ELECTROMETRIC TITRATION OF URANIUM WITH CERIC SULFATE

THESIS FOR THE DEGREE OF M. S.

Mabel Florey Wilson
1930

Volumetric analysis
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Chemistry

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WITH
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THESIS

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In a previous publication (This Journal, 44, 1484 (1922))it was shown by Ewing and Eldridge that the electrometric titration curves for uranium and potassium permanganate, and potassium dichromate had two inflection points. The first denoted the complete oxidation of trivalent uranium to the tetravalent form and the second point, the complete oxidation of the tetravalent form. Gustavson and Knudson (Gustavson and Knudson, This Journal, 44, 2756 (1922))and Müller and Flath (Müller and Flath, Z. Elektrochem., 29 (1923)) titrated uranium electrometrically, but did not note the first inflection point. In commenting on this point of difference it was correctly pointed out by Kolthoff and Furnam (I.M. Kolthoff and N. H. Furnam "Potentiometric Titrations", 1926, P 243-4) that the presence of carbon dioxide and the correct acidity must be obtained in order to form and titrate trivalent uranium. In the previous investigation a special titration cell was used which was designed to eliminate oxygen and the titration was only successful when made in an atmosphere of carbon dioxide or nitrogen.

PREPARATION OF SOLUTIONS

The ceric sulfate solution was prepared by the same method as that used by Willard and Young (H. H. Willard and Philena Young, This Journal, 50, 1322 (1928)). Approximately 300 g. of U.S.P. cerium oxalate were ignited in a platinum crucible, in the open air until all gas was given off, and then for 10 hours in an oven at 600-625°C. This yielded about 150 g. of reddish brown ceric oxide, which was heated approximately 3 hours at 125°-130°C, with 210 ml. of sulfuric acid (1.84 sp. gr.) until a yellow paste was formed. It was then dissolved in about 3.5 liters of distilled water, by heating at 75-80°C and stirring constantly for an hour. This was filtered hot through the undissolved substance.

The ceric sulfate solution was standardized against 0.05 N sodium oxalate solution made from a Bureau of Standards product in a carefully calibrated flask, at 25.0°C. This ceric sulfate solution was found to be 0.05326 N.

The uranium solution was prepared by dissolving 28.283 g. of uranyl acetate in a little distilled water containing 9.8 g. sulfuric acid and carefully diluting to 2 liters.

The uranium solution was standardized by evaporating two 20 ml. portions of stock solution to dryness and igniting to the oxide. From this data the normality of the uranium solution was found to be 0.07113.

An approximately 0.1 N solution of ferrous ammonium sulfate solution was prepared with an excess of free sulfuric acid. It was standardized against the ceric sulfate solution and was found to be 0.1041 N.

APPARATUS

The e.m.f. of the titration cell was determined with a potentiometer which read to one-half of a millivolt.

The titration vessel consisted of a 400 ml beaker with a large cork stopper with six holes for the following pieces:- a burette, a zinc reductor, a mechanical stirrer, an inlet for an inert gas and two electrodes. The standard electrode was a tenth normal calomel half cell and a small bright platinum wire was used for the other electrode.

EXPERIMENTAL PROCEDURE

1.06 ml of concentrated sulfuric acid was added to 30 ml of the uranium solution and evaporated to dryness. This was diluted to 50 ml., heated nearly to boiling and forced through a 50 cm zinc reductor with nitrogen or carbon dioxide. The zinc reductor was washed with 2% sulfuric acid until the total volume of solution in the titrating vessel was 100 ml. This solution while warm was titrated with the standard cerium sulfate reagent. During this procedure nitrogen or carbon dioxide was run through continuously.

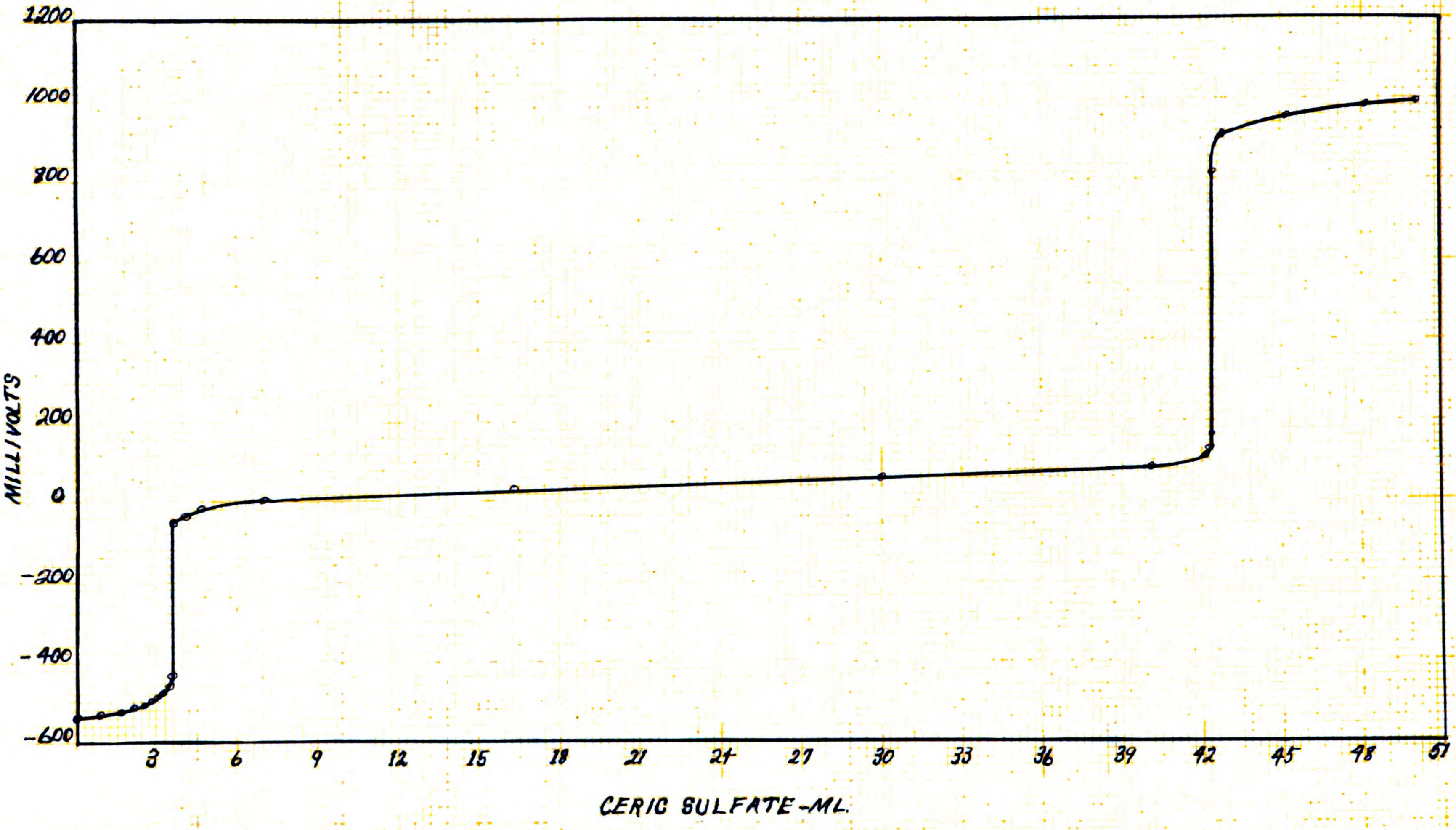
The first end point was approached rather slowly and usually required about 3 ml of the cerium solution. After each addition it was necessary to wait a few moments for an equilibrium reading. After the first end point was established the cerium solution could be added quite rapidly until near the second end point. The behavior of the reaction as the second end point is approached is quite similar to that of any other cerium electrometric titration where equilibrium conditions must be carefully noted.

The volume of ceric sulfate represented by the difference between the two end points was carefully computed, corrected for calibration errors, etc., and from this value the concentration of the uranium solution was found.

Graph 1 (Fig. 1) is typical of the results of many titrations which were made.

In Table 1 are given the results of seven consecutive titrations.

I


MILLIVOLTS
1200
1000
800
600
400
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0
-200
-400
-600
3
6
9
12
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21
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30
33
36
39
42
45
48
51
CERIC SULFATE-ML.

TABLE I

The total volume of the solution titrated was 100 ml and it contained 2 percent sulfuric acid.

Titration Number	Uranium Solution	Ceric Sulfate		ml Ceric Sulfate Solution
		by exp't	calculated	ml uranium
1	29.95 ml	39.88 ml	39.86 ml	1.336
2	29.85 "	39.83 "	39.86 "	1.334
3	29.85 "	39.98 "	39.86 "	1.339
4	29.85 "	39.84 "	39.86 "	1.335
5	29.85 "	39.64 "	39.86 "	(1.327)
6	29.85 "	39.93 "	39.86 "	1.338
7	29.85 "	39.86 "	39.86 "	1.336
Mean		39.87 "		1.336

In experiment number 5 trouble was encountered with the mechanical stirrer.

DISCUSSION OF THE RESULTS.

The stock solution of uranium used in this investigation was prepared from the acetate. Irregular results were obtained in the first titations. The second end point was uncertain and the results were low. This difficulty was not overcome until the acetate was removed. This was accomplished by evaporating the solution with sulfuric acid until the acetate had disapeared. The concentrated solution was diluted with water just previous to reduction.

The color of the freshly reduced acid uranium solution was a dark olive green, and was slightly opaque. Upon addition of ceric sulfate solution it gradually cleared and became a very light green color at the first end point. As oxidation proceeded the color became less intense and gradually changed to a greenish-yellow at the second end point.

Due care must be taken in this titration to make certain that the e.m.f. represents an equilibrium condition. Furnam (N. F. Furman, This Journal, 50, 755, (1928)). in titrating ferrous sulfate allowed one to four minutes after each addition before making the e.m.f. measurements. In titrating uranium with cerium even more time was required for the e.m.f. reading especially at the first end point.

The initial e.m.f. of the reduced solution was usually -500 to -450 mv. This changed gradually about 100 mv.to the first end point when an abrupt change of approximately 400 mv. was noted. A small fraction of a drop of ceric sulfate solution is sufficient to cause this abrupt change. The second end point was also very definite and usually the addition of a small fraction of a drop of the ceric sulfate solution was sufficient to cause the e.m.f. to increase 500 or 600 mv.

Higher concentrations of sulfuric acid, 6%, 15% and 30% by volume, were later titrated. The amount of uranium solution, the total volume and conditions of titration remained the same. In all cases both end points were definite, and the amount of ceric sulphate used between end points was theoretical. Formerly reported titrations (D.T. Ewing and E.H. Eldridge, ibid) stated that high acid concentrations caused the voltage to rise rapidly and the second end point consequently disappeared. In all cases of the higher acid concentrations just mentioned, the shape of the curves remained the same, and all three corresponded closely to the curves obtained from the 2% titration data. The only noticeable effect was the time required for equilibrium to be established at the end points, As the percent acid was increased, a larger time was required for equilibrium. This was particularly noticeable at the second end point, which was fairly rapid in the 2% solution. In this respect the work of Gustavson and Knudson (R.G. Gustavson and C.M. Knudson, ibid) has been confirmed.

TITRATION OF URANIUM WITH CERIUM SULFATE IN HYDROCHLORIC ACID SOLUTION.

Hydrochloric acid may also be used in the titration of uranium with cerium sulfate. Titrations were made using 2M., 4M., 6M., and a combination of 2M. for first end point, with an increase to 4M. immediately after reaching the first end point.

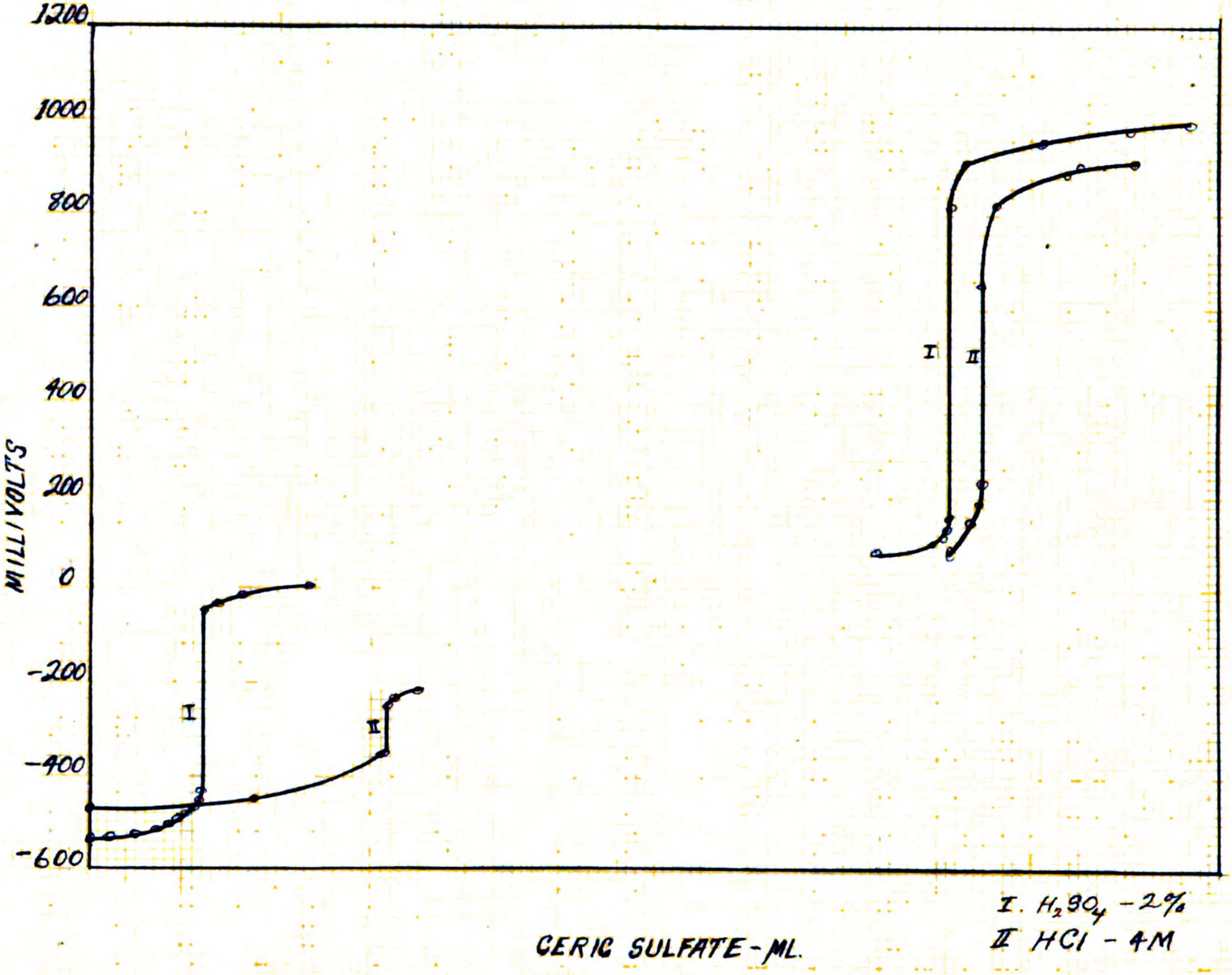
In each case, thirty ml. of the uranium solution was heated to boiling with half the acid, and put through the reductor. This was washed with the remainder of the acid in solution, making a total volume of 100 ml. for titrating. In each case, more reduction to trivalent uranium was noted than in the case of the sulphuric acid titrations. The color of the reduced solution was a very dark red brown and was opaque. Upon the addition of ceric sulfate, the color rapidly changed to the same olive green, noted in the case of sulphuric acid. Colors at the end points were identical.

In no case was the titration with hydrochloric acid as satisfactory as 2% sulfuric. The great difference in effect of these two acids on the titrations, was upon the change of voltage at the end points, and the time required for equilibrium to be established.

Graph number 2 gives a comparison between the deflections in voltage at the two end points in 2% sulfuric acid and 4M. hydrochloric acid titrations.

It will be noticed that the scope of the first end point is 100 mv. with hydrochloric acid and compared with approximately 400 in the case of sulfuric acid; 450^{mv} for hydrochloric compared with

II


MILLIVOLTS
1200
1000
800
600
400
200
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-200
-400
-600
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I
II
CERIC SULFATE-ML.
I. H_2SO_4 -2%
II HCl - 4M

675 for sulfuric at the second end point.

In all cases where hydrochloric acid was used, the first end point was too slow to be practical. In the 2M., the first end point covered about 400 mv., in the 4M., 100 - 200 mv., and in 6M., 50 - 75 mv. With higher acid concentrations, the time required for equilibrium was greater. This was also true of the sulfuric acid solutions, although it did not seem to affect the voltage greatly in case of the sulfuric acid solutions. In exact contrast to the first end point, the stronger the hydrochloric acid, the sharper and quicker the second end point. This is also in exact contrast to the second end point when sulfuric acid was used. In 2M. hydrochloric acid, the equilibrium was very slow, and the change in voltage was approximately 300 - 400 mv; in 4M. it was 400 - 500 mv. and more rapid; in 6M. which compared with 2% sulfuric acid, the change was 600 mv. and more rapid.

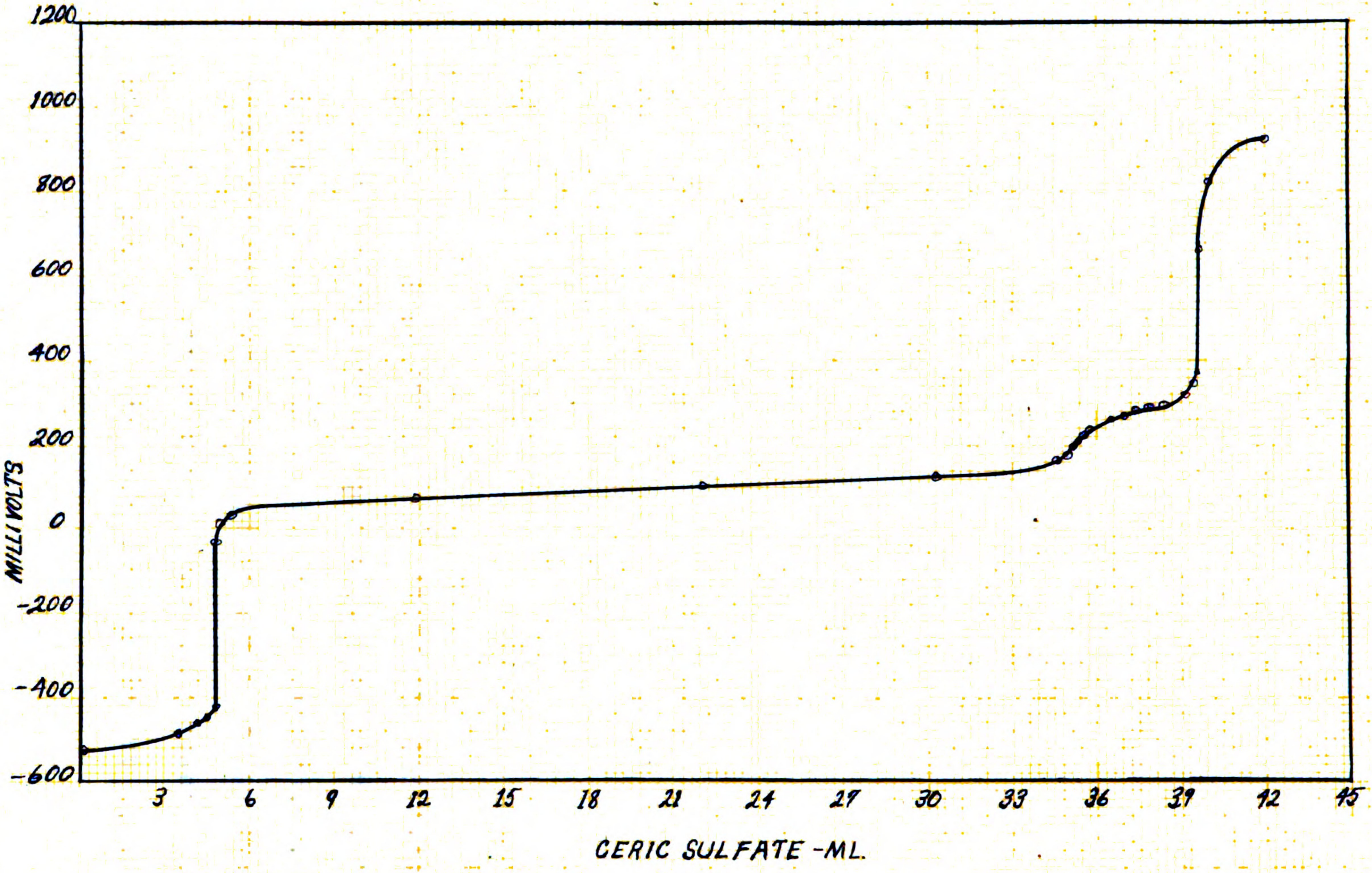
By trying varying combinations of ~~mola~~normalities of hydrochloric acid on the two end points, it was found that a concentration of 2M. hydrochloric acid increased to 4M. after the first end point, gave the best conditions for titration and the most constant results.

A few titrations were made with a combination of the uranium with ferrous ammonium sulphate. Thirty ml. of the uranium solution were prepared and reduced as in the 2% sulfuric acid titrations. Before washing the reductor, 5 ml. of the iron solution were added. The titration was performed in 100 ml. volume, 2% sulfuric acid.

Three end points were obtained: one when trivalent uranium was oxidized to tetravelent, another when tetravelent was oxidized to hexavalent, and a third when the ferrous iron was oxidized to ferric iron. Because of the closely corresponding voltage of the second and third oxidations, it is necessary to plot also, $\frac{de^{(mv)}}{dv^{(ml)}}$, the change in millivolts per change in ml. This gave three definite end points. The amount between the first and second corresponded closely to the theoretical amount of ceric sulphate.necessary to oxidize the uranium present; and the amount between the second and third, very nearly to amount required to oxidize the ferrous iron present. Graph number 3 shows this titration.

Nitrogen was used to exclude the air from

III


MILLIVOLTS
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CERIC SULFATE -ML.

the cell during the titrations. This is essential in successfully titrating the small amount of trivalent uranium present in the reduced solution, due to the rapid oxidation of trivalent uranium in air, as shown by McCoy and Bunzel (Wm. McCoy and H. H. Bunzel, This Journal, 31, 367 (1909)).

SUMMARY

1. When a hot acid solution of uranium sulfate is reduced in a Jones reductor and is titrated in an atmosphere of nitrogen with ceric sulfate as an oxidizing agent, two end points are obtained. The amount of uranium oxidized between the two end points corresponds exactly to the amount of uranium present. 2% sulfuric acid by volume in a total volume of 100 ml. was found to be the best conditions for titration.
2. Uranium acetate in hydrochloric acid solution, when treated in the same way, also gives two end points, difference between which is the amount of uranium present. A concentration of 2M. for the first and 4M.for the second gave the best results.
3. Sharper end points were obtained by the titrations in sulfuric acid, and less time was required for the e.m.f. to come to equilibrium, than in hydrochloric acid.

More consistent results were also obtained with 2% sulfuric acid.

4. When 5 ml. of ferrous ammonium sulfate were added to the reduced 2% uranium solution, three end points were obtained; (1) When trivalent uranium was oxidized to tetravalent, (2) when tetravalent was oxidized to hexavalent, and (3) when ferrous iron was oxidized to ferric.

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