

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY OF THE MICHIGAN STATE COLLEGE]

THE ELECTROMETRIC TITRATION OF URANIUM WITH CERIC SULFATE

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In a previous publication¹ it was shown 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 Knudson² and Müller and Flath³ 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 Furman⁴ that the presence of carbon dioxide and the correct acidity must be obtained in order to form and titrate trivalent uranium. In our previous investigation we used a special titration cell 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 method that was used by Willard and Young.⁵

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°. 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. of sulfuric acid and carefully diluting to 2 liters.

The uranium solution was standardized by evaporating two 2-ml. portions of stock solution to dryness and then igniting to the oxide. From these 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-cc. beaker with a large cork stopper with six holes for the following pieces: a buret, a zinc reductor, a mechanical stirrer, an inlet for an inert gas and two electrodes. The standard

¹ Ewing and Eldridge, *THIS JOURNAL*, **44**, 1484 (1922).

² Gustavson and Knudson, *ibid.*, **44**, 2756 (1922).

³ Müller and Flath, *Z. Elektrochem.*, **29**, 500 (1923).

⁴ I. M. Kolthoff and N. H. Furman, "Potentiometric Titrations," John Wiley and Sons, New York, 1926, pp. 243-244.

⁵ H. H. Willard and Philena Young, *THIS JOURNAL*, **50**, 1322 (1928).

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 almost 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 for 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 electro-metric titration where equilibrium conditions must be carefully noted.

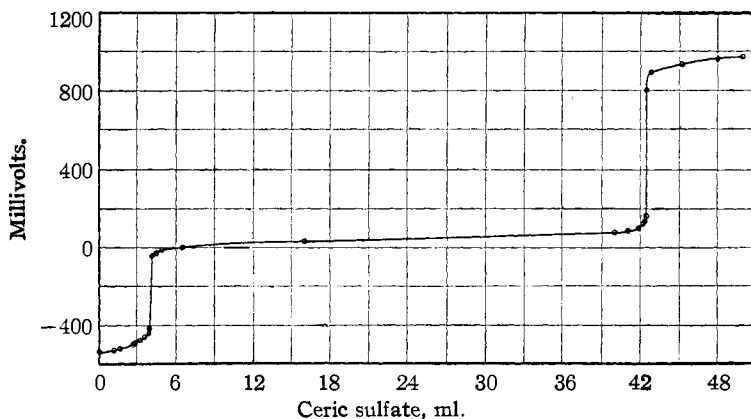


Fig. 1.

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 I are given the results of seven consecutive titrations.

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 titrations.

TABLE I

Total volume of solution titrated, 100 ml.; contained 2% sulfuric acid

Titration number	Uranium solution, ml.	Ceric sulfate, ml.		a/b
		By expt.	Calcd.	
1	29.95	39.88	39.86	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

^a ml. of ceric sulfate solution. ^b ml. of uranium solution.

In Experiment 5 trouble was encountered with the mechanical stirrer.

The second end-point was uncertain and the results 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 disappeared. 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 it was slightly opaque. Upon addition of ceric sulfate solution it gradually cleared and became of 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. measurements represent an equilibrium condition. Furman⁶ 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 sulfate used between end-points was the theoretical. Formerly reported titrations¹ stated that high acid concentrations caused the voltage to rise rapidly and the second end-point

⁶ N. H. Furman, *THIS JOURNAL*, **50**, 755 (1928).

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 percentage of acid was increased, a longer 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 Knudson² has been confirmed.

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

In each case 30 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 sulfuric 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 sulfuric acid. Colors at the end-points were identical.

In no case was the titration with hydrochloric acid as satisfactory as with 2% sulfuric acid. The great difference in effect of these two acids on the titrations was that 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 the 2% sulfuric acid and in the 4 *M* hydrochloric acid titrations. It is noted that the rise in the e. m. f. at the first end-point in the hydrochloric acid solution is approximately 100 mv. and in the sulfuric acid solution the rise is 400 mv. At the second end-point the rise in the hydrochloric acid solution is 450 mv., which compares with a rise of about 675 mv. in the sulfuric acid solution.

In all cases where hydrochloric acid was used, the first end-point was too slow to be of practical use. In the 2 *M* solution, the first end-points covered about 400 mv., in the 4 *M*, 100–200 mv., and in 6 *M*, 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 2 *M* hydrochloric acid, the equilibrium was very slow, and the change in voltage was approximately 300–400 mv.; in 4 *M* it was 400–500 mv. and more rapid;

in 6 *M*, which compared with 2% sulfuric acid, the change was 600 mv. and more rapid.

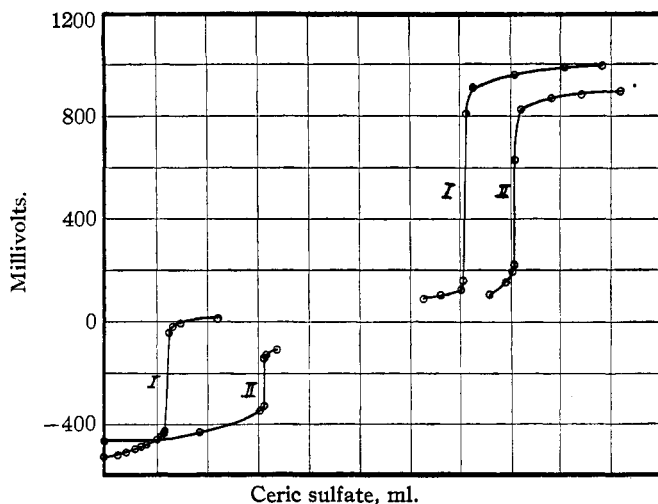


Fig. 2.—I, H₂SO₄, 2%; II, HCl, 4 *M*.

It was found that for hydrochloric acid solutions a concentration of about 2 *M* in hydrochloric acid gave the most definite e. m. f. change for the first end-point. For the second end-point the optimum concentration of hydrochloric acid seemed to be about 4 *M*.

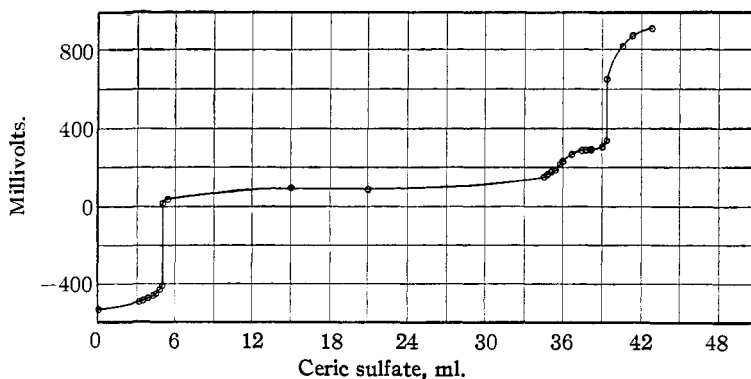


Fig. 3.

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

Three end-points were obtained: one when trivalent uranium was oxidized to tetravalent, another when tetravalent 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 advisable to plot also, $\Delta mv./\Delta ml.$, 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 sulfate necessary to oxidize the uranium present; and the amount between the second and third, very nearly to the amount required to oxidize the ferrous iron present. Graph Number 3 shows this titration.

Nitrogen was used to exclude the air from the cell during the titration. This is essential for 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.⁷

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. A 2% sulfuric acid of uranium sulfate gave satisfactory results.

2. Uranium acetate in hydrochloric acid solution, when treated in the same way, also gives two end-points, the difference between which is the amount of uranium present. A concentration of 2 *M* for the first and 4 *M* for the second gave the best results.

3. Sharper end-points were obtained for 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. Ferrous ammonium sulfate was added to the reduced 2% uranium solution and three end-points were obtained: (1) when trivalent uranium was oxidized to tetravalent, (2) when tetravalent was oxidized to hexavalent and (3) when ferrous was oxidized to ferric iron.

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⁷ H. M. McCoy and H. H. Bunzel, *THIS JOURNAL*, 31, 367 (1909).