

THE ELECTROCHEMISTRY OF URANIUM AND THE SINGLE POTENTIALS OF SOME OXIDES¹ OF URANIUM

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I. INTRODUCTION

The element uranium although classed with chromium, molybdenum and tungsten in the periodic system is peculiar in that it resembles members of other groups of elements as well. Beyond the electrolytic analysis,² the conductivity of the aqueous solutions of its salts,³ the effect of light on the potential of uranous uranyl solutions using platinum electrodes,⁴ and⁵ a similar investigation by Luther and Michie,⁶ very little is found in the literature concerning the electrochemistry of uranium. McCoy and Bunzel⁷ have used potential measurements for determining the rate of oxidation of uranous solutions.

In the paper here presented are contained accounts of experiments on the electrolysis of various uranium compounds. These experiments were made in order to ascertain the electrolytic behavior of different uranium compounds in aqueous solutions, non-aqueous solutions and in fusions. The hope at first was that a method of preparing uranium electrolytically might be found. While metallic uranium was not thus prepared in the pure state, quite a number of compounds of uranium were formed electrolytically. The conditions of the formation of these compounds have been detailed and their single potentials have been ascertained whenever a sufficient amount of pure material was formed in the experiment.

¹ A portion of the thesis submitted to the graduate school of the University of Wisconsin in partial fulfillment of the requirement for the degree of Doctor of Philosophy.

² Smith: *Am. Chem. Jour.*, **1**, 329 (1879).

³ Dittrich: *Zeit. phys. Chem.*, **29**, 449 (1899).

⁴ Baur: *Zeit. phys. Chem.*, **63**, 683 (1908).

⁵ Titlestad: *Zeit. phys. Chem.*, **72**, 257 (1910).

⁶ *Zeit. Elektrochemie*, **14**, 826 (1908).

⁷ *Jour. Am. Chem. Soc.*, **31**, 367 (1909).

The difficulties involved in the electrolysis of uranium compounds are many. The metal does not deposit as such from aqueous solutions of either uranyl or uranous salts but it is deposited as a poorly adhering oxide of variable composition, most probably in the form of the uranyl radicle UO_2 or its hydrates. Prepared in other ways, such as the reduction with metallic potassium¹ or metallic sodium,² by electrolysis of fused double sodium uranous chloride,³ reduction in the electric furnace with carbon⁴ and the reduction with aluminum,⁵ the metal has never been obtained absolutely pure. It is a metal that burns at a low temperature (170°), reacts with cold water and combines with nitrogen, carbon, and oxygen so readily that its preparation in absolutely pure form is well-nigh impossible.

The uranous salt solutions are easily oxidized and for this reason an attempt to electrolyze a uranous solution always results in the formation of uranyl salts around the anode and a deposition of oxide on the cathode. It may also be possible that the reaction of the metal with water is the explanation of the deposit of the oxide at the cathode. Whatever the explanation may be, it has thus far been experimentally impossible to plate pure metallic uranium, especially from aqueous solutions.

Muthmann and Fraunberger⁶ measured the single potential of metallic uranium against a normal solution of potassium chloride and reported a value of 0.19 volt. No analyses indicating the purity of the metal used are given. My own measurements with a sample containing 91.49 percent metallic uranium in normal potassium chloride solution gave a single potential of -0.099 volt which is substantially the same as that developed by the same sample of metal immersed in uranyl nitrate solutions containing 14.3 grams per liter.

¹ Peligot: *Ann. Chim. Phys.*, (3) **5**, 1 (1842).

² Zimmermann: *Liebig's Ann.*, **216**, 14 (1882).

³ Moissan: *Comptes rendus*, **122**, 1088 (1896).

⁴ Moissan: *Comptes rendus*, **116**, 369 (1893).

⁵ Aloy: *Bull. Soc. chim. Paris*, (3) **25**, 153 (1901).

⁶ *Akad. Wiss. München*, **34**, 201 (1904).

It is possible that Muthmann and Fraunberger attach a different meaning to the \approx sign before the figure which they give. On the other hand the uranium they had was undoubtedly of a different state of purity as my own which was contaminated with ferric oxide. Neither result can of course be considered as final since the metal used was not pure.

II. EXPERIMENTAL

NOTE—In all the electrolytic experiments the potential impressed is given in volts and the current density is stated in amperes per square decimeter.

1. Pyridine as a Solvent for Uranyl Salts

Tests upon the solubility of uranyl nitrate, chloride, acetate, sulphate and oxalate were made by treating small portions of the different salts with pyridine. Uranyl nitrate was found to be the most easily dissolved though uranyl chloride and acetate are also appreciably soluble. They are more soluble in cold pyridine than in hot. When heated in a water bath at the boiling temperature, a flocculent yellow precipitate was thrown down in each case. Uranyl sulphate and uranyl oxalate were only slightly soluble in pyridine. The yellow precipitates thrown down on heating the solutions were not dissolved when the solution cooled and could not be brought into solution again in the pyridine.

2. Electrolysis of Uranyl Salts in Pyridine Solution

Many electrolytes are known to yield conducting solutions when dissolved in pyridine and metals have been deposited electrolytically from such solutions,¹ which could not be deposited from aqueous solutions. A saturated solution of uranyl nitrate in pyridine was tried in hopes that metallic uranium might be deposited from this solution electrolytically. The uranyl nitrate used was Merck's "highest purity," while the pyridine used was Baker's pure pyridine. In the preliminary trials the pyridine was not anhydrous. The solution was not a very good conductor. A pressure of 14 volts was

¹ Jour. Phys. Chem., 3, 602 (1899).

required to give any perceptible reading on the milliammeter used. When the voltage was increased to 30 a current density of 0.31 amp. was obtained. The solution became very dark due to the carbonization of the pyridine. After allowing the current to run for three hours the cathode was covered unevenly with a black deposit. The side facing the anode naturally was covered thicker than the other. The excess of pyridine was washed from the deposit with petroleum ether and after drying in the air examined for uranium. The deposit resembled carbon but on dissolving the black material in nitric acid it gave a straw colored solution which when tested qualitatively, showed that uranium was present in considerable quantity.

A fresh solution of uranyl nitrate in pyridine was prepared and electrolyzed with a voltage of 30 and current density of 0.311 amp. In this trial the anode was surrounded by a muslin bag acting as a diaphragm. This arrangement did not prevent the blackening of the pyridine. After three hours the cathode was removed and examined. A black deposit was spread unevenly over the cathode and had a striated appearance. It was washed with gasoline and then allowed to dry in the air. When dry it had a reddish color like partially oxidized copper and was loosely adherent. An attempt was made to measure the single potential of the plated material against a uranyl nitrate solution but as soon as the electrode was dipped into the electrolyte a portion of the coat fell off exposing platinum so that a reliable measurement was not obtained. Diaphragms of other materials were tried including a Schleicher and Schull extraction thimble, a bag made of filter paper and also a bag made of bolting cloth but nothing was found that would prevent the spread of the carbon formed around the anode so that the product on the cathode would not be contaminated. A smoother adhering deposit was obtained by revolving the beaker during electrolyzing but no clear metallic deposit could be obtained nor was the deposit large enough to analyze. The pyridine also charred when uranyl acetate and uranyl chlorides were used as electrolytes,

a positive proof that the nitrate radicle UO_3 was not responsible for the charring of the pyridine. Although uranyl sulphate and uranyl oxalate were both slightly soluble in pyridine neither prevented the charring of the solution when electrolyzed. The anode in both cases became very dark brown but no uranium deposit could be found on the cathode. The voltage used was 100 in each case. The current was not recorded in this case because of a faulty ammeter.

No satisfactory deposit of uranium can be obtained from the solutions of the uranyl salts in pyridine because of (1) the charring of the solvent, (2) the failure of the uranyl radicle to reduce, and (3) the contamination of the deposit by the charred pyridine.

3. Electrolysis of an Ether Solution of Uranyl Nitrate

One gram of uranyl nitrate containing its water of crystallization was dissolved in fifty cubic centimeters of anhydrous ether and placed in a closed cell connected with a reflux condenser. It was electrolyzed under a pressure of 100 volts and gave a current density of 0.12 amp. at the beginning. The side of the cathode facing the anode became covered with a silvery white deposit. After electrolyzing for 6 hours the cathode was removed and the deposit washed with fresh ether. It dried quickly in the air leaving a deposit, white in appearance but slightly tinged with yellow. This deposit did not adhere well to the electrode and was easily brushed off with the finger. It could not be washed off with water but was readily removed with nitric acid. The nitric acid solution gave a qualitative test for uranium.

Further tests made in the same solution under similar conditions and also made with a rotating cathode gave in each case deposits silvery white in appearance at first but when allowed to stand in a calcium chloride desiccator for a while they became yellow. Freshly dissolved uranyl nitrate containing its water of crystallization always conducted better at first. After running for a short time the current gradually fell off finally becoming practically zero. The conductivity

of the ether solution, therefore, appears to be a function of the amount of water present. After the electrolysis has decomposed the water present, the conductivity practically ceases. Solutions made with ether that was not anhydrous were better conducting media than when anhydrous ether was used but eventually they behaved in the same way. Because of the poor conductivity of ether solutions the use of ether as a solvent was abandoned. The nature of the deposit formed was not ascertained. It could only be obtained in small quantities insufficient for analysis.

4. Electrolysis of Ethyl Acetate Solution of Uranyl Nitrate

A solution of uranyl nitrate in ethyl acetate was prepared. No attempt was made to get perfectly anhydrous material for the uranyl nitrate carried water of crystallization. The solution contained 1 gram of uranyl nitrate in 50 cc. It was electrolyzed with a voltage of 95 and at this pressure gave a poorly conducting solution. The current density was 0.2 amp. A deposit began to form on the side of the cathode facing the anode immediately but the opposite side remained clear. The beaker was rotated throughout the run but an even deposit was not obtained. The cathode was removed after two hours, washed with fresh ethyl acetate and dried in a desiccator over calcium chloride. The deposit was dark when first dried but became yellow while standing over night in the desiccator. The weight of the deposit was only 30 milligrams. It was removed from the electrode by 1 drop of concentrated nitric acid and washed back into the solution with ethyl acetate. The addition of the 1 drop of nitric acid increased the conductivity of the solution. The latter was electrolyzed with a voltage of 50, and a current density of 0.21 amp. A flocculent yellow deposit collected around the cathode but did not adhere. It sloughed off at once and piled up under the cathode when stationary. This deposit was not analyzed but to all appearances was the yellow oxide of uranium UO_3 . No trace of uranium could be found on the cathode when removed and washed with fresh ethyl acetate.

Another trial with a freshly prepared solution of uranyl nitrate in ethyl acetate containing no free nitric acid was made. The voltage used was 40 and the current density 0.100 amp. The electrolysis was made without rotation of the solution and was allowed to continue for 12 hours. A yellow deposit was formed on the side of the cathode facing the anode but the other side remained clear. The deposit was spongy and poorly adherent, a part falling off during the electrolysis. The deposit was washed with fresh ethyl acetate and allowed to stand in a calcium chloride desiccator over night. When dry, the deposit weighed only 4.7 milligrams and was easily brushed off. It appeared to be principally the yellow oxide of uranium mixed with a small bit of a black oxide.

Because of the poor conductivity of the solution and the small amount of deposit obtained no analysis of the product was made and no potential reading could be taken because the electrode was not covered entirely with deposit. The use of the ethyl acetate solution for electrolysis had to be abandoned.

5. Electrolysis of an Amyl Alcohol Solution of Uranyl Nitrate

A solution of uranyl nitrate in amyl alcohol was prepared. The solution contained 1 gram of crystallized uranyl nitrate in 50 cc of the alcohol. No attempt was made to prepare anhydrous alcohol because of the water contained in the uranyl nitrate. The solution was poorly conducting, giving a current density of 0.19 amp. under a pressure of 130 volts. A bronze-like deposit, very smooth, was formed on both sides of the cathode. The deposit was quite thin and iridescent. The potential of this deposit was taken with a solution of uranyl nitrate containing 12.3190 grams of anhydrous uranyl nitrate per liter. The single potential was found to be -0.2691 volt. Attempts to get a sufficient quantity of this bronze-like deposit for analysis were futile. In each case only a few milligrams were deposited after electrolyzing under the conditions mentioned above for periods of 12 hours and longer.

On adding 5 cc of water to the amyl alcohol solution, the

conductivity increased. The solution became warm and a heavier deposit was obtained. The maximum current density reached under a pressure of 130 volts was 0.65 amp. The deposit formed under these conditions was black and poorly adherent. It was washed with ether and dried over calcium chloride to constant weight and analyzed for its uranium content. It contained 73.72 percent of uranium and gave a single potential against the uranyl nitrate solution of -0.483 volt.

Sample No. 2, deposited under conditions exactly as the above, gave on analysis 71.36 percent of uranium.

It is evident, that the electrolysis of uranyl nitrate in amyl alcohol solution does not give metallic uranium, and when water is present the composition of the deposit approaches that obtained from aqueous solutions.

6. Electrolysis of Double Potassium Uranyl Cyanide

Moissan¹ states that the cyanides of uranium have not been prepared. When a potassium cyanide solution is added to an aqueous solution of uranium tetrachloride, hydrated uranium oxide is precipitated with evolution of hydrocyanic acid gas. Aloy² prepared uranyl potassium cyanide by precipitating the uranium from uranyl nitrate with potassium cyanide and dissolving the precipitate first formed in an excess of potassium cyanide and then concentrating the solution.

To a solution of Merck's pure uranyl nitrate, potassium cyanide solution was added slowly. A canary-yellow, gelatinous precipitate formed at once and an odor of hydrocyanic acid was noticed. The precipitate was filtered off and washed with cold water to remove the potassium nitrate. The precipitate was removed from the filter and treated with an excess of potassium cyanide. Some of the precipitate would not dissolve in the potassium cyanide solution but was soluble in a solution of hydrocyanic acid.

The hydrocyanic acid was prepared by treating silver nitrate solution with potassium cyanide solution in the molecu-

¹ *Traité de Chimie Minérale*, 4, 885.

² *Ann. Chim. Phys.*, (7) 24, 412 (1901).

lar ratio required to just precipitate all the silver as silver cyanide. This was filtered off and washed with water until free from any slight excess of silver nitrate and then stirred up thoroughly, while kept ice cold, with hydrochloric acid keeping the hydrochloric acid just short of the amount needed to convert all of the silver cyanide to silver chloride. The filtered solution was free from silver and left no residue when evaporated. This solution was used to dissolve the precipitate that remained insoluble in the excess of potassium cyanide. It dissolved completely in the hydrocyanic acid solution. This portion insoluble in potassium cyanide but soluble in hydrocyanic acid was in all probability potassium uranate.

Electrolysis of the double potassium uranyl cyanide solution under a pressure of 4 volts and a current density of 0.62 amp. gave deposits of yellow uranic hydroxide in neutral solution and evolved cyanogen. The deposit sloughed off and settled to the bottom of the cell. The solution became alkaline toward phenolphthalein during the action due to the loss of the volatile acid.

Solutions made acid with hydrocyanic acid likewise evolved cyanogen and deposited yellow uranic oxide on the cathode. This deposit immediately sloughed off but dissolved again as long as there was free acid in the solution.

By the use of a roughened platinum electrode and a higher current density a better adhering product was obtained which was black and uniformly deposited on the cathode.

The weight of the deposit was 67 milligrams and was obtained by electrolyzing the acid solution for three hours under a pressure of 8 volts and a current density of 0.2 amp. The deposit when washed with alcohol and ether gave a single potential of -0.461 volt against the standard uranyl nitrate solution.

The deposition of metallic uranium does not take place in aqueous potassium uranyl cyanide solution either neutral or acid with hydrocyanic acid. With low current density the deposit is uranic oxide. Higher current density changes this to a black hydrated oxide. The composition of the de-

posit was not ascertained since it was only obtained in quantities too small for analysis.

7. Electrolysis of a Solution of Double Sodium Uranyl Oxalate.

The electrolysis was made with an aqueous solution of double sodium uranyl oxalate prepared by dissolving 5 grams of uranium oxalate (E. de Haen, labelled "chemically pure") in 75 cc of water and adding sodium oxalate (Squibb's "C. P. reagent") to the solution in the molecular proportion required to form the double salt. It was electrolyzed with a pressure of 5 volts and a current density of 1.55 amp. There was formed immediately a black deposit, poorly adherent, which sloughed off leaving the cathode exposed in spots. The usual yellow deposit that first forms on electrolyzing aqueous solutions of uranyl salts did not appear. The weight of the deposit after electrolyzing for three hours was 40 milligrams. The greater portion of the uranium had been precipitated during the electrolysis and remained undissolved in the solution.

From this almost depleted solution with a pressure of 7 volts and current density of 0.77 amp. a deposit was obtained which adhered well, was smooth in appearance and showed no trace of the yellow oxide. It weighed 30 milligrams and gave a single potential of -0.381 volt, against the standard solution of uranyl nitrate.

The same solution was made acid with oxalic acid and electrolyzed with a pressure of 10 volts and a current density of 7.75 amp. The solution became warm during the electrolysis. The evolution of gas from the cathode prevented the formation of a smooth deposit. After three hours the deposit formed weighed only 13 mg. No trustworthy single potential could be obtained of this material since the platinum was exposed in spots.

Plating from an aqueous solution of double uranyl sodium oxalate does not deposit metallic uranium. The deposit was not obtained in sufficient quantity for analysis, but its single potential was ascertained.

8. The Electrolysis of an Aqueous Solution of Double Potassium Uranyl Fluoride

Double potassium uranyl fluoride has been prepared by Baker¹ and also by Smithells² by precipitating the uranium from uranyl nitrate with potassium fluoride and also by the action of hydrofluoric acid on potassium uranate or by mixing potassium fluoride and uranyl fluoride in molecular proportions required for the formula $2\text{KF} \cdot \text{UO}_2\text{F}_2$. The double salt of uranium tetrafluoride with potassium fluoride has not been prepared.

Attempts to prepare the latter salt were made by fusing uranium tetrafluoride with the required amount of potassium fluoride to give the salt $2\text{KF} \cdot \text{UF}_4$ corresponding to the analogous double potassium uranium chloride. This was unsuccessful because uranium tetrafluoride is converted into an oxide with loss of fluoride on heating. The residue left was only partly soluble in water but completely dissolved in hydrofluoric acid. The yellow solution thus prepared was used for the electrolysis after evaporating to dryness to remove the excess hydrofluoric acid and redissolving in water.

It was electrolyzed in a hard rubber beaker under a pressure of 6 volts and a current density of 2.32 amp. for one hour. On removing the cathode and washing with water no deposit could be seen. The cathode was treated with concentrated nitric acid and the washings were tested for uranium with negative results. On heating the electrode the platinum first turned a yellow color and on stronger heating became green. The coat now dissolved in nitric acid and gave a splendid test for uranium.

A second experiment made with the same solution gave a deposit silvery white with just a tinge of blue-green. Its weight was uncertain because the glass stem of the electrode had been attached by hydrofluoric acid. The deposit was obtained by electrolyzing the solution for two and one-half hours with a voltage of 7 and a current density of 3.9 amp.

¹ Jour. Chem. Soc., 35, 760 (1879).

² Ibid., 43, 125 (1883).

The single potential of the plated material was measured against the standard uranyl nitrate solution and gave -0.389 volt. Under the same conditions, the same general deposit could always be obtained and the deposits gave nearly the same potential as recorded.

The conditions were varied slightly and a different deposit was found. In this experiment under a voltage of 4 and a current density of 2.54 amp. a white deposit seems to form first but is covered with a black oxide. The deposition was carried on in the same solution as before, except that it had been acidified with hydrofluoric acid. With a higher voltage 8 volts, and a current density of 14 amp. a heavier deposit of the black oxide is formed. The deposit appeared silver white beneath a coat of black. A potential reading of this deposit against the standard solution of uranyl nitrate gave a single potential of -0.470 volt.

The results obtained by plating on the same electrode after running a potential are given in tabular form.

TABLE I

Volts	ND ₁₀₀ in amp.	Time	Weight of Deposit Gram	Color	Single potential
4	3.64	3 hrs.	0.0040	white under black	-0.472 volt
5	2.16	1.5 hrs.	0.0050	white	-0.471 volt
6	2.16	1 hr.	0.0058	black	-0.478 volt
7	2.16	1 hr.	0.0064	black	-0.479 volt
8-9	2.16	2 hr.	0.0080	black	-0.475 volt

The single potential shows that the same material was being deposited throughout. During the successive experiments a portion of the uranium oxyfluoride was reduced to uranous fluoride and this salt separated out during the electrolysis. By thus depleting the solution of its electrolyte it became necessary to increase the voltage to keep up approximately the same current density throughout. From the potential of the clear white and that of the blackened de-

posit it is evident that the two deposits are not the same. The potential of the blackened deposits agrees with those obtained from the nitrate solution in amyl alcohol and also the deposits from the double cyanide and oxalate, in aqueous solution.

Analysis of the Deposit from the Double Fluoride

A deposit, silver white in appearance, was obtained by electrolysis, of a solution of the double potassium uranyl fluoride solution with a pressure of 4 volts and a normal density of 0.485 amp. This was analyzed for its uranium content by heating the electrode until the white deposit had changed to a golden yellow oxide, after which the deposit was dissolved in nitric acid. The uranium was determined by precipitation from the uranyl nitrate solution with ammonia.

TABLE II

	Weight of deposit Gram	U ₃ O ₈ found Gram	Wt. of uranium Gram	% U
Sample 1	0.0522	0.0374	0.0313	57.50
Sample 2	0.0494	0.0362	0.0303	61.45
Sample 3	0.1457	0.1014	0.0818	56.20

Sample 2 was not the clear, white deposit obtained before but showed contamination with the black oxide above mentioned. Sample 3, obtained from a fresh solution of the double salt was white. It was obtained with a voltage of 4 and a current density of 1.63 amp.

The similarity of the behavior of the white deposit, when heated, to the behavior of uranium tetrafluoride when it was heated, suggested that the deposit might be a fluoride of uranium. This was proven to be correct as the following analysis shows: Tests for fluorine were made by placing one of the electrodes in a large platinum dish, adding concentrated sulphuric acid and covering the dish with a glass plate coated with paraffin. The design drawn in the paraffine was not etched in any case though several tests were made in this way.

After failing to find fluorine in this manner an analysis for fluorine was made on a newly prepared deposit.

Method of Analysis

A mixture of sodium and potassium carbonates in such proportion as to give the lowest fusing mixture possible were brought to a quiet fusion in a platinum dish. The electrode with its deposit was then dipped into the fused mass and rotated until the electrode was coated with the fusion material. The temperature was then raised, and the heating continued until the electrode showed a smooth coat of the fused carbonates. The melt was taken up with water and carefully acidified with dilute nitric acid until just neutral or slightly basic. A large portion of the carbon dioxide was removed in this way. The slightly basic solution was then heated to boiling for a short time and allowed to cool. A slight excess of nitric acid was then added and the solution was again made alkaline with a slight excess of ammonia. On boiling the solution several minutes, the remaining carbon dioxide was driven off as ammonium carbonate. At the same time the uranium was precipitated as ammonium uranate. This was filtered off and the fluorine in the filtrate was then determined by precipitation from a neutral solution as calcium fluoride.

TABLE III

Data	Voltage	N.D. ₁₀₀	Wt. of deposit Gram	Wt. of U ₃ O ₈ Gram	% U	Wt. of GaF ₃ Gram	% F
Sample 1	3	1.63	0.2444	0.0880	57.70	0.0404	16.05
Sample 2	3	1.63	0.1076	0.0736	53.40	—	—

The varying results in the uranium content given in Tables II and III would indicate that the deposit was not always uniform. The fluorine result in Sample 2 was lost through breakage. The amount of fluorine found in Sample 1 is very close to the theoretical amount required to form UF₄ with the uranium present. Taking the difference between

100 and the percent of uranium and fluorine as water, the empirical formula for the deposit would be $\text{UF}_4 \cdot 6\text{H}_2\text{O}$. The water was not determined quantitatively directly but its presence was proven qualitatively. The fluorine was proven to be present by testing the precipitate formed with calcium for fluorine.

The white deposit formed when an aqueous solution of potassium uranyl fluoride is electrolyzed, whether in neutral or acid solution, is insoluble uranous fluoride. The uranium is evidently deposited upon the cathode as UO_2 and immediately converted to the fluoride by the hydrofluoric acid present. No metallic uranium is obtained by the electrolysis of the double potassium uranyl fluoride.

The potential of the uranium fluoride deposit is -0.389 volt. Whenever the deposit was blackened, the potential found was the same as that of the black deposit obtained from aqueous solutions of uranyl nitrate and uranyl oxalate.

9. Electrolysis of Potassium Uranyl Fluoride in Ammoniacal Solution

It was found that ammonium hydroxide would not precipitate uranium from aqueous uranyl solutions in the presence of hydroxylamine. The deposition of uranium from alkaline solution was tried with no results. The deposits formed were the color of bronze with a fringe of green. A larger deposit could be obtained in a shorter time than was possible in acid solution and this deposit contained a larger percent of uranium. The composition of the deposit was not constant as shown by analysis.

TABLE IV

	Weight of deposit Gram	Weight of U_3O_8	Weight of uranium	% of uranium
Sample 1	0.3046	0.2237	0.1878	61.55
Sample 2	0.1975	0.1508	0.1264	64.50
Sample 3	0.1386	0.1142	0.0958	69.20

The deposits were obtained by electrolyzing the solution with a pressure of 4 volts and an average current density of 1.8 amp. Stationary electrodes were used and the container rotated. The single potentials of these deposits were not measured.

10. Electrolysis of Fused Potassium Sodium Uranate

A fused bath of potassium sodium uranate was prepared by fusing a mixture of potassium and sodium carbonate in a nickel crucible and adding the green uranium oxide to the melt. This dissolved in the carbonates with evolution of carbon dioxide and formed a molten mass. The first attempt was made with platinum electrodes. The fused material was electrolyzed under a pressure of 3 volts and a current density approximately 33 amp. The alkali metals, which separated out along with the uranium at the cathode, burned near the surface of the melt. The platinum was attacked by the burning alkalies and almost eaten through at the surface of the melt. The portion below the melt was not injured quite so much but became brittle and broke up when the electrode was removed. The electrode was washed first with cold water and finally with dilute acetic acid. The platinum that was below the surface of the melt was gray and would not clear up in treating with concentrated nitric acid. When heated on the lid of a platinum crucible the gray coat became green and could then be dissolved off with nitric acid. Qualitative test indicated that metallic uranium had actually been deposited on the platinum. The black powder that had washed off the electrode with water was uranium oxide.

Electrolysis of a similar bath with nickel electrodes gave a black powder around the cathode. This was insoluble in water and in acetic acid and was difficultly soluble in dilute nitric acid. From its behavior toward nitric acid, it appears to be powdered metallic uranium mixed with some black uranium oxide. The nickel electrode contained no deposit of uranium with which a potential reading could be taken nor was it possible to make an analysis of the small amount of the black powder obtained.

11. The Electrolysis of Uranyl Sulphate Solution

Bunsen¹ and also Carveth and Mott² were able to obtain metallic chromium by electrolyzing a chromous chloride or chromous sulphate solution with high current density. They used an unglazed porous cup as a diaphragm. Because of the strong analogy between chromium and uranium their method of procedure was tried.

Experiments were carried out in various ways. Different current densities were used in different temperatures varying from 0° to boiling. Strong acid solutions, weak acid solutions, neutral solutions, and solutions made alkaline with ammonia after adding hydroxylamine to hold the uranium in solution were tried. Many of the deposits obtained had a metallic appearance, but they were always contaminated with the black oxide or with a sulphate. The electrodes were also varied. The material tried as electrodes were platinum smooth and roughened, copper, carbon, graphite, and nickel. The deposits formed with the different electrodes were always the same in general properties varying with the kind of solution used, the current density, temperature, and length of run. In strongly acid solutions the amount of deposit obtained was always small. The solutions showed by their color a reduction to uranous sulphate and all the solutions remained clear. The solutions neutral at the beginning, soon precipitated a voluminous yellow deposit that settled to the bottom of the container thus depleting the solution of the electrolyte. When this occurred the solution showed an acid reaction, but the acid content was not sufficient to hold the deposit in solution while the current was running. Where a porous cup was used as a diaphragm, the cathode compartment contained reduced uranium sulphate and the solution in the anode compartment remained that of the uranyl salt.

Table V contains the summarized data of the electrolytic experiments.

¹ Pogg. Ann., **91**, 619; Jour. prakt. Chem., **62**, 178.

² Jour. Phys. Chem., **9**, 231 (1905).

TABLE V
Summarized Data of the Electrolytic Experiments

Ex- peri- ment	Cathode	Character of electrolyte	Volts	N.D. ₁₀₀ in amp.	Character of deposit	Time of run	Wt. of deposit Gram	Uranium content Percent	Potential	Remarks
1	Platinum	Acid H ₂ SO ₄	7	14.55	No deposit	2 hrs.
2	Platinum	Slightly acid H ₂ SO ₄	7	10.00	Metallic mixed with black oxide	1 hr.	Too small to weigh	A green hydroxide precipitated
3	Platinum	Slightly acid H ₂ SO ₄	7	17.5	Metallic mixed with oxide	1 hr.	0.0195	Diaphragm used, anolyte 1.12 sp. gr. H ₂ SO ₄
4	Platinum	Slightly acid H ₂ SO ₄	4	2.58	Black oxide with green tinge	3 hrs.	0.1098	62.25	..	Greenish yellow pre- cipitate in cathode compartment
5	Platinum	Strongly acid H ₂ SO ₄	3.5	3.50	No deposit	2 hrs.	Yellow oxide precip- itated in cathode compartment
5	Platinum	Reduced acidity with Na ₂ CO ₃	3.5	2.50	Greenish white with black oxide	2 hrs.	0.0356	Reddish brown pre- cipitate in cathode compartment
6	Platinum	10% solution UO ₂ SO ₄ in water neutral or slightly acid by hy- drolysis	5	2.15	Brownish tinged with green poorly ad- herent	3 hrs.	0.1569	68.20	..	Cathode compart- ment contained a precipitate of yel- low oxide
7	Platinum	10% solution UO ₂ SO ₄ neutral	8.75	3.88	Dense black coat covered with yel- low oxide	1 hr.	Small	Solution in cathode compartment re- duced
8	Platinum	10% solution UO ₂ SO ₄ strongly acid	3	11.6	No deposit	2 hrs.	Solution in cathode compartment com- pletely reduced and dissolved
9	Platinum	10% solution slightly acid H ₂ SO ₄	8.5	2.2	Brown-black deposit with tinge of green	20 min.	0.1854	60.50	..	Cathode compart- ment filled with yel- low precipitate
10	Platinum	10% solution slightly acid H ₂ SO ₄	11	12	Brown-black with yellow adhering	20 min.	-0.6295	

TABLE V—(Continued)

11	Platinum	10% solution UO_2SO_4 acid and treated with formaldehyde	5.5	2.48	Greenish crystals with dark metallic deposit beneath	1 hr.	0.0940	64.60	..	Green crystals when dried were gray-yellow mixed with black beneath diaphragm used
12	Platinum Rotating	10% solution UO_2SO_4 acid and treated with formaldehyde	11	10.82	Black with green crystals stuck to electrode	20 min.	0.0200	Solution boiled deposit poorly adherent. Diaphragm used
13	Platinum Rotating	10% solution UO_2SO_4 1 cc. conc. H_2SO_4	7	15.28	Metallic beneath crystals which washed off	25 min.	0.026	Deposit very hard to remove HNO_3
14	Platinum Rotating	10% solution UO_2SO_4 1 cc. conc. H_2SO_4	10	12.50	Metallic beneath green powder that washed off	25 min.	0.0120	Solution kept cool by ice water bath
15	Platinum Rotating	10% solution UO_2SO_4 1 cc. conc. H_2SO_4	10	13.00	Bronze beneath near surface that broke off	1 hr.	0.0620	...	-0.3259	Brown precipitate in bottom of cathode compartment
16	Platinum Rotating	10% solution UO_2SO_4 1 cc. conc. H_2SO_4	20	27.8	Deposit brown on standing	20 min.	0.050	Solution boiled
17	Platinum Rotating	10% solution UO_2SO_4 1 cc. conc. H_2SO_4	18	5.00	Small amount of white, slimy material that washed off	1 hr.	Cathode compartment full of black precipitate
18	Platinum Rotating	10% solution UO_2SO_4 1 cc. conc. % SO_4	18.5	10.6	Yellowish in spots slightly green in others. Poorly adherent	1 hr.	0.1487	42.00	..	Deposit also had sulphate present. Temp. of bath 40°

As shown in the table the electrolysis of a sulphate solution of uranium has been tried under varying conditions. Wherever sufficient deposit has been obtained for analysis, the analysis has been made. Potential readings could not be obtained on all, because when dried the platinum was exposed. Some of the deposits had a decidedly metallic appearance, were difficultly soluble in nitric acid, and in many respects resembled metallic uranium, but the product was so contaminated with oxide and sulphate that no analysis of the metallic looking portion could be obtained. It is impossible to get a deposit of pure metallic uranium under any of the conditions tried, though some metal seems to be deposited at higher current densities. This, however, is always contaminated with the oxide.

12. Electrolysis of Uranyl Acetate Solution

The electrolysis of a neutral solution of uranyl acetate containing 10 grams of metallic uranium per liter was carried on for 1 hour at 20° with a pressure of 34 volts and a current density of 1.95 amp. The cathode was rotated and a porous cup was used as a diaphragm. The cathode was covered with a thin, iridescent film that appeared metallic. The porous cup in the meantime had become partially filled with the yellow oxide of uranium.

The catholyte was made acid with acetic acid and again electrolyzed with 30 volts and a current density of 3.76 amp. for 1 hour at a temp. of 60°. The electrode became covered with a slight deposit of the yellow oxide mixed with a thin film quite metallic in appearance. The catholyte remained acid throughout and no precipitate of the yellow oxide appeared under these conditions.

A larger voltage, 85, and a current density of 18.2 amp. gave a deposit quite metallic in appearance but contaminated with a small portion of the oxide. Only a little deposit adhered to the cathode, in quantity insufficient for analysis. The solution soon became heated to boiling and the larger portion of the uranium precipitated as a mixture of yellow

and black oxides. Attempts to keep the solution cool were not successful when high current densities were employed. The temperature was kept below 60° by surrounding the cathode with a glass coil through which cold water could be circulated, and by keeping the electrolytic bath surrounded with a mixture of salt and ice.

Pure metallic uranium could not be plated from an aqueous solution of uranyl acetate even with high current densities. The electrolysis under these conditions, always produced a mixture of what seemed metallic uranium mixed with the black oxide. No analysis of the deposit could be obtained.

13. Electrolysis of Uranyl Salts in Acetone

A saturated solution of uranyl nitrate in acetone, when electrolyzed with a voltage of 14 and a current density of 0.77 amp. gave a deposit at the cathode of the yellow oxide. The saturated solution of uranyl chloride under the same voltage and current density gave likewise a deposit of the yellow oxide which sloughed off and piled up below the electrode. When made acid with hydrochloric acid the deposit was the same in appearance, but it dissolved as soon as it fell off. Formaldehyde added to the solution lowered the conductivity but caused the deposit to adhere to the cathode. The deposit was smooth and bronze-like in appearance. On analysis the deposit yielded 46.50 percent uranium. The bronze color was due to some organic matter from the formaldehyde and acetone and the solution had a distinctly caramel odor. No pure metallic uranium was deposited.

14. Electrolysis of an Alkaline Solution of Uranyl Sulphate

A uranyl sulphate solution made alkaline with sodium carbonate was electrolyzed with a rotating cathode using a voltage of 6 and a current density of 6.68 amp. at 58° C. The greater portion of the deposit dropped off the cathode but there was left a small amount, very metallic in appearance, which did not dissolve readily in nitric acid. A portion of the deposit showed it to be the black oxide as usual. The deposit was washed with cold dilute nitric acid and the in-

soluble portion dried and weighed. Its weight was very small. It was dissolved in hot nitric acid and the procedure repeated until the accumulated deposits were large enough for an analysis; The error introduced in this way is great but this deposit was found to be richer in uranium than previous deposits analyzed; 72 percent of uranium was found.

15. Electrolysis of Double Potassium Uranyl Tartrate

An acid solution of potassium uranyl tartrate containing 5 percent uranium was made by dissolving potassium uranate in tartaric acid. It gave a poorly conducting solution and deposited a smooth black coat on the cathode. This like other deposits was poorly adherent and the greater portion fell off the electrode. The temperature at the time of electrolysis was 70° and the voltage 19.5 which gave a current density of 5.45 amp. The portion that adhered was dried and analyzed. It contained 73.8 percent uranium.

A tartrate solution made alkaline with potassium carbonate was electrolyzed with a potential of 15 volts and a current density of 19.4 amp. at boiling temperature. Under these conditions a more adherent deposit was formed which on analysis showed 73.5 percent uranium.

Another sample prepared under similar circumstance gave a uranium content of 76.4 percent. In this run the electrolyte was prepared by dissolving sodium uranate in sodium acid tartrate. The solution was slightly acid during the run.

This same solution when made just alkaline with sodium hydroxide and electrolyzed with a potential of 12 volts and current density of 14 amp. at 76° gave a fairly adherent deposit. It was black with the exception of a few grains that were yellow. The deposit contained 81.5 percent uranium.

With a rotating cathode and a temperature of 80° , a voltage of 9.5, and a current density of 7.5 amp. the deposit formed from this same solution was smooth and well adhering while wet. Its color was black with a slight tinge of brown. When dried with alcohol and ether the brown portion scaled off easily. Analysis showed it to contain 70.8 percent of uranium.

The same solution electrolyzed with a potential of 35 volts and a current density of 35 amp. at a boiling temperature gave a strongly adherent black deposit. This deposit contained 75.8 percent uranium.

The uranium content of deposits obtained from alkaline tartrate solutions approaches and some times exceeds the amount found in the later work with acetate solutions. The products are doubtless the same in general but vary in their uranium content, in the oxygen present and in the amount of hydration. Pure uranium was not obtained.

16. Electrolysis of Double Sodium Uranyl Citrate

A solution containing 5 percent uranium was prepared by dissolving sodium uranate in citric acid in the molecular quantity for producing the double salt. It was electrolyzed at 80° with a potential of 40 volts and a current density of 12.4 amp. The solution was slightly acid at the beginning but soon became basic. A dense, poorly adhering, black deposit formed at the cathode but dropped off rapidly. At the same time there was a precipitate of uranic oxide formed. No deposit was obtained uniform enough in appearance to justify analysis. The black deposit was always contaminated with the yellow oxide.

During the electrolysis the anode became bronze in color. On examination this proved to be carbon contaminated with some uranium salts.

According to Smith¹ a deposit does not form when a double alkali tartrate or citrate is electrolyzed, but this is contrary to my experience.

17. Electrolysis of Uranium Tetrachloride Dissolved in Pyridine

Since the oxides of uranium are deposited from aqueous solutions of either uranyl or uranous salts it would seem possible to obtain metallic uranium from a solution which contains no oxygen. A solution of uranium tetrachloride in anhydrous

¹ Smith: *Am. Chem. Jour.*, **1**, 336 (1879).

pyridine might give the conditions necessary for such an experiment.

Preparation of Materials

Uranium tetrachloride was prepared by passing dry chlorine over an intimate mixture of the green oxide of uranium and carbon heated in a combustion tube to about 600° . The uranium oxide was prepared from Merck's pure uranyl nitrate by ignition. The oxide was mixed with starch paste, and then the starch was carbonized in closed porcelain crucibles. There are formed in the reaction between chlorine, uranium oxide and carbon at least two products and possibly three. The first product comes off at a low temperature and crystallizes in colorless needles on the cooler portion of the combustion tube. At a slightly higher temperature a yellowish green product sublimes. This has all the appearance of anhydrous uranyl chloride. The tetrachloride melts around 400° but does not sublime until heated to 600° and above. It can be slowly driven along the combustion tube and eventually sealed up in small portions of the tube. It is brown when melted and produces brown vapors when sublimed. On cooling the melted product, it crystallizes somewhat, leaving an apple-green mass. In contact with air it fumes and gives off hydrochloric acid and is converted into the more stable salt UO_2Cl_2 . Because of this behavior it had to be kept sealed until used, and then handled rapidly when required.

Anhydrous pyridine was prepared by distilling pyridine that had been standing for two years over potassium hydroxide and barium hydroxide. It was distilled under atmospheric pressure of 726 mm. and only the fraction that came over between 112.7° and 115° was used.

The anhydrous pyridine was placed in a closed cell, and pure, dry hydrogen bubbled through the solution to replace all air from the pyridine and cell. The cell and the sealed tube of uranium tetrachloride were opened quickly, and the uranium salt was dropped into the pyridine. The reaction was not extremely violent but was accompanied with evolution

of heat, considerable hissing, and the formation of dense, white fumes. At the same time the pyridine darkened as though charred and a greenish black, flocculent precipitate was formed.

The closed cell was immediately connected with the battery and the contents electrolyzed, while being stirred with a slow current of pure dry hydrogen. The conductivity was poor, 40 volts across the electrodes were necessary to give a current density of 0.14 amp. Within twenty minutes the potential had to be increased to 64 volts in order to maintain the current density and by the end of two hours the conductivity was practically nil.

The deposit was white, tinged with brown, and did not wash off with gasoline. It was placed over calcium chloride in an atmosphere of hydrogen until dry. Its potential against uranyl nitrate solution was -0.695 volt.

The weight of deposit obtained in consecutive runs was small and analysis of two samples for the uranium content showed 10.65 percent and 10.76 percent of uranium. Another deposit was dried to constant weight and then heated to 120° in a dry test tube by immersing the tube in a bath of paraffin. Pyridine distilled from the solid and condensed in drops on the colder portions of the tube. The deposit formed was a compound containing uranium and pyridine.

No metallic uranium could be obtained in this way.

18. Electrolysis of a Solution of Uranyl Tetrachloride in Acetone

Renz¹ made use of acetone as a solvent for uranium tetrachloride in preparing derivatives of pyridine and quinoline. This reagent was tried as a solvent from which to plate metallic uranium.

The anhydrous acetone was prepared by allowing the commercial product of Mallinckrodt to stand over fused calcium chloride for several days with frequent shaking. The product was distilled and only the portion which came over at 56° used in the experiments.

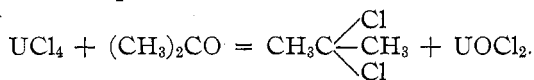
¹ Zeit. anorg. Chem., 36, 110.

The solution was prepared by adding anhydrous UCl_4 directly to the anhydrous acetone in the electrolyzing cell. There was considerable hissing and fuming, and the acetone became blackened. The air was removed from the electrolyzing cell with hydrogen as in the electrolysis of the pyridine solution.

The conductivity of the solution was good, but very little deposit of uranium could be obtained. Electrolysis of the solution for periods varying from one and one-half hours to six hours and longer gave only small amounts of deposit. Hydrogen is evolved copiously during the electrolysis and the solution boils. In all the experiments the solvent was returned to the electrolytic cell with a reflux condenser.

The deposits formed were very dark and gave potentials consecutively around the value -0.64 volt. This value for the potential is of the same order of magnitude as that commonly obtained when uranyl salts are electrolyzed in aqueous solution. No deposit could be obtained of sufficient weight to justify an analysis for the uranium content.

The solvent was subjected to fractional distillation. The first fraction collected between the temperatures 56° and 60° was pure acetone. The second fraction was principally acetone but contained a little methyl alcohol. This fraction was collected between $60-65^\circ$. The third fraction which came over between 65° and 74° had a different odor. Fraction 1 contained no chlorine, fraction 2 a slight amount, and fraction 3 contained a large amount of chlorine. This latter fraction comes over at the boiling point of 2, 2-dichloropropane, and while there might have been present some chloroform, rests showed it to be absent. It seems quite probable that the uranium tetrachloride here plays the same role as phosphorous pentachloride, replacing the oxygen from acetone with chlorine and forming uranium oxychloride according to the equation



It is quite evident from the abundance of hydrogen obtained that this reaction does not explain all that is taking place. The production of hydrochloric acid would be possible only by the formation of substitution products. The boiling points of mono and dichlor acetone eliminate these as products and chloroform was not found. The only other possibility is the breaking up of the acetone and reduction to carbon by the chlorine present. This would seem to be the case from the deep black color of the solution.

No pure uranium could be plated from this solution, and all deposits obtained seemed to be nothing more than the oxide usually obtained with perhaps a small bit of uranium. The deposit formed replaced mercury from mercurous sulphate.

19. Electrolysis of Fused Nitrate Baths

Attempts to plate uranium from a fusion of potassium nitrate and uranyl nitrate were not successful. The uranyl nitrate was decomposed with evolution of oxides of nitrogen and formation of potassium uranate. As long as there was present any potassium nitrate the fused mass would conduct but as soon as the potassium uranate was formed the melt froze and conduction ceased. Examination of the mass around the cathode showed no uranium. There was plenty of the green oxide formed.

The same behavior was observed with a silver nitrate, uranyl nitrate fusion. There was some conductivity at first but the melt soon decomposed, leaving the oxides behind. These fused to form some silver uranate. No metal could be detected at the cathode.

20. Electrolysis of Uranyl Acetate with a Mercury Cathode

A 5 percent solution of neutral uranyl acetate was electrolyzed with a potential of 30 volts and a current density of 4.55 amp., using a mercury cathode to see if the metal could be amalgamated with the mercury. The deposit that first comes out of the solution is the yellow oxide. This settles on the mercury, but, of course, does not enter into it. On continued running of the current the yellow oxide changes to a

darker greenish black and eventually quite black, in all respects similar to the black deposit formed on platinum from aqueous solutions. Portions of the mercury removed and evaporated left no uranium. The uranium is not deposited from aqueous uranyl solutions as metallic uranium but as the oxide.

21. Electrolysis of Fused Double Potassium Uranyl Fluoride

The electrolysis of a fused mixture of uranium tetrafluoride and potassium fluoride was not successful. The uranium fluoride first melted and at the beginning conducted the current, but the mass soon froze and could not be melted again. There was a loss of fluorine accompanied with the formation of potassium uranate with high melting point. No deposit could be found on the cathode that resembled metal.

22. The Character of the Oxide Formed when an Aqueous Solution of Uranyl Acetate is Electrolyzed

In the early work on the quantitative determination of uranium electrolytically Smith¹ determined the composition of the dark deposit to be $U_3O_4 \cdot H_2O$. His results are calculated by using the atomic weight of uranium as 120. If his analysis are calculated using the present atomic weight (238.5) the composition of the deposit becomes $U_3O_8 \cdot 2H_2O$.

Several grams of the black residue were prepared according to Smith's directions and subjected to careful analysis and the results obtained would indicate that the product is not the hydrated green oxide as given. The difference is easily explained on the basis of the analysis made.

The residue left after the determination of the water content was taken to be the green oxide of uranium and calculated accordingly. All analyses made have shown that when the water is driven off by passing a current of air or oxygen over the residue heated in a combustion tube, the residue left is richer in oxygen than the compound U_3O_8 .

Results of analyses are given in the following table. In

¹ Amer. Chem. Jour., 1, 329 (1879).

samples 1 and 2 the uranium content was found by dissolving the material in nitric acid and precipitating the uranium with ammonium hydroxide.

TABLE VI

Sample	Weight Grams	Weight of water Gram	Weight of residue	Weight U_3O_8	% H_2O	% U
1	0.2998	—	—	0.2783	—	78.74
2	0.3021	—	—	0.2800	—	78.62
3	1.0318	0.0385	0.9650	0.9578	3.73	78.73
4	1.0258	0.0403	—	—	3.92	—
5	0.5905	0.0209	0.5511	0.5490	3.54	78.86

The empirical formula as calculated from the results obtained becomes $U_3O_{10.2}H_2O$. Smith explained the discrepancy between the weight of his residue and the weight of water found as due to loss of oxygen, but it is highly probable that the product which he weighed as U_3O_8 was still richer in oxygen than U_3O_8 should be.

23. A New Method for Measuring the Single Potential of Metals and Oxides in Powder Form

The single potentials of metals against their salt solutions are usually measured by using either cast pieces of metal, where this is possible, or an electrode prepared by plating the metal in question on another metal. In case the metal cannot be plated or cast, the determination of the single potential is difficult.

The measurement can be made on metals and oxides in powder form by pasting the finely powdered metal on platinum or any other good conducting metal, with gelatin. In the experiments tabulated below the electrodes were prepared by first moistening a platinum electrode with a solution of gelatin and then spreading the finely divided metals or oxides over the platinum and pressing them firmly with a spatula. Each measurement was compared with results obtained by other investigators using electrolytes of the same strength as have been used in this investigation. The results are given in Table VII.

TABLE VII
Results of Potential Measurements of Some Metals and Oxides

Chain	Observer	Form	Value given	Value found by pasting with gelatin
Zn/ZnCl ₂ N/1//KCl.Hg ₂ Cl ₂ N/1/Hg	Neumann	Cast	0.5030 volt	0.5026 volt
Cu/CuSO ₄ N/1//KCl.N/1Hg ₂ Cl ₂ /Hg	Neumann	Plated	-0.515 volt	-0.516 volt
Ag/AgNO ₃ N/10KNO ₃ N/1//KCl.N/1Hg ₂ Cl ₂ /Hg	Kahlenberg	Plated	-1.018 volt	-1.0024 volt
MnO ₂ /Mn(NO ₃) ₂ N/5.HNO ₃ N/20//KCl.Hg ₂ Cl ₂ /Hg	Egli	Plated	-0.993 volt	-1.1156 volt (fresh pasted)
	Tower	Plated	-1.5042 volt	-1.3621 volt (left in air)
				-1.5159 volt (plated)
				-1.7145 volt (fresh pasted)
				-1.7794 volt (after 2 hrs.)
				-1.7475 volt (fresh pasted)
PbO ₂ /H ₂ SO ₄ 2N//KCl.N/1Hg ₂ Cl ₂ /Hg	Dolezalck	Plated	-1.893 volt	-1.8203 volt (after 2 days)

NOTE.—Values taken from Landolt-Börnstein.

The zinc used was Bakers "C. P." zinc dust. The copper was precipitated electrolytically from a copper sulphate solution by metallic zinc and the excess zinc removed by digesting with dilute sulphuric acid. The silver was prepared by reduction of the pure oxide in hydrogen. The gelatin was the commercial product labelled "Gold edge." The solution was prepared by dissolving 0.5 gram in 25 cc of water and applied while still liquid.

The measurements made with metals show that the method is reliable.

The manganese dioxide was Merck's "C. P." product and the lead peroxide Mallinckrodt's preparation, labelled "C. P." The potentials obtained by plating manganese dioxide give higher values than the pasted material. This is no doubt due to a different state of hydration. An electrode, when prepared by plating, always gave lower readings after it had dried in the air. The moist, pasted electrode gave higher readings when left exposed to the air. This was also true of the lead peroxide when pasted, but the potentials found are of the same order of magnitude and possess the same polarity. The potential measurements for manganese dioxide as made by Tower¹ were obtained immediately upon removal from the plating bath.

24. The Single Potential of Uranium and Its Oxides

With the exception of the green oxide of uranium, the oxides are difficult to prepare in absolutely pure form. The hydrated oxide $\text{UO}_3\text{H}_2\text{O}$ is first deposited when an aqueous solution of any uranyl salt is electrolyzed but the product obtained is usually contaminated with a black oxide especially when the uranium is almost depleted. Uranous oxide UO_2 can be obtained in a fair state of purity by reducing ammonium uranate in a current of pure, dry hydrogen. This, however, is pyrophoric and absorbs oxygen from the air, becoming U_3O_8 . This is especially true when prepared from the uranyl salts of organic acids such as the oxalate and acetate.

¹ Zeit. phys. Chem., **32**, 566 (1900).

Anhydrous UO_3 has been prepared by heating uranyl nitrate to 250° for several hours.¹ However, the purity of the product is questionable unless the work is done in an atmosphere of oxygen since the green oxide U_3O_8 tends to form.

Other oxides have been described in the literature, but their existence as definite compounds is more or less questionable.

The green oxide U_3O_8 , being the high temperature oxide, is most easily prepared by igniting ammonium uranate in the air to constant weight. The pure oxide was prepared in this way and used for the potential measurements herein recorded. The finely ground powder was pasted on a platinum electrode with gelatin and the single potential was then measured against a solution of uranyl nitrate which contained 14.3 grams of anhydrous uranyl nitrate per liter. The half element was the usual form of a normal mercury calomel electrode. The results are given in volts and are fairly constant for the different electrodes prepared from different samples of the oxide.

TABLE VIII

Sample	Observed potential
1	—0.778 volt
2	—0.787 volt
3	—0.779 volt
4	—0.785 volt

A sample of pure uranium oxide U_3O_8 obtained from Dr. S. C. Lind of the Bureau of Mines, Boulder, Colorado, when pasted on platinum with gelatin, gave a single potential of —0.773 volt.

A sample of uranous oxide UO_2 prepared by heating ammonium uranate in a current of hydrogen was used for measuring the potential. It gave an analysis 87.65 percent uranium. By calculation pure UO_2 contains 88.17 percent uranium.

¹ Jacquelin: Chem. Pharm. Centralblatt, 1845, 193.

The potential of this material gave a value for three different electrodes prepared with gelatin.

—0.778 volt
—0.773 volt
—0.776 volt

With UO_2 the value is the same as that found for U_3O_8 . It is possible that there is a superficial oxidizing effect which causes the result to be the same.

The hydrated yellow oxide was prepared by electrolysis of a neutral solution of uranyl acetate. It was deposited in small quantities with a voltage of 6 and a current density of 0.108 amp. at room temperature. The first deposit formed is entirely yellow, but if allowed to remain until considerable free acetic acid is present, the yellow compound is contaminated with the lower black oxide. As soon as the cathode showed a slight blackening, the electrolysis was interrupted and the solution filtered from the yellow deposit. By proceeding in this way with other portions of fresh uranyl acetate, enough yellow hydrated oxide of a high grade of purity was obtained for analysis and for potential measurements. Ammonium hydroxide or fixed alkali hydroxide added during electrolysis of an acetate solution reduces the acidity and prevents the formation of the black deposit but the product obtained in this way is the alkali uranate and not the yellow oxide.

Analysis of the product showed:

U 76.53 percent, water 7.36 percent, oxygen by difference 16.11 percent. The formula of the product thus becomes $\text{UO}_3\text{H}_2\text{O}$.

The single potential of the product measured against the standard solution of uranyl nitrate gave a constant value of —0.860 volt. The value given was obtained on four different electrodes prepared by pasting the oxide on platinum with gelatin.

The black deposit formed when an aqueous solution of a uranyl salt is electrolyzed when pasted on platinum with gelatin gives a single potential of —0.6872 volt. This is conclusive evidence that the deposit is not U_3O_8 as formerly sup-

posed, and both the potential and the analysis support this conclusion.

A sample of metallic uranium prepared by Schuchardt was analyzed and found to contain uranium 91.49 percent, ferric oxide 8.34 percent.

It was used for making a single potential measurement by pasting the finely powdered material upon platinum with gelatin. The maximum potential obtained in this way was -0.093 volt for the sample. The potential decreases rapidly in contact with the uranyl nitrate solution which indicates a rapid oxidation of the metal.

25. The Single Potential of the Black Oxide Plated on Platinum

By using an electrode covered with platinum black a smooth, adherent deposit of the black oxide can be obtained. Single potentials of this measured against the standard uranyl nitrate solution gave variable results depending upon the treatment given the deposit. The first deposit obtained with a pressure of 13.5 volts and a current density of 3.11 amp. gave the same potential formerly obtained from aqueous uranyl salt solutions, namely, -0.497 volt. With this sample, the small amount of the yellow oxide present was washed off with dilute acetic acid.

The electrode was used for obtaining a heavier deposit, and under similar treatment gave for the second reading a maximum of -0.361 volt. The value diminished rapidly.

Electrolyzed again for one hour with all factors identical the maximum potential reading was -0.302 volt.

When the electrolysis was allowed to continue until the uranium was depleted, the value for the potential was much greater. If the potential is measured immediately upon removal from the electrolytic bath higher values will be found. Voltages as high as -0.4999 volt have actually been measured. This product when allowed to stand in contact with the standard uranyl nitrate solution or in the air gives decreasing values. The voltages fall off gradually and change polarity due to

slow oxidation of the deposit. When washed with dilute acetic acid before taking the potential, the initial value was repeatedly found to be about \pm O potential, but here the value was dependent upon the time which elapsed between the removal from the electrolytic bath and the measurement of the potential.

These variable results are no doubt due to occluded hydrogen in the deposit. However, experiments showed that this deposit does not serve as a hydrogen electrode in the same manner as platinum black does. No constant value for hydrogen was obtained, and the potential readings decreased in the usual manner when the deposit was used as a hydrogen electrode. No constant values could be obtained upon which to base a conclusion.

26. Reaction of Uranium Tetrachloride with Paraffin

An attempt to prepare metallic uranium by allowing uranium tetrachloride to react with metallic sodium under molten paraffin was not successful. Instead of reacting with the sodium the uranium tetrachloride reacts with the paraffin, evolving hydrochloric acid. The exact nature of the reaction is as yet unknown. When the excess paraffin is removed by petroleum ether and washed free from all chlorides present there is left a brownish black material insoluble in ice water. The product gives a potential exactly the same value as U_3O_8 . In this respect it behaves like UO_2 produced by reduction in hydrogen. From its polarity and potential, it is probably an oxide of uranium rather than metallic uranium.

The analysis of the substance dried to constant weight over sulphuric acid gave 52.67 percent metallic uranium and 46.54 percent carbon. A portion of the carbon was probably oxidized by the nitric acid used to separate the uranium from the mixture. Further examination of the reaction of uranium tetrachloride with organic material will be made.

III. SUMMARY OF RESULTS

The conclusions drawn from the experimental results, briefly stated, are:

1. In aqueous solutions with low current density uranyl salts deposit first the hydrated uranic oxide $\text{UO}_3 \cdot \text{H}_2\text{O}$, which is later changed by the action of current to a black oxide of varying composition.

2. With higher current density uranyl sulphate is reduced to uranous sulphate, but in the presence of free acid the deposit obtained is small in amount and poorly adherent though metallic in appearance. In neutral or alkaline solution, the deposit formed is a mixture of the black and yellow oxides.

3. The use of a porous cup as a diaphragm does but little good. The deposit is the same in character as when no diaphragm is used.

4. The deposit obtained when alkaline uranyl tartrate and citrate solutions are electrolyzed is an oxide much richer in uranium than that deposited from solutions acidified with tartaric or citric acid.

5. The conductivity of non-aqueous solutions of uranyl salts is a function of the water present, and the deposits formed are oxides contaminated with organic matter.

6. Anhydrous pyridine treated with anhydrous uranium tetrachloride forms solutions conducting electricity. From these deposits a compound containing uranium and pyridine may be obtained on the cathode.

7. Anhydrous acetone, when used as a solvent for uranium tetrachloride, gives a solution which conducts well but deposits no pure metallic uranium. The deposit replaces mercury from mercurous sulphate. The uranium tetrachloride reacts with acetone forming 2,2-dichloropropane and also further decomposes acetone. Hydrogen is evolved during electrolysis of the solution.

8. Solutions of potassium uranyl fluoride, whether neutral, acid or alkaline, form a deposit containing fluorine. In acid solution the deposit is $\text{UF}_4 \cdot 6\text{H}_2\text{O}$. Neutral and alkaline solutions give a mixture of UF_4 and uranium oxide.

9. Deposits from double potassium uranyl cyanide solutions, when neutral, consist of potassium uranate. When

acid with hydrocyanic acid, the deposit is the yellow hydrated oxide contaminated with some of the black oxide.

10. The single potential of metals and oxides in powder form can be measured accurately by pasting the finely powdered material on a platinum electrode with gelatin.

11. The single potentials of the more stable oxides of uranium have been measured.

12. Uranous oxide UO_2 gives a single potential identical with that obtained for the green oxide U_3O_8 .

13. The black deposit formed when uranium salts are electrolyzed is not $\text{U}_3\text{O}_8 \cdot 2\text{H}_2\text{O}$ as claimed by Smith but it is a product having the composition $\text{U}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$. Further, it does not give the same potential as U_3O_8 .

14. The position of uranium in the electrochemical series has not been definitely fixed because of inability to make pure uranium, but the potential of a sample of uranium containing 91.49 percent uranium and 8.34 percent ferric oxide has been measured.

This work was undertaken at the suggestion of Professor Kahlenberg and carried out under his direction.

*University of Wisconsin
Madison, June 20, 1919*