The crude hydroxides were dissolved in the minimum quantity of hydrochloric acid by boiling, diluted with water and nearly neutralized with sodium hydroxide solution. The liquid, after the addition of a little formic acid, was treated with a slight excess of sodium formate, and the precipitate filtered off and washed thoroughly to insure complete removal of zinc. The filtrate gave a faint gallium line indicating that the precipitation of gallium was not complete.

The precipitate and filter paper were removed to a casserole, stirred with water and thoroughly saturated with hydrogen sulfide. A quantity of 1% hydrochloric acid was added and after standing for some time, the insoluble tin and cadmium sulfides were removed by filtration. Since the filtrate was too large in volume to work with, the gallium was precipitated by making the liquid slightly alkaline with ammonium hydroxide and boiling until faintly acid to litmus. The gallium and aluminum hydroxides were separated by filtration, dissolved in the minimum quantity of hydrochloric acid, and an excess of sodium hydroxide solution added. By electrolizing with a current of 1.5 amperes, using platinum electrodes of about 3 sq. cm., the gallium was deposited on the cathode in extremely bright globules which dropped off as they became larger.

When the gallium ceased to be deposited, the solution was removed and the metal washed several times with water, and the globules then united by the addition of a drop or two of conc. hydrochloric acid. The latter was immediately removed by washing with water and finally with alcohol.

Any gallium remaining in the liquid and wash waters, after electrolysis, was regained by precipitating in the usual manner as the ferrocyanide from a strongly (hydrochloric) acid solution.

DURHAM, N. H.

SELENIC ACID AND COPPER SELENATE.[1]

BY L. M. DENNIS AND J. P. KOLLER.

This article deals with the extraction of selenium from smelter flue-dust and from anode slime; the preparation of pure selenium dioxide and selenious acid; the preparation of pure selenic acid; the detection of selenious acid present in selenic acid, and the detection of sulfuric acid present in selenic acid; attempts to prepare perselenates; the hydrates of copper selenate, and the ammonates of copper selenate.

[1] This article is based upon the thesis presented to the Faculty of the Graduate School of Cornell University by Joseph Peter Koller in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

A. THE EXTRACTION OF SELENIUM.

1. Extraction of Selenium from Smelter Flue-Dust.

One source of selenium for this investigation was a smelter flue-dust that contained about 22% of selenium, small amounts of silica, iron, and aluminum as the principal impurities, and a trace of tellurium.

The flue-dust was finely ground and was fused with sodium carbonate and sodium peroxide in nickel crucibles. A mixture that was found to give complete oxidation with but slight excess of sodium peroxide, and to yield a product that easily disintegrated in water, consisted of 300 g. of flue-dust, 200 g. of anhydrous sodium carbonate, and 775 g. of sodium peroxide. The flue-dust and sodium carbonate were ground together, the sodium peroxide was then added, and the materials were thoroughly mixed on paper. A small amount of the mixture was placed in a large nickel crucible and was heated to quiet fusion. More of the mixture was then added in small portions at a time, the heat of reaction being sufficient to maintain the mass in fusion without further application of external heat. When the crucible was nearly filled with the fused mass, it was allowed to cool, the product was treated with water, and any insoluble material was removed by filtration. The filtrate was then nearly neutralized with conc. hydrochloric acid which precipitated the greater part of the aluminum and zinc as hydroxides. These were removed by filtration through a Büchner funnel.

To this filtrate three times its volume of conc. hydrochloric acid was added and the liquid was boiled for 30 minutes to reduce selenic acid to selenious acid. Any silica that here separated was filtered off. The filtrate was heated to somewhat above 80°, and sodium sulfite in amount two or three times that theoretically required for the reduction of the selenious acid was added in small portions at a time. The liquid was digested at about 80° for several hours to convert all of the selenium into the gray modification. This was then collected on a filter paper in a Büchner funnel and was thoroughly washed with hot water to remove the sulfates that were present.

The addition of sodium sulfite to a hot solution was found to precipitate the selenium in a more finely divided and more easily filterable form than when the reducing agent is added to a cold solution of selenious acid.

Examination of the residue showed that this method gave complete extraction of the selenium from the flue-dust.[1]

2. Extraction of Selenium from Anode Slime.

A considerable amount of anode slime was kindly presented to us by the Nichols Copper Company. Analysis showed that this material con-

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[1] Subsequent to our development of this method of extracting selenium from flue-dust there appeared an article by Meyer and Heider (*Ber.*, 48, 1154 (1915)) in which they oxidized selenium dioxide with sodium peroxide to form sodium selenate.

tained 96% of selenium and a considerable amount of tellurium. Conc. nitric acid was placed in a large evaporating dish and was diluted with $1/_5$ of its volume of water. The dried, finely-ground anode slime was then added, whereupon a vigorous reaction took place. When this reaction abated, the contents of the dish were heated to carry the reaction to completion. The small amount of insoluble matter was removed by filtration through an asbestos pad on a Witt plate. The filtrate was viscous and was dark green in color. It was evaporated to dryness to remove the excess of nitric acid, the temperature being carefully controlled to prevent sublimation of selenium dioxide. The residue was treated with hydrochloric acid (3:1) and selenium was precipitated from the resulting solution by sodium sulfite or sulfur dioxide. The precipitated selenium, which still contained traces of impurities, was filtered and washed in the manner above described.

B. THE PREPARATION OF SELENIUM DIOXIDE AND SELENIOUS ACID.
1. The Preparation of Selenium Dioxide by Sublimation.

A portion of the selenium obtained as described under A was treated with nitric acid and the solution was freed from excess of nitric acid by evaporation. To ensure complete removal of the acid, the residue was dissolved in a small amount of water and evaporation to dryness was repeated. The selenium dioxide thus obtained was sublimed in a glass tube 85 cm. long and 3.5 cm. internal diameter. The tube was provided with a loose-fitting cylindrical cover of asbestos paper, and was placed in a gas combustion-furnace 60 cm. long. A plug of glass wool 2 cm. thick was placed midway in the tube. Selenium dioxide was then introduced upon one side of this plug, and a current of dry air was passed through the tube. The tube was so placed in the furnace as to leave but a short part of the exit end projecting from the furnace. Upon then heating the tube, selenium dioxide condensed near the exit end. The tube was then gradually pushed out of the furnace and the sublimed selenium dioxide condensed nearer and nearer to the middle of the tube. When the sublimation was complete the tube allowed to cool and was then placed in a perpendicular position, with the exit end downward, in a beaker of water. Water was drawn up into the tube nearly to the plug of glass wool, whereupon the sublimed selenium dioxide dissolved. 150 g. of selenium dioxide was used in each charge.

2. The Crystallization of Selenious Acid.

Berzelius[1] states that selenious acid crystallizes readily from aqueous solution.

Weber[2] crystallized selenious acid from its solution in water, dried the

[1] *Lehrbuch der Chemie*, 5th edition, Vol. II, p. 206.
[2] *Pogg. Ann.*, **118**, 479 (1863).

crystals for a short time over sulfuric acid, and found on analysis that the product was $SeO_2.H_2O$.

Clausnizer[1] evaporated an aqueous solution of selenious acid until it was of sirupy consistency. Slow cooling of this solution yielded large crystals of H_2SeO_3.

Since these statements make it clear that selenious acid crystallizes readily from aqueous solution, it was thought probable that the direct preparation of this compound from the anode slime, and recrystallization of the product, might rapidly lead to a pure substance. For these reasons, 3000 g. of the crude anode slime was treated with nitric acid, and the solution was evaporated to sirupy consistency. Large crystals of selenious acid separated from the solution on standing. These were freed from the mother liquor on a Büchner filter, were dissolved in water, and the selenious acid was again separated by crystallization. Four such recrystallizations yielded a selenious acid that was colorless and that was found to be free from iron, tellurium, and sulfur, which were the principal impurities in the anode slime. The test for tellurium in the selenious acid was made by dissolving from 10 to 20 g. of the acid in hydrochloric acid (sp. gr. 1.16), heating the solution to 90°, and saturating it with sulfur dioxide. The precipitated selenium was removed by filtration and the filtrate was diluted with an equal volume of water. This solution was saturated in the cold with sulfur dioxide. If tellurium is present it is immediately precipitated in a black form. Any small amount of selenium that was not removed in the first precipitation with sulfur dioxide will here appear as a red precipitate. The test for tellurium is more sensitive if this element is precipitated in the final filtrate by potassium iodide instead of sulfur dioxide.

1200 g. of crystalline selenious acid was obtained from the 3000 g. of anode slimes. The ease of operation of this method and the purity of the resulting product renders the procedure well adapted to the extraction and purification of selenium from crude material, and it is surprising that so few cases of its employment are recorded in the literature.

C. PREPARATION OF PURE SELENIC ACID.

Selenic acid was first prepared by Mitscherlich[2] in 1827, who suspended lead selenate in water and precipitated the lead by hydrogen sulfide.

This method was also employed by von Gerichten[3] and later by Diemer and Lenher.[4]

Wohlwill[5] treated copper selenate with hydrogen sulfide and removed

[1] *Ann.*, **196**, 265 (1879).

[2] *Pogg. Ann.*, **9**, 623 (1827).

[3] *Ber.*, **6**, 162 (1873).

[4] *J. Phys. Chem.*, **13**, 505 (1909).

[5] *Ann.*, **114**, 169 (1860).

the precipitated copper sulfide by filtration. This method was criticized by Topsöe,[1] and by von Gerichten,[2] who found that the precipitated copper sulfide was oxidized during the washing, and that this contaminated the selenic acid with sulfuric acid. This difficulty was avoided by von Hauer,[3] who prepared cadmium selenate and removed the cadmium from this solution by precipitation with hydrogen sulfide.

Meyer and Heider[2] oxidized selenium dioxide with perhydrol (30% H_2O_2) and obtained a yield of 70% selenic acid.

Metzner[4] found that selenium dioxide is quantitatively oxidized to the trioxide by potassium permanganate. Mathers[5] oxidized selenious acid to selenic acid with potassium permanganate in a hot solution containing nitric acid. Metzner prepared pure selenic acid by pouring a solution of selenious acid into a solution of permanganic acid, removing the separated manganese dioxide by filtration, and then concentrating the filtrate. The product is said to be free from selenious acid but to contain a small amount of manganese. Metzner also prepared selenic acid by first oxidizing selenium dioxide with either chlorine or bromine, neutralizing the acid solution with copper oxide, separating the copper selenate from the copper chloride that is present by fractional crystallization, and then electrolyzing an aqueous solution of the copper selenate to remove the copper. He states that the resulting selenic acid contains neither copper, chlorine, nor selenious acid.

Thomsen[6] converted selenious acid into selenic acid by shaking silver selenite with water and bromine. The precipitate of silver bromide is removed by filtration, and the filtrate was said to contain pure selenic acid that was free from selenious acid. This method has also been employed by Diemer and Lenher,[2] by Benger,[7] and by Klason and Mellquist.[8]

The electrolytic oxidation of sodium selenite to sodium selenate was effected by Müller.[9] Glauser[10] electrolyzed a solution of selenious acid to selenic acid and prevented the separation of selenium at the cathode and increased the yield of selenic acid by adding conc. nitric acid to the electrolyte. This electrolytic oxidation was further studied by Meyer and Heider,[2] who use a solution of selenium dioxide in conc. nitric acid as electrolyte.

[1] *Krist-kem. Unters. ov de selens. Salts*, Copenhagen, **1870**, p. 5.
[2] *Loc. cit.*
[3] *Wien. Akad. Ber.*, **39**, 299 (1860).
[4] *Ann. chim. phys.*, [7] **15**, 203 (1898).
[5] THIS JOURNAL, **30**, 1374 (1908).
[6] *Ber.*, **2**, 598 (1869).
[7] THIS JOURNAL, **39**, 2171 (1917).
[8] *Z. angew. Chem.*, **25**, 514 (1912).
[9] *Ber.*, **36**, 4262 (1903).
[10] *Chem. Ztg.*, **31**, 630 (1907).

Mathers[1] prepared selenic acid by electrolytic decomposition of lead selenate that rested upon the cathode, and that was covered with a dilute solution of selenic acid.

Manuelli and Lazzarini[2] studied the amount of oxidation and reduction that occurs in the electrolysis of a solution of selenious acid.

Three methods for the preparation of selenic acid were studied by the authors of this paper; the oxidation of silver selenite by bromine, the oxidation of selenious acid by chlorine in the presence of copper carbonate, and lastly, the electrolytic oxidation of selenious acid.

1. The Oxidation of Silver Selenite by Bromine.

Silver selenite was prepared by slowly adding a solution of 400 g. of silver nitrate in 1500 cc. of water to a solution of 150 g. of pure selenious acid in 2 liters of water, the second solution being vigorously stirred while the silver nitrate was being run in. The precipitate was twice washed by decantation, was then transferred to a Büchner funnel and was further washed with water until free from silver nitrate. The silver selenite was kept under a small volume of water until used. The filtrate was nearly neutralized with sodium carbonate to precipitate the greater portion of the silver selenite that was still present in the liquid because of the reversible character of the reaction.

$$2AgNO_3 + H_2SeO_3 \rightleftarrows Ag_2SeO_3 + 2HNO_3.$$
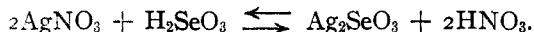
The silver selenite thus recovered was thoroughly washed and was added to the first portion.

The silver selenite was then treated with bromine that had been purified by shaking the bromine with a 15% solution of potassium bromide and then distilling the bromine from calcium bromide to free the bromine from chlorine.[3] About 50 g. of silver selenite was suspended in 3 liters of water and the bromine was slowly added while the solution was vigorously agitated with a stirrer making 700 r. p. m. It was found that rapid stirring hastened the reaction. When bromine sufficient in amount to give to the solution a tinge of orange color had been added, another portion of about 50 g. of silver selenite was introduced and bromine was again added in excess. About 250 g. in all of silver selenite was used in a single operation. At the close of the treatment of each portion, there should be sufficient bromine present to give an orange color to the solution and the liquid should then be allowed to stand for at least two hours to ensure complete oxidation.

$$Ag_2SeO_3 + 2 Br + H_2O = H_2SeO_4 + 2 AgBr.$$
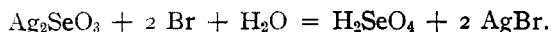
The supernatant liquid that contained the selenic acid was tested for the

[1] *Loc. cit.*

[2] *Gazz. chim. ital.*, **39**, 50 (1909).

[3] Richards, *Proc. Am. Acad. Arts Sci.*, **37**, No. 14; *Chem. News*, **85**, 223 (1902).

presence of selenious acid by first passing through a sample of it a current of air to remove the free bromine and then adding a solution of potassium iodide. (See under D.)

The silver bromide was filtered off on an asbestos pad on a Witt plate. It was in each case tested for the presence of silver selenite, and since this compound was always found· to be absent, the reaction between silver selenite and bromine appears to go to completion. The filtrate was freed from most of the free bromine by blowing a current of air through it. It was then evaporated down to a volume of about 200 cc. at a temperature not exceeding 70°. At the end of the evaporation it was found always to contain selenious acid and hydrobromic acid. These products were apparently due to the formation of hydrobromic acid through the action of the bromine upon water, and the reduction of selenic acid by this hydrobromic acid.[1]

Eder found[2] that when a solution of bromine in water is allowed to stand either in the light or in the dark, there is a steady diminution in the amount of free bromine in the solution. On the other hand, Richards and Stull[3] state that there is very slight reaction between bromine and water when the solution is exposed to the action of diffused daylight at a temperature of 23°.

In view of the conflicting testimony on this point, qualitative experiments were made to ascertain whether hydrobromic acid is formed when a solution of bromine in water is allowed to stand in the light. Carefully purified bromine was shaken with water and was permitted to stand in diffused daylight for two hours. The excess of bromine was then driven out by passing a current of air through the solution. The completeness of the removal of the bromine was evidenced by the fact that a portion of this residual solution did not liberate iodine from a solution of hydriodic acid. When a little nitric acid and a dilute solution of silver nitrate were added to the remainder of the solution, an appreciable precipitate of silver bromide resulted. In a second test the aqueous solution of bromine was allowed to stand for 12 hours in diffused daylight. This then yielded a heavy precipitate of silver bromide. An aqueous solution of bromine was boiled and was then found to give a heavy precipitate of silver bromide. These experiments show that hydrobromic acid is formed by the action of the excess of bromine upon water in the oxidation of silver selenite to selenic acid, and this explains the presence of selenious acid with selenic acid in the filtrate from the silver bromide.

To avoid reduction of selenic acid by hydrobromic acid the method was then modified as follows:

[1] Gooch and Scoville, Z. anorg. Chem., 10, 256 (1895).
[2] Monatsh., 6, 502 (1886).
[3] Z. physik. Chem., 41, 547 (1902).

Silver selenite was suspended in such an amount of water as would finally yield a 3% solution of selenic acid, and bromine was then added until the solution assumed an orange color. After two hours the precipitated silver bromide was filtered off and a current of air was passed through the filtrate to remove the excess of bromine. A solution of silver nitrate was then carefully added to precipitate the hydrobromic acid that had been formed. To ensure the absence of silver nitrate from the solution, a slight amount of bromine water was then added, and any precipitate that was formed was removed by filtration. The filtrate was then evaporated on a steam bath to $^1/_2$ its volume and was further concentrated under a pressure of 25 mm. at a temperature of 120° to remove nitric acid.

2. The Oxidation of Copper Selenite by Chlorine.[1]

A small amount of pure basic copper carbonate was added to a solution of selenious acid containing 500 g. of selenium dioxide in 5.5 liters. Chlorine gas was then passed through the liquid. The copper carbonate gradually dissolves owing to the formation of soluble copper selenate and copper chloride. Additional amounts of the copper carbonate were added from time to time and the passage of chlorine was continued until the solution assumed a distinct green color. A small amount of solid copper carbonate remained in excess after the chlorination was complete. The reactions that here take place are expressed by the equations

$$H_2SeO_3 + Cl_2 + H_2O = 2 HCl + H_2SeO_4,$$

$$2CuCO_3 + 2HCl + H_2SeO_4 = CuCl_2 + CuSeO_4 + 2CO_2 + 2H_2O.$$
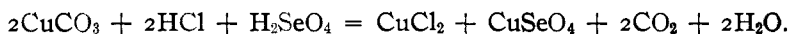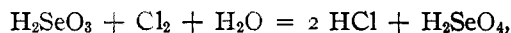
The solution was freed from solid matter by filtration and was then evaporated to small volume at a temperature that was not allowed to rise above 65°. At higher temperatures a basic copper selenate forms. The solution was then allowed to cool and a large crop of small crystals was obtained. These crystals were separated from the mother liquor and were recrystallized from water. This final product consisted of copper selenate carrying 1 to 2% of copper chloride.

Copper chloride is readily soluble in acetone. Copper selenate is very slightly soluble in acetone. These facts were utilized to remove the copper chloride from the copper selenate. The crystalline product was dried in the air, was finely ground, and 75 g. of it was placed in a Soxhlet extraction apparatus in which the end of the siphon tube was covered by a piece of filter paper. The extractor was then inserted in the neck of a flask containing pure redistilled acetone and an upright condenser was attached to the extractor. After extraction with the acetone, the material remaining in the extractor was freed from acetone by exposure to the air, and was found to contain only very slight traces of copper chloride. This latter substance was then completely removed by one further crystallization of

[1] Metzner, *Ann. chim. phys.*, [7] **15**, 203 (1898).

the copper selenate from water. The copper selenate remaining in the mother liquor from this crystallization can be recovered almost quantitively by adding to the concentrated solution an equal volume of acetone, which precipitates the copper selenate and holds the copper chloride in solution.

Selenic acid was prepared from this purified copper selenate by electrolytic precipitation of the copper. 430 g. of the crystalline copper selenate ($CuSeO_4.5H_2O$) was dissolved in 1.7 liters of water and was placed in a glass cylinder. The anode consisted of two pieces of sheet platinum, each of which had a surface of 60 sq. cm. These were placed on opposite sides of the cathode. The cathode consisted of a flat piece of copper gauze of 180 sq. cm. surface, and a platinum cylinder of 45 sq. cm. that was rotated at a speed of about 300 r. p. m. The current was maintained at 1.5 to 2 amperes when the solution was stirred, and at 0.08 ampere when the solution was not stirred. The cathode current density did not exceed 0.89 ampere per sq. dcm., and it was finally reduced to 0.2 ampere when the copper concentration had become low. Low current density was necessary in order to avoid the reduction of selenic acid. The use of the copper gauze cathode in addition to the platinum cathode at the beginning of the electrolysis permitted the employment of a larger current for the removal of most of the copper while still maintaining a low current density. For the removal of the last trace of copper, a copper cathode was disadvantageous, and for that reason toward the end of the electrolysis the copper cathode was removed and only the rotating platinum cathode was employed, the current being dropped to 0.08 ampere (0.2 ampere per sq. dcm.) when this change was made. About 75 hours was required for the complete electrolytic removal of the copper.

The electrolyte now consisted of selenic acid of a concentration of about 9%. It was also found to be free from selenious acid by the test with potassium iodide that will be described later.

100 cc. of this dilute solution of selenic acid was evaporated at 95° at a pressure of 23 mm. for 12 hours. The resulting acid was found to be entirely free from selenious acid and it possessed a specific gravity of 2.16, corresponding to a concentration of 82%. When it was attempted still further to concentrate this acid by heating it to 175° under a pressure of 20 mm. for 5 hours, it was found that a small amount of selenious acid was produced, one part of selenious acid to 3000 parts of anhydrous selenic acid.

3. The Electrolytic Oxidation of Selenious Acid to Selenic Acid.

Earlier investigations upon the electrolytic oxidation of salts of selenious acid have already been cited. No systematic study of electrolytic oxidation of selenious acid to selenic acid, however, seems to have been made. This was therefore examined to ascertain whether this procedure would

give results comparable with or superior to those of the methods that have already been described.

Before taking up the electrolytic oxidation of selenious acid, neutral potassium selenite was first used as the anolyte.   100 cc. of a solution of this salt that contained 30 g. of selenium dioxide was electrolyzed in a beaker with a platinum wire cathode and an anode of sheet platinum of a surface of 55 sq. cm.   At the beginning of the electrolysis the current was 0.5 ampere which was increased as selenic acid formed to a final value of 1.5 amperes, the voltage being between 5 and 6.   At the end of 100 hours there was still a trace of selenious acid in the solution, and further electrolysis for 20 hours failed to remove this.   There was a very slight reduction to free selenium, a thin red coating of the element appearing on the cathode.   Under these conditions, therefore, the oxidation to selenic acid proceeds with but little reduction to free selenium at the cathode, but complete oxidation of the selenious acid is not attained.

In the next experiment 300 cc. of an aqueous solution of selenious acid containing 11.2 g. of selenium dioxide was electrolyzed with the apparatus just described except that the cathode was surrounded by a Soxhlet extraction thimble.   After electrolysis at 0.45 ampere for 60 hours, the solution still contained a trace of selenious acid.   Moreover, free selenium separated at the cathode and offered a very high resistance to the passage of the current.   It was necessary to remove this deposit several times during the electrolysis.   The total amount of selenium thus reduced was 1.06 g., about 12% of the amount originally taken.   The cathodic reduction to free selenium became less as the concentration of selenic acid rose, and toward the end of the electrolysis the quantity of selenium that was reduced was not of such an amount as to necessitate its removal. Continuation of the electrolysis of this solution, after the oxidation of selenic acid had been effected, resulted in the separation of 0.07 g. of free selenium in 30 hours.   This agrees with the observations of Manuelli and Lazzarini.[1]   Oxidation of the selenious acid took place very slowly at the beginning of the electrolysis, but proceeded more rapidly as the concentration of selenic acid increased.   The amount of selenious acid in the solution was determined by the method of Gooch.[2]   This consists in adding to the solution an excess of a standard solution of potassium permanganate and then titrating with oxalic acid.   If both selenious acid and selenic acid are present, the amount of the latter may be ascertained by determining the total acidity by titration with sodium hydroxide, using methyl orange as indicator and deducting from this result the selenious acid found by the Gooch method.   It should be borne in mind that, in the titration with sodium hydroxide, selenious acid is monobasic and selenic acid is dibasic.

[1] Gazz. chim. ital., 39₁ 50 (1909).
[2] Z. anorg. Chem., 9, 360 (1895).

Using this method of analysis it was found that the above electrolysis of selenious acid gave a product that contained 0.03865 g. of selenic acid per cc., and 0.075 mg. of selenious acid per cc.

In the next electrolysis a solution of selenious acid served an anolyte, and the catholyte, which was placed in a paper thimble, consisted of a mixture of 5 cc. of a 6% solution of selenic acid, 10 cc. of a 10% solution of sodium selenate, and 10 cc. of water. The solution of selenious acid contained 20 g. of selenium dioxide in 300 cc. Two pieces of platinum gauze served as anode, and platinum wire as cathode. A porous cup was first used instead of the thimble but it was found that this gave too high resistance. The electrolysis was continued for about 100 hours at 1 to 1.5 amperes. No selenious acid was present in the electrolyte at the end of the run, but the amount of selenium that separated at the cathode was still high, 1.8 g.

Electrolytic oxidation of selenious acid to which nitric acid had been added gave a product free from selenious acid and only a slight deposit of selenium on the cathode. The selenic acid was here of course contaminated by the nitric acid that had been used.

The next experiment was undertaken to ascertain whether electrolysis could be used to oxidize selenious acid that was present in small amount in selenic acid, and thus free the latter from this lower oxidation product. A sample of selenic acid of sp. gr. of 1.8 that contained a considerable amount of selenious acid was used as the anolyte. 50 cc. of this solution was diluted to 200 cc., yielding a selenic acid of 16%. A piece of sheet platinum served as anode. The cathode solution, which was placed in a small porous cup, contained 5 g. of potassium selenate, 5 cc. of a 20% solution of selenic acid, and 10 cc. of water. This solution was kept cool by immersing in it a coil of glass tubing through which cold water was passed. The cathode consisted of a piece of platinum gauze of 20 sq. cm. surface. The current ranged from 2 to 4 amperes at from 5 to 6.5 volts. At the end of 24 hours all but a trace of selenious acid had been oxidized, the anolyte showing 0.35 mg. of selenium dioxide in 10 cc. of solution. Only a very light deposit of selenium separated upon the cathode.

The electrolysis was repeated with a 30% solution of selenic acid containing some selenious acid. At the end of the experiment it was found that the platinum anode had decreased in weight and that the anolyte had assumed a yellow color. This indicated that the selenic acid had dissolved some platinum during the electrolysis.

A comparison of the efficiencies of anodes consisting of smooth platinum, rough platinum, and lead dioxide was next made. We prepared lead dioxide anodes by electrolytically depositing the substance upon platinum gauze from a solution of lead nitrate containing 10% of free nitric acid, using a current of 0.5 ampere. The electrode was subsequently

heated to 180°. The cathode in this experiment consisted of strips of metallic copper of a total surface of about 10 sq. cm. In one cell (No. 4), the cathode was placed in an extraction thimble. The 4 cells were connected in series and the electrolyte consisted of 100 cc. of a 5% solution of selenious acid. The current was 5 amperes and the duration of the electrolysis was 8 hours. The selenic acid present in $1/8$ of each of the 4 solutions was determined by precipitation with bairum chloride. The results were as follows:

TABLE I.

Efficiencies of Anodes.

Cell number.	Anode.	Wt. $BaSeO_4$, G.
1	Smooth platinum	0.3126
2	Platinum gauze	0.2885
3	Lead dioxide	1.1535
4	Lead dioxide (Thimble used)	1.2997

These results show that an anode of smooth platinum gives a somewhat higher yield than does platinum gauze, and that lead dioxide is decidedly more efficient than is either form of platinum. Further, the placing of the cathode within a thimble increases the yield.

The above experiments on the electrolytic oxidation of selenious acid show that it is difficult to obtain complete oxidation of the acid to selenic acid and that there is usually loss of selenium through cathodic reduction. The method is, however, of value in freeing selenic acid from all but a trace of any selenious acid that it may contain. Furthermore, it is shown that an anode of lead dioxide is superior to one of platinum.

The results of our study of the preparation of selenic acid may now be summarized.

The oxidation of silver selenite by bromine yields a product that contains some selenious acid. Diemer and Lenher[1] and Benger[1] removed the selenious acid by treatment of the solution with hydrogen sulfide, but Benger states that selenic acid is also reduced by hydrogen sulfide with the formation of selenium and sulfur, and probably some sulfur dioxide. Diemer and Lenher state that the selenic acid prepared by the action of bromine upon silver selenite is free from sulfuric acid and selenious acid, but they do not describe the method that they employed in testing for the presence of these two substances in the presence of selenic acid. In our own experiments selenious acid was always found in the product from this reaction.

The electrolytic oxidation of selenious acid under the conditions described above yielded in only one case a product that was free from selenious acid.

The oxidation of copper selenite by chlorine with subsequent crystalliza-

[1] *Loc. cit.*

tion of the copper selenate, extraction of copper chloride by acetone, and removal of the copper by electrolysis, yields a selenic acid that is free from selenious acid and chlorine. The method also is suitable for the preparation of selenic acid on a comparatively large scale. For these reasons we regard it as the best of the three procedures that we have examined.

D. DETECTION OF SELENIOUS ACID PRESENT IN SELENIC ACID.

Hydriodic acid reduces selenious acid according to the equation

$$H_2SeO_3 + 4HI = Se + 4I + 3H_2O.$$
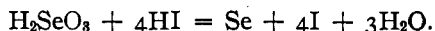
A concentrated solution of selenic acid is reduced by hydriodic acid to selenious acid, which is then further reduced to free selenium if an excess of hydriodic acid is present. Below a certain concentration, however, selenic acid is reduced very slowly by hydriodic acid, and it is possible so to adjust the conditions as to effect the reduction of selenious acid in the presence of selenic acid without causing reduction of the latter. The appearance of a yellow tint in the solution after the addition of hydriodic acid does not in itself prove the presence of selenious acid. That is established only by the appearance of reduced selenium The trace of selenic acid that may be reduced by hydriodic acid may at times produce a yellow color in the solution due to the liberated iodine, but under proper conditions no free selenium is formed. Consequently, if the liberated iodine is reduced and thus decolorized by the addition of just the necessary amount of a solution of sodium sulfite, the yellow color due to liberated iodine will disappear, and the red tinge that is caused by finely suspended selenium will then become visible. When such a solution is viewed lengthwise in a test-tube or in a 50 cc. Nessler tube, very small amounts of selenium can be detected.

To establish the delicacy of this method of detection, experiments were first made upon the action of hydriodic acid on solutions of selenic acid of different concentrations. The hydrochloric acid used was a 10% solution. The solution of potassium iodide was freshly prepared and was of 10% strength. The solution of sodium sulfite was 2%. The solutions were placed in 25 cc. test-tubes, 150 × 12 mm., and were viewed lengthwise through the tube which was held against a white background. The solution of selenic acid was first placed in the tube, hydrochloric acid was then added, and then the solution of potassium iodide. Two drops of the solution of sodium sulfite usually suffices to reduce the liberated iodine.

These results show that selenic acid of a strength of 0.8% or less is not appreciably reduced under the conditions here described.

Experiments were next made upon the delicacy of the reaction between hydriodic and selenious acid, one drop of the solution of selenious acid containing 0.2 mg. of selenium dioxide.

TABLE II.

Delicacy of the Colorimetric Method.

	Composition of solution.				Observation.	
Test No.	H₂O. Cc.	HCl. Cc.	KI. Cc.	H₂SeO₄. Cc.	In ½ hour.	After addition of sulfite.
1....	0.5	..	4.5	....	Colorless	....
2....	3.5	1	0.5	....	Colorless	....
3....	...	..	0.5	4.5 of 8.0%	Orange	Slightly pink
4....	...	1	0.5	3.5 of 8.0%	Cloudy orange	Decidedly red
5....	...	1	0.5	3.5 of 0.8%	Slightly yellow	Colorless
6....	...	1	0.5	3.5 of 0.08%	Trace yellow	Colorless
7....	...	1	0.5	15 of 0.08%	Trace yellow	Colorless

TABLE III.

Delicacy of the Reaction Between Hydriodic Acid and Selenious Acid.

	Composition of solution.				Observation.	
Test No.	H₂O. Cc.	HCl. Cc.	KI. Cc.	H₂SeO₃ drop.	In 20 minutes.	After addition of sulfite.
1........	4.5	..	0.5	1	No color	....
2........	3.5	1	0.5	1	Cloudy orange	Much selenium
3........	15	1	0.5	1	Decidedly orange	Strong red

Hydrazine hydrate and hydrazine hydrochloride were next used.

TABLE IV.

Delicacy, Using Hydrazine Salts.

	Composition of solution.				Observation.	
Test No.	H₂O. Cc.	HCl. Cc.	H₂N.NH₂. Cc.	H₂SeO₃. drop.	In 20 minutes.	After addition of sulfite.
1........	4.5	..	0.5	1	No color	....
2........	3.5	1	0.5	1	No color	....
3........	3.5	1	0.5	3	Strong red	Strong red

The results given in Tables III and IV show that it is necessary to acidify the solutions to obtain reduction of selenious acid, and that hydriodic acid reduces selenious acid more actively than does hydrazine.

Tests were then made of the delicacy of the detection of selenious acid in the presence of selenic acid. The total volume in each case amounted to about 15 cc., and the liquid contained one cc. of 10% hydrochloric acid, 0.5 cc. of 10% potassium iodide, and the volumes of selenic acid and selenious acid given in the table. The selenic acid had a concentration of 0.8%, and the selenious acid contained 0.02 mg. of selenium dioxide per cc. After addition of the potassium iodide, the solutions were allowed to stand for 10 minutes. Two drops of sodium sulfite were then added and the observation was made.

These results show that 0.02 mg. of selenium dioxide in 15 cc. of solution, or one part in 750,000, can clearly be detected by this method; that 120 mg. of selenic acid in 15 cc. of solution yields no reduced selenium; and that one part of selenious acid may be clearly detected in 2200 parts of selenic acid.

TABLE V.

Detection of Selenious Acid in the Presence of Selenic Acid.

Composition of Solution.

Test No.	H₂SeO₄. Cc.	H₂SeO₃. Cc.	Observation.
1..............	..	1	Pink tinge
2..............	..	2	Pink tinge
3..............	15	..	Colorless
4..............	13	2	Pink tinge

The delicacy of the test was still further increased by the use of 50 cc. Nessler tubes which permit the observation of a column of liquid 20 cm. in height. Into such a tube there were placed 46 cc. of an 0.8% solution of selenic acid, 3 cc. of 10% hydrochloric acid, and one cc. of 10% potassium iodide. In Test No. 1 there was also added one cc. of a solution of selenious acid containing 0.02 mg. of selenium dioxide. After the solutions had stood for 5 minutes, two drops of the sodium sulfite solution were added to each and the liquids were then observed against a white background.

TABLE VI.

Delicacy, Using a 50 Cc. Nessler Tube.

Composition of solution.

Test No.	H₂SeO₃. Cc.	Observation.
1......................	1	Slight pink
2......................	..	Colorless

These results show that under the above conditions 0.02 mg. of selenium dioxide can be detected in the presence of 0.368 g. of selenic acid or one part of selenium dioxide in 18,400 parts of selenic acid. It was further established by Test No. 1 that one part of selenium dioxide in 2,500,000 parts of solution may be detected by this method.

E. THE DETECTION OF SULFURIC ACID IN THE PRESENCE OF SELENIC ACID.

Definite details for the detection of small amounts of sulfuric acid in the presence of an excess of selenic acid have thus far not appeared in the literature, nor has the sensitiveness of any of the described methods been given. Jannasch and Heimann[1] ascertained that selenic acid is quantitatively reduced to selenium by hydroxylamine hydrochloride, and that sulfuric acid is not affected by this reagent. It was found upon experiment that hydrazine would also quantitatively reduce selenic acid to free selenium in the presence of a small amount of hydrochloric acid and that the reagent had no effect upon sulfuric acid. This reaction was utilized for the detection of selenic acid in the presence of sulfuric acid in the following manner:

The selenic acid was diluted with water until it has a strength of not over 4 %. The solution was placed in a 350 cc. beaker, 10 cc. of a 90%

[1] *Ber.*, **31**, 2386 (1898).

solution of hydrazine hydrate was added, and the liquid was heated to about 60°. Sufficient conc. hydrochloric acid to make the solution distinctly acid (about 5 cc.) was then added, and the liquid was heated to a temperature near the boiling point for one hour. It was then cooled and the separated selenium was removed by filtration. More hydrazine hydrate was added to the filtrate which was then acidified with hydrochloric acid and again heated. This treatment was repeated until no further separation of selenium resulted. The filtrate thus freed from selenic acid and selenium was evaporated to about 25 cc., 2 cc. of a 10% solution of barium chloride was added, and the solution was allowed to stand at a temperature of about 80° for at least one hour. One mg. of barium sulfate in this solution was easily observable. The results of a determination of the delicacy of the test for selenic acid in the presence of sulfuric acid were as follows:

TABLE VII.

Delicacy of Test for Selenic Acid in the Presence of Sulfuric Acid.

| Test No. | Composition of solution. | | Observation. |
	H_2SeO_4. G.	H_2SO_4. G.	
1	4	....	No precipitate
2	4	0.0004	Strong precipitate

These results show that by this procedure one part of sulfuric acid in 10,000 parts of selenic acid may clearly be recognized.

F. ATTEMPTS TO PREPARE PERSELENIC ACID AND PERSELENATES.

Selenic acid and sulfuric acid resemble each other very closely in their chemical and physical properties. Persulfuric acid and various persulfates have been prepared. In 1901 Dennis and Brown published a preliminary note[1] descriptive of experiments that had been performed by Mr. Brown in 1898, which seemed to indicate the formation of potassium perselenate when a solution of potassium selenate was electrolyzed under specified conditions. This question was again taken up by the authors of the present paper. Solutions of pure potassium selenate and of pure selenic acid were electrolyzed under conditions most favorable to the formation of potassium persulfate and persulfuric acid, but in no case was there any indication of the formation either of a perselenate or perselenic acid.

G. HYDRATES OF COPPER SELENATE.

Metzner has described the monohydrate and pentahydrate of copper selenate, the former resulting when the pentahydrate is heated to 100°.

This preparation of the monohydrate was repeated, using carefully purified samples of the pentahydrate. This substance was found to lose weight steadily and slowly when heated to 50°, but after a period of 30 hours it had not yet reached constant weight, the loss amounting to 15.35%

[1] THIS JOURNAL, **22**, 358 (1901).

of its original weight. When heated to 95° for 5 hours longer, the loss amounted to 23.81% but constant weight was not yet obtained. It was only when the sample was heated to a temperature of 104° that constant weight resulted. The loss of weight at this point was 24.12%, and the loss calculated for the monohydrate is 24.28%. Another sample heated for two hours at 102° gave a loss agreeing almost exactly with that calculated for the formation of monohydrate.

Since no statement was found in the literature as to the temperature at which crystalline copper selenate is entirely dehydrated, this was determined by further heating of the monohydrate. It was found that complete dehydration is effected at a temperature lying between 230° and 235°, and that the resulting anhydrous copper selenate is stable up to a temperature of 280°.

When copper selenate was freed from copper chloride by extraction with acetone, it was observed that the selenate appeared to lose some of its water of crystallization. The extent of this dehydration was ascertained by placing a sample of copper selenate pentahydrate, ground to pass a 150-mesh sieve, in a Soxhlet extraction thimble and extracting it with acetone for 10 hours. The resulting product was dried over calcium chloride and then possessed a pale blue color, which was noticeably lighter than that of the original material. A determination of copper in this salt gave 24.38%. The calculated percentage of copper in $CuSeO_4.3H_2O$ is 24.37%. Determinations of selenium agreed fairly well with the amount calculated for the trihydrate. It therefore appears that when the pentahydrate of copper selenate is extracted with acetone by the procedure earlier described, two molecules of water are removed.

H. AMMONATES OF COPPER SELENATE.

Horn and Taylor investigated the hydrated ammonates of copper sulphate,[1] and they described the preparation and properties of $CuSO_4.4NH_3.H_2O$. Their methods have here been followed in the preparation of the analogous selenium compounds. As preliminary, however, to the study of these ammonates, it was necessary to perfect a method for the determination of selenium in such compounds, and to test the accuracy of the usual methods for the determination of ammonia and copper when applied to the analysis of the ammonates of copper selenate.

1. Methods of Analysis Employed.

a. **Determination of Selenium in Selenates.**—The most satisfactory method for determining selenium in selenates is by reduction of the selenic acid. Of the various reducing agents that may be employed, Gutbier[2] and Meyer[3] give preference to hydrazine hydrate. Jannasch and Müller[4]

[1] *Am. Chem. J.*, **32**, 253 (1904).

[2] *Z. anorg. Chem.*, **41**, 291 (1904).

[3] *Z. anal. Chem.*, **53**, 145 (1914).

[4] *Ber.*, **31**, 2393 (1898).

use hydrazine sulfate for the reduction of selenious acid. Pierce[1] reduces selenic acid with hydriodic acid and weighs the resulting selenium. Gooch and Scoville[2] boil selenic acid with hydrobromic acid, pass the liberated bromine into a solution of potassium iodide, and titrate the liberated iodine.. It has been a somewhat common practice to reduce selenic acid to selenious acid by adding strong hydrochloric acid, and heating the solution to boiling. This procedure, however, results in loss of selenium dioxide through volatilization unless it is conducted with great care.[3]

˙Hydrazine reduces selenic acid so readily and so completely that no preliminary reduction to selenious acid is necessary.

Preliminary tests of a qualitative nature upon the reduction of selenic acid by hydrazine hydrate were first made. Two cc. of an 8% solution of selenic acid was diluted with 10 cc. of water, and 2 cc. of a 90% solution of hydrazine hydrate was added. Conc. hydrochloric acid was then added until there was 0.5 cc. of this acid in excess. A heavy precipitate of selenium at once resulted. The solution was digested for two hours on a water bath, the gray selenium was filtered off, and the filtrate was found to be free from selenic acid and selenious acid. The reduction therefore was complete. When 2 cc. of an 8% solution of selenic acid was treated with 2 cc. of hydrazine hydrate in a total volume of about 12 cc., no precipitate resulted in the cold from this weakly alkaline solution. The solution was then heated upon a steam bath for 2 hours, but only a very slight amount of free selenium separated. The solution was then cooled, diluted with water, and acidified with a slight excess of hydrochloric acid. When barium chloride was added to a portion of this solution, a heavy precipitate of barium selenate resulted. When a solution of potassium iodide was added to another portion of the solution, no immediate precipitation of selenium and iodine appeared as would have been the case if even a small amount of selenious acid had been formed. It is therefore evident that hydrazine hydrate reduces selenic acid but slightly when the reagent is not present in large excess. It was found, however, that a solution of selenious acid is slowly reduced in the cold by the addition of such an amount of hydrazine hydrate as will render the solution strongly alkaline, and that quantitative reduction of selenious acid to selenium takes place when this solution is heated.

On the basis of these qualitative experiments the following quantitative method was developed: The solution of selenic acid containing from 0.1 to 0.5 g. of selenium is diluted with water to about 150 cc. Five to ten cc. of a 90% solution of hydrazine hydrate is added and the solution is

    [1] Z. anorg. Chem., 12, 409 (1896).

    [2] Ibid., 10, 256 (1895).

    [3] Gutbier and Engeroff, Z. anal. Chem., 54, 193 (1915); Boutzoureano, Ann. chim. phys., [6] 18, 296 (1889); Gooch and Evans, Z. anorg. Chem., 10, 148 (1895).

warmed to 60°. Conc. hydrochloric acid is then added cautiously to avoid too violent a reaction and its addition is continued until the hydrazine hydrate is neutralized, and there is about 3 cc. of hydrochloric acid in excess. The liquid is held just below the boiling point for about two hours to permit the colloidal selenium to coagulate and to convert the selenium to the gray form. The solution is then allowed to cool for about one hour, when the precipitate is collected in a Gooch crucible, washed with hot water, dried at 105°, and weighed. It sometimes occurs that the filtrate has a red tinge that is due to passage through the filter of a slight amount of selenium. In such case the filtrate is treated with 0.5 cc. of hydrazine hydrate and sufficient hydrochloric acid to render the solution acid, and is evaporated to about 100 cc. at a temperature near the boiling point. The selenium is then collected in a Gooch crucible, as before. This treatment of the filtrate entirely removes any colloidal selenium that may have passed through the first filter.

In the analysis of the selenates of copper, it is necessary first to remove the copper by electrolysis before precipitating the selenium with hydrazine.

The accuracy of the method was tested with portions of a standard solution of selenic acid with the following results:

TABLE VIII.
Accuracy of Method.

Run number.	Wt. selenium taken. G.	Wt. selenium found. G.
1	0.1184	0.1192
2	0.1184	0.1191
3	0.1184	0.1178

b. **Determination of Copper in Copper Selenates.**—Copper was determined in the various ammonates of copper selenate by dissolving, in water, samples containing from 0.1 to 0.5 g. of copper, adding 3 cc. of conc. sulfuric acid and 0.5 cc. of conc. nitric acid, diluting the solution to 200 cc. and electrolyzing with a platinum gauze cylinder as cathode. The cathode was rotated at about 300 r. p. m. The current for the first 10 minutes was 0.8 ampere and after that 0.4 ampere. This regulation was necessary to avoid the formation of selenium through cathodic reduction. The deposits of copper were slightly dull in appearance, but they adhered tenaciously to the cathode and gave consistently agreeing and accurate results.

c. **Determination of Ammonia in Ammonates of Copper Selenate.**—The Kjeldahl method was used. Twenty cc. of diluted sulfuric acid (1 : 1) was placed in a 750 cc. Erlenmeyer flask and the weighed sample was dropped into the acid and allowed to dissolve. 200 cc. of water was then added, together with a piece of granulated zinc. A solution of potassium hydroxide of sp. gr. 1.45 was introduced into the flask through a separatory funnel. A Chamot safety bulb was inserted in the neck of the flask and

the bulb was connected with a spiral condenser that dipped into a measured amount of standard acid. A blank experiment demonstrated the purity of the reagents used.

2. Copper Selenate Tetrammonate Monohydrate, $CuSeO_4.4NH_3.H_2O$.

To prepare this compound, 100 g. of pure copper selenate pentahydrate was treated with 125 cc. of ammonium hydroxide (sp. gr. 0.96) until the substance was completely dissolved. Ammonia was then passed through the solution. The gas was rapidly absorbed and there separated in a short time clusters of very small, needle-like crystals of a deep blue-violet color that nearly matches the tint BV-Shade 2 of Mulliken's Color Standard.[1] The passage of ammonia was continued for two hours and the separated crystals were then collected in a Büchner funnel and washed twice with ammonium hydroxide (sp. gr. 0.96). Suction was continued through the funnel for some minutes; the crystals were then spread upon a cover-glass and allowed to stand in the air for 10 minutes, whereupon most of the ammonium hydroxide evaporated. They were then transferred to a desiccator containing quick-lime. This substance removes the water of the adhering ammonium hydroxide but does not absorb the ammonia. Consequently there was present in the desiccator a slight amount of ammonia, which tended to equalize the vapor tension of the ammonia in the compound. The water in the compound was removed by lime in from 36 to 72 hours. Analysis of the resulting compound gave the following results:

Calc. for $CuSeO_4.4NH_3.H_2O$: Cu, 21.71; Se, 27.01; NH_3, 23.25.

Found: Cu, 21.98, 2197, Av. 21.975; Se, 27.15; NH_3, 23.17, 23.31, Av. 23.24.

This copper selenate tetrammonate monohydrate is quite stable when kept over lime or when preserved in a glass-stoppered bottle which the substance nearly fills. When exposed to the air it slowly gives off ammonia and the crystals become dull in appearance. When observed under the microscope the crystals are seen to be slender prisms whose behavior toward polarized light indicates that they belong to the orthorhombic system as do the crystals of the analogous compound of sulfuric acid. When dropped into a small amount of water the crystals dissolve, forming a deep blue solution. When this is diluted with water, the color becomes lighter and basic copper salts separate.

3. Copper Selenate Triammonate Monohydrate, $CuSeO_4.3NH_3.H_2O$.

Finely ground crystals of the tetrammonate monohydrate were exposed to the air for 14 hours at a temperature of about 20° and then a slow current of air was passed over the crystals at room temperature for 10 hours longer. The substance lost ammonia during the early part of this treatment. Ammonia then ceased to be given off and the product ap-

[1] "Identification of Pure Organic Compounds", by S. P. Mulliken.

parently assumed a stable form. Its color is a pure blue which lies between B-Tint and B-Normal Tones of Mulliken's Color Standard. Analysis of the compound gave the following results:

Calc. for $CuSeO_4.3\ NH_3.H_2O$: Cu, 23.04; Se, 28.72; NH_3, 18.52.

Found: Cu, 23.06, 23.07, Av. 23.065; Se, 28.66; NH_3, 18.52, 18.42, Av. 18.47.

Determination of the copper in a second preparation of the compound gave 23.07%. This agreement with the first results indicates that the substance is a stable compound of definite composition. When dropped into a little water, it dissolves to a blue solution which, when diluted, becomes of lighter tint and separates a basic copper salt.

4. Copper Selenate Tetrammonate, $CuSeO_4.4NH_3$.

This was prepared from the copper selenate tetrammonate monohydrate by making the latter substance in the manner above described, collecting the crystals on a Büchner funnel, removing some of the adhering ammonium hydroxide by suction, pressing the crystals between filter paper, and then placing them immediately upon a filter paper in a desiccator over lime, and drying them for 7 days at a pressure of 25 mm. Determinations of the copper and selenium in this product, and of ammonia in a sample that had remained in the desiccator 4 days longer, gave the following results:

Calc. for $CuSeO_4.4\ NH_3$: Cu, 23.13; Se, 28.80; NH_3, 24.79.

Found: Cu, 23.25, 23.15, Av. 23.20; Se, 28.40, 28.40, Av. 28.40; NH_3, 24.85, 24.99, Av. 24.92.

It seems peculiar that the copper selenate tetrammonate monohydrate loses its molecule of water under the above conditions but does not lose ammonia. A similar result, however, was obtained by Bouzat,[1] who prepared copper sulfate tetrammonate by heating copper sulfate tetrammonate monohydrate. Copper selenate tetrammonate is of a lighter blue-violet color than the tetrammonate monohydrate, and is nearly identical in tint with BV-Normal Tones of Mulliken's Color Standard. The compound gives off ammonia slowly when exposed to the atmosphere. It is quite stable when kept over lime even at low pressure. It is also apparently stable when preserved in a glass-stoppered bottle which the substance nearly fills.

Summary.

1. The separation of selenium from tellurium by the crystallization of selenious acid is described.

2. Three methods for the preparation of selenic acid were studied, and that involving the oxidation of copper selenite by chlorine, crystallization of the resulting copper selenate, extraction of copper chloride by acetone, and removal of copper by electrolysis was found to be the most satisfactory.

3. A method for the detection of slight amounts of selenious acid in

[1] *Ann. chim. phys.*, [7] **29**, 305 (1903).

selenic acid has been developed, as well as one for the detection of small amounts of sulfuric acid in the presence of selenic acid.

4. It has been demonstrated that the electrolysis of selenic acid or of its salts under conditions favorable to the formation of persulfates from the analogous compounds of sulfur yields neither perselenic acid nor perselenates.

5. The dehydration of crystalline copper selenate was studied and the temperature of its complete dehydration was determined.

6. A method for the determination of selenium in selenates by the use of hydrazine hydrate is described.

7. The preparation and properties of three new ammonates of copper selenate are described.

ITHACA, N. Y.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

AN ELECTROMAGNETIC HYPOTHESIS OF THE KINETICS OF HETEROGENEOUS EQUILIBRIUM, THE STRUCTURE OF LIQUIDS, AND COHESION.

BY WILLIAM D. HARKINS AND H. H. KING.

While Gibbs[2] in his remarkable treatise "On the Equilibrium of Heterogeneous Substances" has given a very broad treatment of his subject from the thermodynamic standpoint, nothing is included which would give any idea of the probable distribution of any component (A) between a set of phases (a), (b), (c), ——, from a knowledge of the properties of (A) alone, and those of the phases (a), (b), (c), ——, before any of the component (A) has been mixed with them. It is the purpose of this paper to indicate that the general nature of such a distribution can be predicted in most cases from the standpoint of the hypothesis that it is conditioned not only by the motion of the molecules (vibrations apparent as temperature, and probably rotations as well), but also by the intensity and the nature of the electromagnetic field surrounding them. Since all recent theories of the structure of the atom assume it to consist of a system of negative electrons built up around a positively charged nucleus, the atom, and therefore the molecule, would on this basis be surrounded by an electric field. Inasmuch as there is considerable evidence that the electrons are in motion (the magnetic properties of substances, etc.), this is also