[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

APPLICATIONS OF CERIC SULFATE IN VOLUMETRIC ANALYSIS. V. POTENTIOMETRIC STUDY OF THE REACTION BETWEEN FERROCYANIDE AND CERIC IONS

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Introduction

In previous papers of this series[1] it has been shown that solutions of ceric sulfate, containing sulfuric acid, are suitable for use in volumetric analysis, especially with the aid of the potentiometric method of determining end-points. Independently of this series of studies, H. H. Willard and Philena Young[2] and I. A. Atanasiu[3] have studied some of the uses of ceric sulfate in volumetric analysis. H. Rathsberg[4] has recently employed the reagent in the determination of antimony and arsenic as did Willard and Young[2] and Furman and Wallace (unpublished).

In addition to the advantages of ceric sulfate that have already been pointed out by the investigators whom we have cited, *viz.*, (a) stability, (b) high normal oxidation–reduction potential, (c) simplicity of valence change as contrasted with the relations in case of permanganate, there is another that is of some interest: (d) ceric salts are almost unique among the stable powerful oxidizing agents in having a cation as the primary active constituent.[5] In most of the other cases, that is, permanganate, dichromate, chlorate, bromate, iodate, etc., the active constituent is an anion, or at least can only be liberated by the destruction of an anion. Owing to mutual attraction of oppositely charged ions, ceric salts might therefore be expected to be somewhat more effective, other things being equal, in the oxidation of anions than dichromate, or even permanganate. This appears to be true in the oxidation of nitrite, for example.

The Reaction between Ceric Sulfate and Ferrocyanide.—The reaction $Ce^{++++} + Fe(CN)_6^{----} \rightleftarrows Ce^{+++} + Fe(CN)_6^{---}$ proceeds quantitatively from left to right in acid solution and quantitatively from right to left in alkaline medium (30% potassium carbonate solution). Browning and Palmer[6] used the latter reaction as a basis for the volumetric de-

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[1] N. H. Furman, THIS JOURNAL, **50**, 755, 1675 (1928).

[2] Willard and Young, *ibid.*, **50**, 1322, 1334, 1368, 1372, 1379 (1928); **51**, 139, 149 (1929); *Ind. Eng. Chem.*, **20**, 972 (1928).

[3] I. A. Atanasiu, *Bull. Soc. Roum. Chim.*, **30**, 1 (1927); Atanasiu and V. Stefanescu, *Ber.*, **61**, 1343 (1928).

[4] Rathsberg, *ibid.*, **61**, 1664 (1928).

[5] W. D. Treadwell (private communication) called attention to the possible importance of this factor.

[6] Browning and Palmer, *Am. J. Sci.*, **26**, 83 (1908).

termination of cerium. Tomiček[7] has shown that the end-point may be determined potentiometrically.

Atanasiu and Stefanescu[3] have published data on but a single titration of ferrocyanide with ceric solution, and give no test analyses regarding the accuracy of the method. They state that the concentration of sulfuric acid does not alter the inflection in any way. We find that there is a fairly definite upper limit of acidity. We have also studied the reverse titration.

Experimental

The potentiometric titration apparatus did not differ in any essential respect from that which was used in the earlier investigations of this series. The indicator electrode was a bright platinum wire; the reference electrode, a normal calomel electrode.

The ceric solutions which were used in this investigation were prepared from commercial rare earth oxides[8] containing 45% of CeO_2 (44.94 and 45.24% of CeO_2 [bismuthate method)].

Prior to ignition the material dissolves readily and practically completely in dilute sulfuric or nitric acid. After ignition it is readily decomposed by heating with concentrated or dilute sulfuric acid (1 vol. acid of sp. gr. 1.84 : 1 vol. water). Over 90% of the available cerium is found to be present in the ceric condition in the resulting solutions. A solution approximately 1 *N* in sulfuric acid and others from 3–4 *N* in acid were prepared; the latter solutions were found to be stable, whereas the former decreased slowly in strength.[9]

The ceric sulfate was standardized potentiometrically against pure sodium oxalate. Addition of hydrochloric acid as suggested by Willard and Young[10] makes the potentiometric standardization convenient, whereas in sulfuric acid solution the standardization is accurate, although extremely tedious.[11]

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[7] O. Tomiček, *Rec. trav. chim.*, **44**, 410 (1925).

[8] We are indebted to Dr. H. S. Miner of the Welsbach Company, Gloucester, N. J., for this material, which is a commercial rare-earth oxide mixture that is available in quantity. The mixture usually contains about 55% per cent. of CeO_2 on a dry basis, the other oxides being chiefly those of lanthanum and neodymium, with smaller quantities of praseodymium and samarium oxides. We have found this to be the best available raw material for the preparation of ceric sulfate solutions. *Cf.* also Willard and Young, THIS JOURNAL, **51**, 149 (1929).

[9] The decrease in strength is not due to reduction but to the gradual precipitation of ceric ion in part, at least, in the form of phosphate. The phosphate occurs in the crude rare-earth oxides and is brought into solution by the more concentrated acid which is first used to dissolve the oxide. Upon dilution a gradual separation of ceric salt begins and may continue for a week, or even longer, depending upon the conditions of acidity and dilution of the ceric salt.

[10] Willard and Young, THIS JOURNAL, **50**, 1325 (1928).

[11] Furman, *ibid.*, **50**, 761 (1928).

Potassium permanganate solutions were standardized potentiometrically against the pure sodium oxalate.[12]

Approximately 0.1 or 0.05 *N* potassium ferrocyanide solutions were prepared. The content of the solution was checked at frequent intervals by potentiometric titration with the potassium permanganate.[13] The data thus obtained were used as a basis of judging the accuracy of the titration of ferrocyanide with ceric sulfate.

Titration of Ferrocyanide with Ceric Sulfate.—The titrations were made at room temperature (20–25°). Appropriate quantities of the ferrocyanide solution and of acid and water were measured out. The rate of addition of ceric salt had little effect upon the accuracy of the titration. The results are summarized in Tables I and II.

TABLE I

TITRATION OF APPROXIMATELY 0.05 *N* FERROCYANIDE WITH 0.05 *N* CERIC SULFATE

	1	2	3	4	5	6
Initial acid concn., *N*	...	1.5	5.0	...	0.5	0.8
Ceric soln. found, cc.	25.30	25.31	25.34	25.11	25.11	25.08
Ceric soln. calcd., cc.	25.32	25.32	25.32	25.09	25.09	25.09
Error, cc.	−0.02	−0.01	+0.02	+0.02	+0.02	−0.01

The total initial volume was 100 cc.; in Nos. 2 and 3 the acid was hydrochloric, in 5 and 6, sulfuric.

Weighed portions of a dried specimen of "c. p." commercial potassium ferrocyanide required, respectively, 0.13, 0.17, 0.17, 0.14, 0.13 and 0.10% less than the calculated quantity of ceric sulphate. Unpurified potassium ferrocyanide would probably serve as a secondary standard in much the same way as does "c. p." Mohr's salt.

TABLE II

TITRATION OF 0.1002 *N* FERROCYANIDE WITH 0.1028 *N* CERIC SULFATE

A. In Hydrochloric Acid Solution

	1	2	3	4	5	6	7	8
Initial vol., cc.	100	100	60	100	100	60	60	100
Initial acid concn., *N*	0.9	0.9	...	0.6	0.9	1.0	2.0	0.6
Ceric soln. found, cc.	24.42	24.35	9.75	24.36	24.31	9.78	9.77	24.33
Ceric soln. calcd., cc.	24.37	24.37	9.75	24.37	24.37	9.75	9.75	24.37
Error, cc.	+0.05	−0.02	±0.00	−0.01	−0.06	+0.03	+0.02	−0.04

B. In Sulfuric Acid Solution

	1	2	3	4	5	6
Initial vol., cc.	60	60	60	60	60	60
Initial acid concn., *N*	1.0	1.5	3.0	1.0	2.0	3.0
Ceric soln. found, cc.	24.32	24.37	24.36	9.74	9.76	9.78
Ceric soln. calcd., cc.	24.37	24.37	24.37	9.75	9.75	9.75
Error, cc.	−0.05	±0.00	−0.01	−0.01	+0.01	+0.03

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[12] C. del Fresno, *Z. Elektrochem.*, **31**, 199 (1925); S. Popoff and J. Whitman, THIS JOURNAL, **47**, 2259 (1925).

[13] E. Müller and H. Lauterbach, *Z. anal. Chem.*, **61**, 398 (1922); I. M. Kolthoff, *Rec. trav. chim.*, **41**, 343 (1922).

The general nature of the titration graph in the neighborhood of the end-point is indicated in Fig. 1. The character of the reverse titration is also indicated. The potential readings become steady almost at once except in the immediate region of the end-point, where the establishment of a steady potential reading requires one to three minutes, depending upon the conditions.

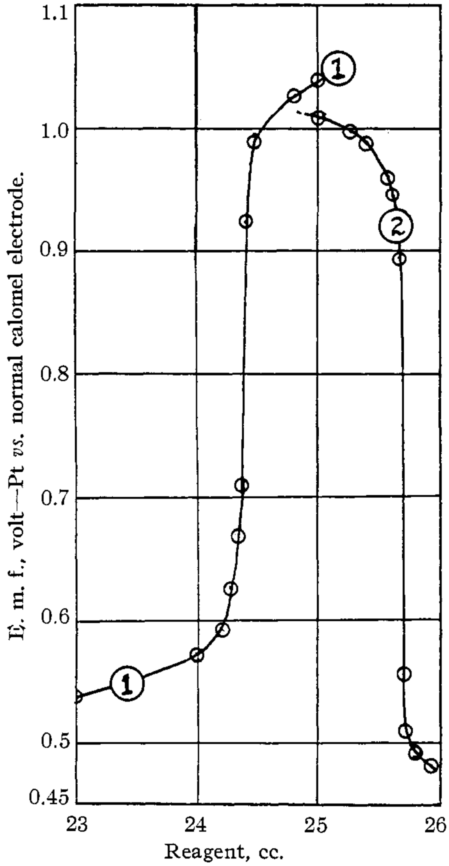

Fig. 1.—Curve 1, titration of 25 cc. of 0.1002 *N* ferrocyanide with 0.1027 *N* ceric sulfate. Initial volume, 60 cc. 1 *N* in sulfuric acid. Found, 24.36. Calcd., 24.37 cc. of ceric sulfate. Curve 2, the reverse of (1). Initial volume 75 cc., about 1 *N* in sulfuric acid. Calcd., 25.65 cc. Found, 25.66 cc. of ferrocyanide.

The concentration of acid should not be too high. With a ceric solution that is 1 *N* in sulfuric acid the initial concentration of sulfuric acid in the ferrocyanide solution should not exceed 5 *N*. If the initial acid concentration is too low, and if the acidity of the ceric solution is low, a white precipitate may be formed during the titration. With much more than 5 *N* original acid concentration, the end-point potential readings are established sluggishly, and some decomposition of the ferro- or ferricyanide may occur. With hydrochloric acid the results are excellent in the range 0.5–2 *N*. If the acid concentration is as high as 4 *N* at the end-point the rise in potential is not sharp.

The jump in potential at the end-point usually amounted to 0.15–0.25 volt per 0.05 cc. of 0.05 *N* solution, or 0.2–0.3 volt per 0.05 cc. of 0.1 *N* ceric solution.

The titration appears to be very accurate and much less circumscribed than the permanganate titration, where a very limited range of acidity is essential.

Visual End-Point.—During the titrations with ceric sulfate a greenish coloration is formed during the progress of the titration. This is apparently due to the formation of ferric ferrocyanide with a trace of iron that is found to be present in the ceric solution (thiocyanate reaction). Apparently the excess of ferrocyanide aids in keeping the ferric ferrocyanide in colloidal form.[14] The greenish coloration disappears quite sharply at the end-point when the last traces of ferrocyanide are oxidized.

It is possible to use the disappearance of the greenish color as a visual indication of the end-point. During the potentiometric studies the color end-point was observed to precede the potentiometric by 0.03, 0.00, 0.03, 0.00, 0.00, 0.04, 0.03 and 0.02 cc. The background was not very satisfactory for observation of the color change in these cases. A series of determinations was made by the visual method using a white tile background: found, 23.47, 23.48, 23.50, 23.49 cc. of approximately 0.1 *N* ceric solution per 25 cc. of ferrocyanide. Twenty-five cc. portions of the ferrocyanide were then titrated potentiometrically: found, 23.47, 23.47, 23.51, 23.49 cc. of ceric solution. The two methods are therefore in excellent agreement.

A portion of the ceric solution was treated with a slight excess of hydrogen peroxide and then boiled to decompose the latter. After appropriate dilution and withdrawal of an aliquot portion, the iron was estimated colorimetrically to be 1.00 ± 0.05 mg. per 25 cc. of ceric solution.

If a trace of ferric iron is added to a ferrocyanide solution that is being titrated with permanganate, the same greenish coloration forms and is destroyed in the same manner at the end-point.

Titration of Ceric Sulfate with Ferrocyanide.—This titration is only practicable under very limited conditions. The most important single factor is speed of titration. If the rate of titration is too small some ceric sulfate is apparently consumed by a side reaction, probably with ferricyanide, and too little ferrocyanide is used. For example, if the titration was interrupted after addition of 10 and 20 cc. of ferrocyanide, respectively, in order to take potential readings, only 25.53 cc. of ferrocyanide was required instead of 25.65 cc., the calculated quantity. The erratic nature of the results is indicated by the following figures, cc. of ferrocyanide (0.1002 *N*) found:

1	2	3	4	5	6	7	8	9
25.17	25.34	25.27	25.44	25.41	25.51	25.55	25.53	25.57

The amount theoretically required was 25.65 cc. in each case. In No. 1 the rate of addition was 5 cc. per minute. In instances 2–5 a relatively large number of interruptions was made for potential readings. In cases 6–9 only two readings were taken, one after rapid addition of 10 cc. and the other after 10 cc. more of ferrocyanide had been added. The titrations were then finished slowly. Under like conditions of operation the results are quite reproducible but seriously in error.

If from 80 to 97% of the theoretical amount of ferrocyanide is added very rapidly (fifteen to twenty-five seconds) the titration may be finished in the usual manner and the results are accurate, as is indicated in Table III.

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[14] *Cf.* G. Rossi and M. Marzari, *C. A.*, **22**, 1262 (1928).

TABLE III

TITRATION OF 0.1028 *N* CERIC SULFATE WITH 0.1002 *N* FERROCYANIDE

Initial vol., cc.	55	50	50	50	75	75	100	100
Ferrocyanide soln., cc.	25.60	25.60	25.65	25.67	25.66	25.68	25.63	25.65
Error, cc.	−0.05	−0.05	±0.00	+0.02	+0.01	+0.03	−0.02	±0.00

In each case 25.65 cc. of ferrocyanide should have been used The initial acid concentration ranged from 1 to 2.5 *N*. In the first instance 20 cc. of ferrocyanide was added, within about fifteen seconds, to the well-stirred ceric solution; in the other cases from 24.5–25 cc. was added rapidly before any potential readings were taken. The break in potential per 0.03 cc. of ferrocyanide at the end-point amounted to 0.23–0.34 volt. The readings were steady except in case of the drop that caused the large break in potential. From one to three minutes were required before the reading was steady. A drop of ferrocyanide in excess caused the appearance of the greenish coloration and was a reliable indication that the end-point had been passed. The general character of the potential curve is indicated in Fig. 1.

Summary

The potentiometric titration of ferrocyanide with ceric sulfate has been found to be accurate throughout a wide range of conditions and can be recommended for precise work.

The reverse titration is only accurate if the major portion of the ferrocyanide is added very rapidly. This method cannot therefore be recommended for general application.

The presence of a small quantity of ferric iron in the ceric solution causes a greenish coloration (ferric ferrocyanide) which disappears sharply at the end-point of the oxidation of the ferrocyanide. This visual end-point is practically identical with the potentiometric one.

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