial. So much platinum was dissolved by the aqua regia formed that it was deemed advisable to substitute a fused quartz dish for that of platinum. All of the salt used in this investigation was precipitated six times as chloride in quartz vessels. The chloride so obtained was then recrystallized six times more in platinum vessels. In all cases the crystals were separated from the mother liquor by centrifugal drainage. The salt, as finally prepared, exhibited no lines other than those of potassium. A sample weighing 0.4 gram was volatilized in a platinum boat in nitrogen and left no ponderable residue. This was regarded as sufficient evidence that silica had not been introduced through the use of silica vessels.

Apparatus.

The anode used was of platinum similar to those employed in previous work. It was made up of three discs of platinum gauze 5 cm. in diameter and 30 meshes per cm. The edges of the discs were slightly fused. These discs were mounted on a shaft 10 cm. in length and 1 mm. in diameter, the shaft passing perpendicularly through the center of the discs holding them parallel at a distance of 8 mm. apart. The anode was plated with silver before each analysis. The silver deposited on the anode averaged about 15 grams.

In plating with silver, this electrode was made the cathode in a concentrated solution of the double oxalate of silver and ammonia. A platinum wire, bent in the form of a right angle, was made the anode and inserted between the discs to insure that the inner portions might be completely covered with silver. The electrode to be plated was rotated at about 200 r. p. m. A current of 1 ampere at 1.5 volts was used. Later the current was increased to four amperes. A heavy, porous ring of silver was deposited on the shaft of the electrode just above the upper disc. The purpose of this was to prevent the solution from ascending the shaft and coming in contact with the exposed platinum above. The plated electrode was dipped in dilute hydrochloric acid, washed thoroughly by boiling repeatedly with water, heated nearly to redness in a Bunsen flame, cooled in a desiccator and weighed.

This method was used in the preparation of the anode in all cases except those particularly noted.

The cell was essentially the same as those used in previous work. A crystallizing dish, 12 cm. in diameter and 6 cm. in height, was the outer vessel. An open glass triangle fitting closely within this vessel supported a bottomless beaker 6 cm. in diameter and 49 mm. in height. The triangle was of such size that the beaker would just slide within it when out of the dish, but when the triangle was wedged within the larger dish, the pressure was sufficient to hold the beaker in any desired position. The height of the inner beaker was such that when the heavy cover glasses were placed over the dish, the lower edge of the beaker was exactly 4 mm. from the bottom of the dish when the upper edge of the beaker touched the cover glasses. A ring of six turns of platinized platinum wire was placed about the beaker in position in the dish. When mercury was poured into the outer vessel to a depth of 1 cm., it sealed the opening between the beaker and the dish, forming a two compartment cell. Contact between the platinum wire and the mercury was made at three points.

During electrolysis the anode was supported in a chuck on the end of a shaft driven by a small motor of German manufacture. Current for the electrolysis of the salt was supplied from the lead accumulators with which the laboratory is equipped. Electrical measurements were made on a Weston voltmeter graduated to 0.5 volt and a Weston ammeter graduated to 0.01 ampere. The current was regulated by means of a Ward Leonard rheostat.

For the purpose of heating the anode an electrically heated oven was constructed. This consisted of a porcelain cylinder 7 cm. in diameter and 12 cm. in length. Number 39 B. & S. gauge "nichrome" ribbon $^1/_{16}$ inch wide was wound about this cylinder throughout its length. Over this was placed a sheet of asbestos paper and another coil of ribbon was wound over the paper from end to end of the cylinder. The two coils so formed were connected in parallel. A preparation composed of clay, asbestos fiber and infusorial earth was made into a paste with water and the entire cylinder covered to a depth of 3 cm. When dry this material allowed very little heat to radiate. The whole apparatus was enclosed in a cylindrical box of tin-plated iron. Sheets of mica were used for covers. On 110 volt D. C. circuit, using an external rheostat it was possible to obtain any desired temperature up to 600°.

The balance used for all weighings was one of Troemner design. The weights were of platinum and brass and carefully calibrated. Their density was taken as 8.3.

The nephelometer used was similar to that described by Richards and Wells[1] and had been used in previous work in this laboratory.

Drying and Weighing Potassium Chloride.—Richards[2] found that to remove water entirely from crystals of potassium chloride it was necessary to fuse the salt. If potassium chloride be fused in platinum in the presence of oxygen the platinum is attacked, as is evidenced by the loss in weight of the platinum vessel. Fusion in an atmosphere of nitrogen obviates this difficulty. All samples of potassium chloride were fused in a platinum boat in a tube of fused quartz in an atmosphere of nitrogen. The quartz tube was a part of the familiar bottling apparatus devised by Richards. Heat was supplied by a double coil of "nichrome" ribbon wound about

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[1] *Am. Chem. J.*, 31, 235.

[2] *Z. physik. Chem.*, 46, 189 (1903).

the tube and protected in a manner similar to that described in the preparation of the oven for heating the anode. Nitrogen was prepared by the method of Wanklyn by passing air saturated with ammonia gas over a hot copper gauze. The gas then passed through a large quantity of dilute sulfuric acid, concentrated sulfuric acid and over stick potash.

The temperature in the tube was slowly increased until the salt barely fused. This could be observed through an opening made in the insulating material about the tube. The salt was then allowed to solidify in an atmosphere of nitrogen. The latter was then replaced by a current of pure dry air. When all of the nitrogen was expelled the boat was pushed into a weighing bottle, the bottle stoppered and removed with its contents to the balance for weighing. A counterpoise was used in all weighing, both of the fused salt and anode. In spite of the care taken to exclude oxygen, the boat lost weight during every fusion. This loss, however, never exceeded one-tenth of a milligram. Careful tests of the gas leaving the tube failed to reveal the presence of oxygen.

After weighing, the contents of the boat were dissolved in pure water. In every case the salt dissolved to a perfectly clear solution. No insoluble particles were noticed at any time. The solutions so obtained were carefully washed into the beaker of the decomposition cell. In addition, the boat and beaker were washed again and all washings collected for estimation of their chlorine content by means of the nephelometer, as will be described later.

Electrolysis.—The cell was set up as previously described. A layer of pure mercury was poured into the dish to a depth of 10 mm., rising above the bottom of the beaker to a depth of 6 mm. The solution to be electrolyzed was then washed into the inner beaker. Five cc. of a saturated solution of sodium chloride were poured into the outer compartment of the cell. About 200 cc. of water were added to this, bringing the level of the liquid well above the platinum wires.

The previously weighed anode was then brought into position in the liquid in the inner cup. The anode was placed 1 cm. from the surface of the mercury and performed two hundred revolutions per minute. Electrical connection was made with the mercury serving as cathode by means of a platinum wire encased in glass. A constant potential of 3.5 volts was maintained throughout the electrolysis. The initial current varied from 1.2 amperes to 0.9 ampere, depending on the amount of salt in solution. The dilution was approximately 55 cc. Cover glasses were fitted over the apparatus with openings for the passage of the anode shaft and wire connecting with the mercury.

When the current was turned on the chlorine passed to the anode, which rapidly darkened, due to the action of light on the silver chloride formed. Potassium passed into the mercury and the decomposition of the amalgam formed was soon apparent in the outer compartment. The current was allowed to fall as the decomposition of the salt proceeded until 0.03 ampere was reached. The current was then interrupted, the cover glasses were washed with pure water and the washings preserved. The anode was then removed from the solution, carefully washed with pure water and heated in the electric oven for thirty minutes at a temperature of 400°. The anode was then cooled in a desiccator and weighed. The solution was carefully pipetted from the inner cup to a calibrated 250 cc. flask and the cell washed repeatedly with water. All washings, including those from the boat and the beaker in which the salt was dissolved, were introduced into the calibrated flask and the flask filled to the mark. The chlorine in the solution in the flask was estimated by means of the nephelometer.

It was early noticed that on washing the anode with pure water the wash water became cloudy, due to the well-known fact that colloidal silver chloride is formed. It was obviously necessary that this amount of silver chloride should be estimated, particularly since the silver present in it represented silver dissolved from the anode. The analysis of this solution was made by means of the nephelometer in the following manner.

The solution contained silver chloride, potassium chloride and some potassium hydroxide from the decomposition of potassium amalgam in the inner cup. A solution of sodium chloride was prepared containing exactly 0.0001 gram of chlorine in 250 cc. This was used as the standard for comparison. Three test tubes of equal capacity were prepared for use in the nephelometer, by painting the bottoms and also around the tops to prevent undue reflections. Platinum plates on platinum wires were used as stirrers. To one tube was added 1 cc. of silver nitrate solution (10 grams in 250 cc.) and 1 cc. of nitric acid (1 : 10). The tube was then filled with the standard chlorine solution.

To the second tube were added 2 cc. of nitric acid. This tube was then filled with the solution to be examined. Comparison of the cloudiness produced in this tube with the standard served as a means of estimating the silver chloride in the solution.

To the third tube, 1 cc. of nitric acid and 1 cc. of silver nitrate were added. When this tube was compared with the standard it was possible to estimate the total chlorine content of the solution. The difference between the amount of chlorine present as silver chloride and the total chlorine is evidently the chlorine still present as undecomposed potassium chloride. While the amount of silver chloride found in this way varied with each experiment, it fell within the limits of 0.00190 gram and 0.00016 gram.

Forty determinations in all were made after this manner. In every case decomposition of amalgam was noticed within the inner cup. In twelve determinations the salt was measured by fusing and weighing directly. In the remaining determinations, 25 cc. portions were pipetted from solutions standardized by precipitating similar portions with silver nitrate, taking the usual precautions observed in the estimation of silver chloride.

All weighings were reduced to the vacuum standard. The density of potassium chloride was taken as 1.995. For every apparent gram of potassium chloride a correction of +0.000456 was made. For every apparent gram of silver attacked by chlorine 0.00003 was subtracted; for every apparent gram of silver chloride formed 0.000071 was added. These corrections applied to normal pressure and a temperature of 20°. The necessary corrections for variations from these conditions were made.

The following table gives results taken from a few typical experiments. The chlorine content of potassium chloride was calculated from the values K = 39.11, Cl = 35.462.

KCl used. Gram.	Cl calculated. Gram.	Cl found. Gram.	Error. Gram.
0.88313	0.41996	0.39656	—0.02340
1.11147	0.52855	0.50756	—0.02098
1.15214	0.54789	0.53838	—0.00951
1.32455	0.62987	0.62695	—0.00292
1.02716	0.48845	0.48270	—0.00575
1.26060	0.59946	0.58565	—0.01381

Results from standard solutions:

Cl present Gram.	Cl found. Gram.	Error. Gram.
0.4755	0.4680	—0.0075
0.5242	0.5119	—0.0123
0.4710	0.4534	—0.0176
0.4710	0.4541	—0.0169

Throughout all these experiments a constant search was maintained for the source of error. Chlorine could not be detected escaping from the solution and repeated tests failed to reveal the presence of chlorates or hypochlorites in the solution. An examination of the mercury, however, did reveal a small quantity of silver but as this was an accumulation from twenty experiments, the small quantity found (0.0005 gram) would not account for the sum of the errors. Finally a test of the solution in the outer compartment offered a clue to the source of error. On substituting a solution of pure potassium nitrate for the sodium chloride used as electrolyte in the outer compartment, a voluminous precipitate of silver chloride was obtained when silver nitrate was added to this solution after the electrolysis of a portion of potassium chloride.

The natural assumption was that the depth of the layer of mercury was insufficient to overcome the centrifugal pressure exerted by the particles of the solution when whirled about by the revolving anode.

The depth of the layer of mercury was increased to 15 mm., bringing the upper surface of the mercury 11 mm. above the lower edge of the beaker. A solution of potassium chloride containing 0.4709 gram of chlorine was electrolyzed under the conditions observed before. The solution was carefully pipetted from the outer compartment and after acidulating with pure nitric acid was tested with silver nitrate for the presence of chlorides. A precipitate was produced. This was filtered through a weighed Gooch crucible and the amount of silver chloride determined. After weighing the anode, the deposit of silver chloride was removed by rotating the anode in successive portions of strong ammonia until these solutions no longer gave a precipitate when acidulated with nitric acid. The combined ammonia solutions of silver chloride from the anode were then acidulated with nitric acid when all of the silver chloride was reprecipitated. This was collected in a Gooch crucible and weighed. This experiment was repeated. The results obtained are tabulated below:

	1.	2.
Increase in weight of anode	0.4596	0.4656 gram
Chlorine found by solution and reprecipitation of AgCl on anode	0.4628	0.4673 gram
Weight of chlorine found in outer cup	0.0079	0.0029 gram
Weight of AgCl and Cl found by nephelometer	0.0003	0.0005 gram
Total chlorine found	0.4710	0.4707 gram
Weight of chlorine in solution	0.4709	0.4709

The observation that the increase in weight of the anode did not represent the true weight of the chlorine that had attached itself to it was not new. Earlier experiments on the solution and reprecipitation of silver chloride from the anode had indicated this to be true.

It was at once evident that solution from the inner cup was transferred to the outer vessel. How this was possible was a matter of speculation. The only explanation that suggested itself was that the solution wets the glass, which the mercury does not, and thus forms a film between the glass and the mercury, thereby offering a channel of escape into the outer vessel. It is evident that this "seepage" is not always the same, and that the variation in results previously obtained can be ascribed at least for the most part to this previously unobserved phenomenon.

With the idea of preventing solutions passing between the glass and mercury a method was sought to make the mercury "wet" the lower edges of the inner cell. The expedient of cementing bands of metals to the lower edge of the inner cup did not prove very satisfactory. A cup was then prepared with the lower edges "platinized" by painting with a mixture of chloroplatinic acid and glycerol. After drying in an oven at 300°, the lower edge bearing the platinum was heated just to the point of fusion in a burner flame. The platinum on the glass was then made the cathode in a solution of mercurous nitrate and a heavy deposit of mercury was plated on to the platinum surface. When new, this form of vessel prevented the escape of solution into the outer cup but the platinum soon dissolved off the glass. A new cup was then platinized on the bottom edge and on the outside, the platinum coating outside forming a band 4 mm. in width around the bottom of the vessel. The platinum was made the cathode in a solution of the double cyanide of silver and potassium and a heavy coating of silver was deposited on the platinum. This deposit was very adherent and in use was not dissolved by the mercury to any appreciable extent.

The dimensions of the cup so prepared were identical with those of the cup used in the early experiments. A layer of mercury 8 mm. in depth was sufficient to form a perfect seal. Tests made in fifty-three analyses performed using this form of cup failed to reveal any chlorides in the outer compartment at any time. Using a cup of this description it was at once noticed that the increase in weight of the anode approached closer to the weight of the chlorine in the solution. The amount of amalgam decomposed in the inner vessel seemed to influence the results. Whenever considerable decomposition was noticed, the results were invariably lower than when the decomposition was slight. When little decomposition was noticed, however, the results were decidedly better. Efforts to prevent, or at least minimize this decomposition, were made as described later. Twenty-eight analyses were made with this cup, using a constant potential of 3.5 volts. The initial current varied from 1.9 amperes to 0.9 ampere, depending on the concentration of the solution. The final current was 0.03 ampere in all cases. The time required varied from 90 minutes to 2 hours and 40 minutes, depending on the quantity of salt electrolyzed. Some typical results are given in the tables below.

From portions of salt measured by direct weighing of the fused sample:

KCl used. Gram.	Cl calculated. Gram.	Cl found. Gram.	Error. Gram.
0.90761	0.43160	0.43117	—0.00044
1.33460	0.63465	0.63420	—0.00045
1.62881	0.77456	0.77399	—0.00057
1.19750	0.56946	0.56928	—0.00018
1.20245	0.57181	0.57143	—0.00038
1.01564	0.48298	0.48285	—0.00013
1.00355	0.47723	0.47742	+0.00019

From portions of salt measured by pipetting out 25 cc. portions of solutions standardized by precipitation:

Cl present. Gram.	Cl found. Gram.	Error. Gram.
0.47845	0.47868	+0.00023
0.47845	0.47833	—0.00012
0.47845	0.47741	—0.00104
0.47851	0.47830	—0.00021
0.47851	0.47796	—0.00055

In the course of these experiments it was noticed that the voltage might be increased above the potential that had been previously used without endangering the success of the determination. The initial voltage of 3.5 volts was allowed to rise as high as 12.3 volts on two occasions. A tendency to form colloidal solutions of silver chloride characterized these determinations, together with an increase in the decomposition of amalgam in the inner cell.

With the idea in mind of decreasing the decomposition of amalgam in the inner cell a section 8 mm. in height was cut from the bottom of a beaker 40 mm. in diameter. This was cemented in an inverted position in the center of the crystallizing dish by means of zinc oxychloride. The union of the edges of the inverted beaker with the bottom of the dish was painted over with hot paraffin to prevent the solution from entering and softening the cement. When the inner cup was placed in position and mercury poured into the outer vessel, the cathode surface of the cell was reduced to a ring of mercury about 10 mm. in width. This device caused the concentrated amalgam to be formed as closely as possible to the outer vessel, where it could quickly find its way, and be decomposed. Using a cell of this description it was found possible to use a constant electromotive force of 6.5 to 7 volts, with an initial current of 1.6 amperes to 2 amperes. As much as 1.09 grams of potassium chloride could be decomposed under these conditions in one hour. Ten analyses were made with a cup of this type. Typical results are given below.

From portions of salt measured by direct weighing of the fused sample:

KCl used. Gram.	Cl calculated. Gram.	Cl found. Gram.	Error. Gram.
1.34162	0.63799	0.63786	—0.00013
1.37128	0.65209	0.65182	—0.00027
1.09926	0.52274	0.52262	—0.00012

From portions of salt measured by pipetting out 25 cc. portions of solutions standardized by precipitation:

Cl present. Gram.	Cl found. Gram.	Error. Gram.
0.47851	0.47865	+0.00014
0.47851	0.47785	—0.00066
0.47851	0.47837	—0.00014

It is evident from the results obtained that it is possible to make very accurate determinations of the chlorine content of potassium chloride by this means, particularly if the entire contents of the cell are washed out and the mercury thoroughly washed. To completely wash the mercury without loss of manipulation is difficult to accomplish. Further, the dilution of the solution obtained is such that accurate measurements by means of the nephelometer are difficult to obtain.

Further study of the electrolytic method of determining anions is in progress, and it is hoped that it may ultimately be possible to employ this process to determin the ratio in which potassium and chlorine are combined in potassium chloride.

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[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 alkalin 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