Assumption (III) requires that there be no heat effect not due to combination of hydrogen on the calorimeter. This is proved by the blank experiment. It also requires that all the monatomic hydrogen passing through the small holes recombine on the platinum calorimeter. The mean free path at the pressures in the calorimeter is long enough to insure that every hydrogen atom will strike the calorimeter at least once. From the geometry the probable number of collisions is at least 3. The coefficient of recombination of hydrogen atoms on a platinum surface is not known but all qualitative information indicates it is very high. If it is above 80%, the error introduced is less than 1%. Such incomplete recombination would mean that our value was too low.

This determination was made at constant pressure. The corresponding value at constant volume would be some 600 calories smaller.

Summary

A new direct method for the determination of the heat of formation of molecular hydrogen has been described. The mathematical theory and a description of the apparatus have been given.

The results of three experiments and one blank determination have been presented with a discussion of the possible experimental and theoretical errors.

The value of the heat of formation of molecular hydrogen has been determined by this method as 105,000 ± 3500 calories.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

CERIC SULFATE AS A VOLUMETRIC OXIDIZING AGENT. I. PREPARATION AND STANDARDIZATION OF SOLUTIONS. DETERMINATION OF CALCIUM

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RECEIVED FEBRUARY 15, 1928 PUBLISHED MAY 5, 1928

Introduction

The use of ceric salts as oxidizing agents has been suggested by a number of authors. Lange[2] in referring to the oxidizing properties of ceric sulfate recommends it as a volumetric reagent; Sonnenschein[3] suggests it instead of permanganate for the titration of iron; A. Job[4] speaks of the stability and strong oxidizing properties of acid solutions of ceric salts and of their possible use in cases where permanganate is not applicable as in the esti-

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[1] From a dissertation submitted by Philena Young to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] Lange, *J. prakt. Chem.*, 82, 129 (1861).

[3] Sonnenschein, *Ber.*, 3, 631 (1870).

[4] Job, *Compt. rend.*, 128, 101 (1899).

mation of oxalochlorides, the excess of the reagent being determined with hydrogen peroxide. This last author states that the oxidizing solution may be prepared from ordinary commercial cerium compounds as the presence of the other monazite metals has no influence on results. G. Barbieri[5] discusses the volumetric determination of nitrous acid by means of tetravalent cerium, the factor of which is determined iodimetrically or with hydrogen peroxide. He remarks that ceric compounds are reduced by hydrazine and hydroxylamine salts in the cold. Sommer and Pincas[6] find that salts of quadrivalent cerium immediately effect the complete oxidation of hydrazoic acid in neutral or acid solution, and Martin[7] has developed an iodimetric method for determining the excess of ceric sulfate used in this oxidation. Benrath and Ruland,[8] in a paper on the oxidizing action of ceric sulfate, discuss the oxidation of a number of organic compounds as tartaric acid, oxalic acid, anthracene, hydrazine, hydroxylamine, as well as sodium thiosulfate, sulfurous acid, hypophosphorous acid. Ceric salts have been used in the electrolytic oxidation of organic compounds and a number of volumetric methods for the estimation of cerium have been worked out.[9] No one, however, has yet used ceric salts in the direct titration of reducing agents.[10]

An extensive development of analytical methods based upon the use of ceric salts as volumetric reagents would have been difficult before the advent of the potentiometric method of determining an end-point. Though a visual change or an internal indicator may be used in some cases, the end-point in many of the titrations must be determined electrometrically. Since the oxidation potential of the most powerful oxidizing agents such as that of permanganate in acid solution is very close to that of ceric compounds in a similar medium,[11] the latter should prove to be very strong oxidizing agents and should behave in many reactions in a manner similar to permanganate. A ceric salt has, however, one great advantage, namely, that only trivalent cerium can be formed in its reduction, whereas with permanganate several reduction products are possible and it is not always easy to avoid the formation of more than one of these in a given reaction. Ceric salts may be used in solutions containing a high concentration of

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[5] Barbieri, *Chem.-Ztg.*, **29**, 668 (1905).

[6] Sommer and Pincas, *Ber.*, **48**, 1963 (1915).

[7] Martin, THIS JOURNAL, **49**, 2133 (1927).

[8] Benrath and Ruland, *Z. anorg. allgem. Chem.*, 114, 267 (1920).

[9] Lessnig, *Z. anal. Chem.*, 71, 161 (1927), gives a brief summary of the methods for cerium.

[10] After these papers were submitted to THIS JOURNAL, a paper appeared by Furman, THIS JOURNAL, **50**, 755 (1928), in which he showed that ceric sulfate could be standardized against oxalate or ferrous sulfate in sulfuric acid solution. The authors' results confirm the accuracy of these methods and considerably extend the usefulness of these reactions.

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

hydrochloric acid and are very stable toward heat, while the use of permanganate under such conditions is almost always out of the question. The authors have therefore made a systematic study of ceric salts as oxidizing agents in volumetric analysis, the results of which will appear in a series of papers.

Experimental

Preparation of Ceric Sulfate

The supply of U. S. P. cerous oxalate available was found by Metzger's bismuthate method[12] to contain 48.22% of CeO_2 in the ignited oxide. While a pure cerium compound was not necessary for our purpose because no interference from the other rare earths was to be expected, it seemed better to use material containing a higher percentage of cerium. On the other hand, a material not too pure has certain advantages: a mixed oxide of the rare earths containing about 85% of CeO_2 is attacked readily by sulfuric acid, sp. gr. 1.5, with the formation of ceric sulfate, while a very pure sample of CeO_2 must be treated with concentrated sulfuric acid to obtain the sulfate.[13] The pure oxide is a relatively expensive reagent, but a ceric oxide containing other rare earths is inexpensive.

A slight modification of Roberts' permanganate process[14] for concentrating cerium in a rare earth mixture was used. The solution of the nitrates, diluted considerably with water, was heated to boiling, stirred mechanically and treated with sodium carbonate solution until a slight permanent precipitate was formed. This was dissolved in nitric acid, added drop by drop, and to the boiling hot liquid a solution, 0.25 molar in potassium permanganate and 1 molar in sodium carbonate, was added until a fair excess of permanganate was present. By this procedure all of the cerium was precipitated as dioxide along with some of the other rare earth oxides. Roberts' directions were followed in converting these oxides into chlorides and subsequently into oxalates. A considerable quantity of material was worked up by this method and the chloride solutions were combined and stirred thoroughly so that the entire oxalate precipitate would be of the same composition. The ignited oxides from this oxalate contained 85.1% of CeO_2. When the oxalate was ignited at 600–625° for ten hours, slightly more than 99% of the cerium in it was converted into CeO_2. If this was dissolved in sulfuric acid, sp. gr. 1.5, diluted and titrated directly for ceric content, 91.2% of the CeO_2 in the oxide was found as ceric sulfate. While the conversion into oxide was more nearly complete at a higher temperature, the yield of ceric salt was somewhat lower.

To prepare a large amount of ceric sulfate solution, portions of the oxide, ignited at 600–625°, were treated with sufficient sulfuric acid, sp. gr. 1.5, to make the final solution 0.5 or 1 molar in acid when it was diluted sufficiently to give a 0.1 N ceric sulfate solution. This oxide–acid mixture was kept at 125–130° and stirred mechanically until the pale pinkish brown oxide, which was converted first into a deep red material, became a bright yellow in color. This material was diluted almost to the volume required for a 0.1 N solution and kept at 75–80° for an hour while being stirred mechanically. It was filtered hot from the small amount of undissolved material, which appeared to be unchanged CeO_2 and was combined with similar precipitates to be worked up later. If the U. S. P. oxalate was ignited, this impure oxide dissolved readily in sulfuric acid of sp. gr. 1.3.

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[12] Metzger, THIS JOURNAL, 31, 523 (1909).

[13] Meyer and Aufrecht, *Ber.*, 37, 140 (1904); Spencer, *J. Chem. Soc.*, 107, 1265 (1915).

[14] Roberts, *Am. J. Sci.*, [IV] 31, 350 (1911).

Some of this ignited oxide was treated with 95% sulfuric acid at a temperature of 150–155°, and was converted fairly rapidly into the bright yellow ceric sulfate. This, when cool, was added slowly to water at room temperature. Nearly all of the solid dissolved and the actual yield in ceric sulfate from a given weight of the ignited oxide was very nearly the same as that in the process described above. The first method was somewhat more convenient.

A further supply of 0.1 *N* ceric sulfate was made from C. P. CeO_2, very pale yellow in color, by treatment with concentrated sulfuric acid as described above. From the strength of the solution obtained, it was found that 98.2% of the oxide used in the process was converted into ceric sulfate.

During a three months' interval, the normality factor of this ceric sulfate solution was constant to within one part in a thousand.

Different cerium compounds were used to prepare 0.1 *N* ceric sulfate, the purpose being to compare the cost of a liter of these solutions. Pure ceric sulfate and pure ceric ammonium nitrate, converted into sulfate by evaporation with sulfuric acid, were out of the question because of the expense. The approximate cost of the cerium compound for a liter of 0.1 *N* solution from C. P. CeO_2 was eighty-five cents, from U. S. P. cerous oxalate ten cents. While this last material is satisfactory for the preparation of such a volumetric solution, an oxalate containing 80–85% of the theoretical quantity of CeO_2 is perhaps preferable.

Standardization of Ceric Sulfate

Since it is very desirable to use a primary standard for this purpose, a study was made of the titration of sodium oxalate in hot solution with ceric sulfate, the reaction being

$$Na_2C_2O_4 + 2Ce(SO_4)_2 = Na_2SO_4 + 2CO_2 + Ce_2(SO_4)_3.$$

Portions of a standard solution of sodium oxalate from the U. S. Bureau of Standards were acidified with sulfuric acid, heated nearly to boiling and titrated electrometrically with 0.1 *N* ceric sulfate prepared from the ignited oxide containing 85.1% of CeO_2. Two cc. of sulfuric acid was contained in the ceric sulfate used. In all of this work a silver chloride–platinum electrode system was used. The silver chloride electrode in 0.1 *N* potassium chloride was placed directly in the liquid to be titrated. The results are shown in Table I.

These data indicate that concordant results may be obtained when the volume of the solution is varied from 100–300 cc. (larger variations in volume were not studied) and when the weight of sodium oxalate is changed over wide limits. The end-point equilibrium is quite rapid if not more than 2.5 cc. of concd. sulfuric acid is present per 100 cc. of solution at the time of titration. The high result obtained in the last experiment is probably due to the low acid content of the solution. No acid was added before the titration and only 1.85 g. of sulfuric acid was present in the ceric sulfate. It is probable that not quite all of the cerous oxalate was dissolved. In the other experiments in which no acid was added, a considerable quantity of cerous oxalate precipitated on the addition of the first portion of ceric sulfate and then dissolved as more of the reagent was added.

TABLE I

EFFECT OF SULFURIC ACID

$Na_2C_2O_4$, g.	Initial vol., cc.	H_2SO_4, sp. gr. 1.83, at beginning, cc.	$Ce(SO_4)_2$, normality	Character of end-point
0.2679	200	0	0.1067	Rapid
.2679	200	5	.1067	Fairly rapid
.2679	200	10	.1067	Slow
.2679	300	0	.1067	Rapid
.2679	300	7.5	.1068	Fairly rapid
.2679	300	15	.1068	Slow
.2679	100	0	.1067	Rapid
.2679	100	2.5	.1067	Slow but usable
.2679	100	5	.1068	Too slow
.1339	300	7.5	.1067	Rapid
.5358	300	0	.1067	Rapid
.1339	300	0	.1081	Fairly rapid

Experiments showed that the equilibrium at the end-point was reached too slowly in all cases if the temperature of the solution at the end of a titration was below 70°. At or above this temperature results were as indicated in Table I.

The results were identical no matter whether the ceric sulfate solution was added slowly to the oxalate, as would be necessary in a permanganate titration, or rapidly from a pipet.

Portions of a standard solution of sodium oxalate were acidified with hydrochloric acid, heated nearly to boiling and titrated electrometrically with 0.1 *N* ceric sulfate. The equilibrium at the end-point was rapid in all cases. The results are shown in Table II.

TABLE II

EFFECT OF HYDROCHLORIC ACID

$Na_2C_2O_4$, g.	Initial vol., cc.	HCl, sp. gr. 1.18, at beginning, cc.	$Ce(SO_4)_2$, normality
0.2679	200	0	0.1043
.2679	200	5	.1043
.2679	200	20	.1042
.2679	200	40	.1043
.2679	200	60	.1043
.2679	100	10	.1042
.2679	300	30	.1042
.1339	300	30	.1041
.5358	300	30	.1043

It is seen that ceric sulfate may be used with no special precautions in strong hydrochloric acid solutions and thus has a decided advantage over permanganate. The end-point break in the above experiments averaged about 175–200 mv. per 0.02 cc. of 0.1 *N* ceric sulfate, and fifteen minutes after the completion of a titration not the slightest decrease in potential had occurred.

Experiments similar to those made in Tables I and II showed that as much as 60 cc. of 73% perchloric acid or 50 cc. of glacial acetic acid per 200 cc. of solution could be used instead of sulfuric or hydrochloric acid and the end-point equilibrium was rapid. The presence of even 5 cc. of concd. nitric acid in this same volume however, gave too high a value for the ceric sulfate, showing that this acid had a slight effect on the oxalate. Phosphoric and hydrofluoric acids must be absent, even if considerable hydrochloric acid is present, as they cause the formation of insoluble cerium salts. In the titration of ferrous ion in hydrochloric acid solution with ceric sulfate, which is described later, the presence of a moderate amount of phosphoric acid causes no interference, probably because this reaction is a more rapid one than the oxalate–ceric sulfate reaction. Experiments using ceric sulfate solution prepared from pure CeO_2 gave the same results.

Since in the titration of oxalate the solution is colorless until an excess of ceric sulfate is present, the possibility of using a visual end-point was investigated. An initial volume of 200 cc., containing 10–20 cc. of concd. hydrochloric acid, was used. If an equal volume of water is taken as a comparison liquid, the slightest change in color at the end-point is easily seen. A blank determination made at 70° on 200 cc. of water containing 20 cc. of concd. hydrochloric acid and 3–5 cc. of concd. sulfuric acid (the volume in the ceric sulfate added) showed that 0.05 cc. of 0.1 N ceric sulfate was required to give a pale yellow color. Unless sulfuric acid was added, the ceric sulfate was reduced. When this amount was subtracted from the volume of ceric sulfate used in a titration the normality corresponded exactly to that obtained electrometrically.

Quantitative results were obtained in the reverse titration of ceric sulfate with sodium oxalate in hot solution when as much as 5 cc. of concd. sulfuric acid was present per 200 cc. of solution. If more sulfuric acid was used, the equilibrium at the end-point was too slow. Twenty-five cc. of perchloric acid (73%) or 5–20 cc. of concd. nitric acid in the same volume gave quantitative results with a fairly rapid end-point equilibrium. Hydrochloric acid had a reducing effect on the ceric sulfate present in the hot solution. The end-point breaks amounted to 150–200 mv. per 0.03 cc. of 0.1 N sodium oxalate except in the nitric acid solutions where they were of about half this magnitude. It was found that this electrometric titration with oxalate could be used after a bismuthate oxidation,[12] but the equilibrium in the region of the end-point was quite slow, due to the large amount of acid present.

Iodine Chloride as Catalyst

Later work which showed the value of certain iodine compounds as catalyst in the reaction between arsenite and ceric salt[15] suggested the

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[15] To be described in a later paper of this series.

possibility of titrating oxalate at room temperature in the presence of such a catalyst. It was found that the titration of oxalate in hydrochloric acid solution containing iodine chloride proceeded rapidly and quantitatively at room temperature. Iodine chloride was chosen although iodide or iodate worked equally well, because it necessitated no blank correction in the volume of ceric sulfate used, since the final form of the catalyst in all cases was iodine chloride. The catalytic action of iodide or iodate seemed a little slower than that of iodine chloride and the blank required for either was an objection.

The action of the catalyst in this reaction is not clear. It was found that iodine chloride is not reduced at all by oxalate in hydrochloric acid solution in thirty minutes, nor does it catalyze at room temperature the action of oxalate in hydrochloric acid solution with (1) potassium permanganate, (2) potassium dichromate or (3) potassium iodate. Its catalytic action seems to be confined to the ceric salt titration and this suggests the possibility that the ceric ion is an important factor, since cerous salt was found not to catalyze the action between iodine chloride and oxalate. This same conclusion was drawn from work with the arsenite titration. This subject is being investigated.

The iodine chloride solution was prepared by dissolving 0.279 g. of potassium iodide and 0.178 g. of potassium iodate in 250 cc. of water and adding all at once 250 cc. of concd. hydrochloric acid.[16] The solution thus obtained was 0.005 *M* in iodine chloride. It was adjusted electrometrically by adding the proper amount of dilute potassium iodide or iodate.

Measured portions of a standard solution of sodium oxalate were acidified with hydrochloric acid. Iodine chloride was added and water to a total volume of 100 cc. The end-point was determined electrometrically. The results are shown in Table III.

TABLE III

TITRATION OF OXALATE, IODINE CHLORIDE AS CATALYST

$Na_2C_2O_4$, 0.1 *N*, cc.	HCl, sp. gr. 1.18, at beginning, cc.	ICl, cc.	$Ce(SO_4)_2$, 0.1 *N*, cc.	Character of end-point
10	10	10	9.98	Slow
10	15	10	9.99	Rapid
10	25	10	9.98	Rapid
10	20	5	9.99	Rapid
10	15	20	9.99	Rapid
50	15	10	49.94	Rapid
50	25	10	49.90	Slow
10	20	10 cc. 0.0025 *M* KI	10.49	Rapid
10	15	5 cc. 0.0025 *M* KIO_3	9.54	Fairly slow

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[16] G. S. Jamieson, "Volumetric Iodate Methods," The Chemical Catalog Company, New York, 1926, pp. 8, 9.

In the lower acid range (first experiment) the reaction is at first more rapid than in the higher acid range (third experiment), but the equilibrium at the end point is slower. The addition of 15–25 cc. of concd. hydrochloric acid per 100 cc. of solution, not considering the acid present in the iodine chloride solution, gives the most favorable conditions for a titration. The values of the blanks in the last two experiments, +0.49 cc. and −0.46 cc., correspond very closely with the volumes of ceric sulfate theoretically required, +0.48 cc. and −0.46 cc., to convert either of the catalysts used into iodine chloride. The potential at the beginning of a titration is approximately 625–675 mv., but drops to 400–450 mv. during the addition of the first few cubic centimeters of oxidizing solution. At the end-point the break in potential averaged 200–250 mv. per 0.03 cc. of 0.1 *N* ceric sulfate.

Methylene blue has been proposed by Sinnatt[17] instead of starch in iodimetric titrations, and Atack[18] has discussed its use as a volumetric reagent in oxidation-reduction reactions. This dye was found to give an excellent end-point in the titration of oxalate with ceric salt in the presence of iodine chloride as catalyst, provided that certain rather narrow experimental conditions were maintained.

During this titration the solution is pale yellow, and as the end-point is approached becomes a deeper yellow, due to the presence of free iodine. As the last portion of ceric sulfate (0.2–0.3 cc.) converts this into iodine chloride, the yellow color gradually fades out. In a titration in which the end-point equilibrium is rather slow, the electrometric break in potential is indicated when the solution is still somewhat yellow and two or three minutes or longer may be required for this color to bleach out. The color disappears much more quickly when conditions are such that the end-point equilibrium is rapid. Experiments have shown that methylene blue cannot be added until within 0.4 cc. of the end-point, and the color change is much sharper if it is not added until within 0.2–0.3 cc. Therefore conditions for a rapid end-point equilibrium must be chosen. When 2 drops of the indicator are added to a pale yellow solution, the solution turns green, and with each succeeding drop of ceric sulfate becomes more blue until a final drop or two of the oxidizing agent causes the whole liquid to turn a deep pink color, which in five to ten seconds changes to a permanent blue shade. Under some conditions the entire solution will not become pink, in which cases, as well as in the above, the end-point is taken as the reading for the last drop which caused the appearance of any pink color in the solution.

Measured portions of a standard solution of sodium oxalate were taken. Iodine chloride and hydrochloric acid were used after sufficient water had

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[17] Sinnatt, *Analyst*, **35**, 309 (1910); **37**, 252 (1912).

[18] Atack, *J. Soc. Dyers and Colourists*, **31**, 183 (1915).

been added to make the total volume of the solution 100 cc. at the time of titration. Two drops of a 0.1% solution of methylene blue in water were added when within 0.2–0.3 cc. of the end-point. The results are shown in Table IV.

TABLE IV

TITRATION OF OXALATE—METHYLENE BLUE INDICATOR

$Na_2C_2O_4$, 0.1 *N*, cc.	HCl, sp. gr. 1.18, at beginning, cc.	$Ce(SO_4)_2$, 0.1 *N*, cc.	Character of end-point color change
10	15	10.01	Satisfactory
10	20	9.98	Excellent
10	25	9.99	Excellent
10	35	?	Not satisfactory
25	10	24.99	Fairly satisfactory
25	15	24.97	Satisfactory
25	20	24.99	Excellent
25	25	?	Not satisfactory
50	20	49.83	Satisfactory
50	15	49.90	Excellent

The amount of iodine chloride was varied, but 10 cc. was found to give the best results.

Titration of Ferrous Iron with Ceric Sulfate

To be able to compare the titrations of ceric sulfate against (1) oxalate and (2) ferrous sulfate as a further check on this method of standardizing a ceric salt, the conditions necessary for the ferrous iron–ceric salt reaction were determined.

$$2FeSO_4 + 2Ce(SO_4)_2 = Fe_2(SO_4)_3 + Ce_2(SO_4)_3$$

The same volume of ceric sulfate was required in each of 6 titrations of 40 cc. of 0.1 *N* ferrous sulfate in which the volume was varied from 100–300 cc. and the sulfuric acid, sp. gr. 1.83, from 0–25 cc. per 100 cc. of solution. The end-point was determinede lectrometrically; the end-point equilibrium was rapid in every case and the break in potential amounted to 250–300 mv. per 0.02 cc. of 0.1 *N* ceric sulfate.

Similar results were obtained when hydrochloric or perchloric acid was used. With as much as 40 cc. of concd. hydrochloric acid or 40 cc. of perchloric acid (73%) per 100 cc. of solution, the end-point equilibrium was rapid and the break in potential large. Nitric acid, however, was detrimental, and the presence of 5 cc. of it per 100 cc. of solution caused a decided decrease in the volume of ceric salt used.

The titration of ceric salt with ferrous sulfate[19] went smoothly when considerable sulfuric or perchloric acid was present. Five cc. of concd. hydrochloric acid per 100 cc. of solution containing 25 cc. of 0.1 *N* ceric

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[19] Since the completion of this work an article by Someya, *Z. anorg. allgem. Chem.*, **168**, 56 (1927), has appeared in which the electrometric titration of ceric sulfate with ferrous sulfate is described.

sulfate caused no interference if the titration was made without delay. If the solution was allowed to stand for five to fifteen minutes before titration, the reducing action of the acid became evident. Quantitative results were obtained with the use of as much as 30 cc. of concd. nitric acid per 100 cc. of solution.

Comparison of Standardizations against Oxalate and Iron

A weight buret was used for the ceric sulfate solution. The samples of sodium oxalate were from the Bureau of Standards and the impurities in the electrolytic iron had been accurately determined. In the titrations of oxalate, in one series, 0.35–0.40-g. samples were dissolved in 200 cc. of water, 10 cc. of concd. hydrochloric acid added and the solutions heated nearly to boiling before titration; while in the second series the samples were dissolved in 75 cc. of water, 15 cc. of concd. hydrochloric acid and 10 cc. of iodine chloride added before titration. In the third series, the samples of electrolytic iron were dissolved in hydrochloric acid, any ferric chloride reduced with a slight excess of stannous chloride, the cooled solution diluted to 150 cc., 10 cc. of saturated mercuric chloride solution added and the solution titrated.[20] The electrometric method was used in all cases. During the titration an atmosphere of carbon dioxide was maintained above the solution to prevent any oxidation of the ferrous iron by air. Later work showed that if this precaution was not taken there was an error of approximately one part in a thousand.

Table V

Weight Normality of Ceric Sulfate by Different Methods

Against	(1) Electrolytic Fe, 99.97% Fe	(2) $Na_2C_2O_4$ in hot soln.	(3) $Na_2C_2O_4$ at room temp. with ICl as catalyst
	0.09410	0.09410	0.09406
	.09414	.09416	.09409
	.09408	.09407	.09409
	.09409	.09406	.09404
Average =	.09410	.09410	.09407

Fig. 1 shows typical curves for the titration of oxalate and of ferrous iron with ceric sulfate. The results are expressed in terms of a platinum-1 *N* calomel electrode system.

Determination of Calcium with Ceric Sulfate

It is obviously possible to use ceric sulfate like permanganate for the volumetric determination of calcium. A. Job[4] has referred to the estimation of oxalic acid in oxalochlorides by addition of excess of ceric salt solution, the excess being determined with hydrogen peroxide, but he gives no experimental data. Benrath and Ruland[8] in a study of the oxi-

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[20] The stannous chloride reduction method for iron followed by titration with ceric sulfate is described in paper II of this series.

dizing action of ceric sulfate state that oxalic acid is oxidized to carbon dioxide and that sulfuric acid and normal sulfates retard the reaction. Since the gravimetric determination of calcium oxide by precipitation as oxalate and ignition in air at 475–550° to carbonate[21] is a very accurate method, the results obtained in this way were compared with those obtained by volumetric titration with ceric sulfate.

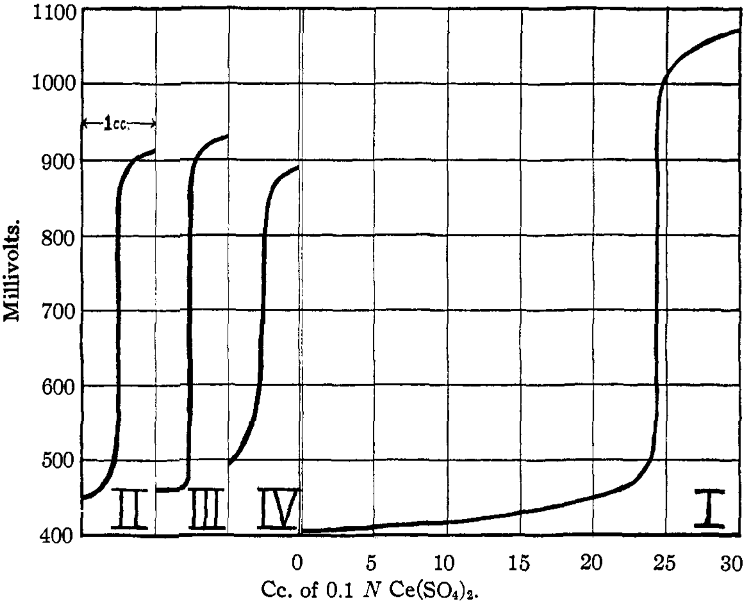

Fig. 1.—Curve I.—25 cc. of 0.1 *N* $Na_2C_2O_4$ titrated with 0.1 *N* $Ce(SO_4)_2$; 3 cc. of concd. H_2SO_4 in initial vol. of 200 cc. Curve II.—End-point in titration of 0.1 *N* $FeSO_4$ with 0.1 *N* $Ce(SO_4)_2$; 15 cc. of concd. HCl in initial vol. of 100 cc. Curve III.—End-point in titration of 0.1 *N* $Na_2C_2O_4$ with 0.1 *N* $Ce(SO_4)_2$; 15 cc. of concd. HCl in initial vol. of 200 cc. Curve IV.—Same as III but 10 cc. of 0. 005 *M* ICl added.

In the following analyses the standard procedure of neutralizing with ammonia a hydrochloric acid solution containing calcium and oxalate ions was followed. The precipitate was collected in a filtering crucible and ignited to carbonate in a *muffle* at 500–525°. In the volumetric method the precipitate was washed into a beaker with water and the paper then washed thoroughly with dilute hydrochloric acid (60 cc. of water + 10 cc. of HCl) and finally with water. The solution was diluted to 200 cc., heated nearly to boiling and titrated either electrometrically or to a visual end-point with ceric sulfate which had been standardized electrometrically against sodium oxalate. Iodine chloride was not used as a catalyst, though such a method would be equally applicable.

[21] A method tested in this Laboratory but not yet published.

TABLE VI

SUMMARY OF ANALYSES FOR CALCIUM OXIDE

Sample		Percentage of CaO: Titration with $Ce(SO_4)_2$ Electrometric	Visual	Weighing as $CaCO_3$
1 Iceland Spar		55.93	55.96	55.97
		55.92	55.93	55.99
		55.93	55.94	56.00
	Average	55.93	55.94	55.99
2		26.60	26.64	26.65[a]
		26.59	26.62	...
		26.66	...	...
		26.60	...	...
	Average	26.61	26.63	26.65[a]
3		20.00	19.94	19.94[a]
		19.97	20.01	...
		20.03	...	...
	Average	20.00	19.97	19.94[a]

[a] These values represent an average of accurate analyses made gravimetrically by another person.

Summary

1. A solution of ceric sulfate is easily prepared by dissolving in sulfuric acid CeO_2 obtained by igniting the oxalate. Pure material is not necessary as the other rare earths do not interfere in oxidation-reduction reactions.

2. This reagent is in some cases a stronger oxidizing agent than permanganate in acid solution and has a number of advantages over the latter: only one valence change is possible, namely, from $Ce^{++++} \longrightarrow Ce^{+++}$; it may be used in a solution containing a high concentration of hydrochloric acid and is stable toward heat. The normality factor of the solution remains constant over a long period.

3. Ceric sulfate may be accurately standardized against sodium oxalate in hot sulfuric, hydrochloric or perchloric acid solution, the end-point being determined either electrometrically or visually by a change from colorless to yellow. The titration of ceric salt with oxalate is quantitative in hot sulfuric, perchloric or nitric acid solution.

4. The oxalate titration with ceric sulfate may be carried out with the same accuracy at room temperature by the use of iodine chloride as catalyst. The end-point is determined either electrometrically or with methylene blue as internal indicator.

5. Ferrous iron may be determined volumetrically in sulfuric, hydrochloric or perchloric acid solution with ceric sulfate. The reverse titration proceeds quantitatively in a sulfuric, perchloric or nitric acid solution.

6. A method for calcium has been developed, based upon precipitation

as oxalate, solution in hydrochloric acid and titration with standard ceric sulfate.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

CERIC SULFATE AS A VOLUMETRIC OXIDIZING AGENT. II. DETERMINATION OF IRON

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RECEIVED FEBRUARY 15, 1928 PUBLISHED MAY 5, 1928

The possibility of titrating ferrous iron with ceric sulfate has been investigated by the authors[2] and has been found to give quantitative results in either hydrochloric, sulfuric or perchloric acid solution. Furman[3] has also studied this reaction in sulfuric acid solution. It seemed important to study the application of this titration to the analysis of iron ores in which the iron was reduced in hydrochloric acid solution with stannous chloride, the excess of the latter being removed with mercuric chloride, because some of the present methods for titrating the iron after such a reduction have certain undesirable features. If permanganate is used as the oxidizing agent, the concentration of hydrochloric acid must be small because of its reducing action. Manganese sulfate is added[4] but even with this precaution the end-point obtained is fleeting, and some experience with the method is required for accurate results. This end-point has been determined electrometrically.[5] If the titration is made with dichromate, potassium ferricyanide may be used as an external indicator, an inconvenient process, or diphenylamine as an internal indicator,[6] the change in color being from a green to a deep blue shade. Many persons find it difficult to obtain a sharp color change in this latter case. The determination of the end-point electrometrically is very satisfactory.[7]

Experimental

A standard iron solution was made by dissolving electrolytic iron (99.97% Fe) in hydrochloric acid. The ferrous chloride was largely

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[1] From a dissertation submitted by Philena Young to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] Willard and Young, THIS JOURNAL, **50**, 1322 (1928).

[3] Furman, *ibid.*, **50**, 755 (1928).

[4] Barnebey, *ibid.*, **36**, 1429 (1914).

[5] Erich Müller, "Elektrometrische Massanalyse," Th. Steinkopff, Dresden, 1926, pp. 152–153; Müller and Möllering, *Z. anorg. allgem. Chem.*, **141**, 111 (1924).

[6] Knop, THIS JOURNAL, **46**, 263 (1924); Mehlig, *J. Chem. Education*, **3**, 824 (1926).

[7] Hildebrand, THIS JOURNAL, **35**, 847 (1913); Kolthoff, *Chem. Weekblad*, **16**, 450 (1919); Hostetter and Roberts, THIS JOURNAL, **41**, 1337 (1919); Eppley and Vosburgh, *ibid.*, **44**, 2148 (1922).