According to the method of Horn,[3] the sensitivity curve (Fig. 7) shows that with 50cc. Nessler tubes the best range of the test is from 0.01 to 0.2 mg. When glycerine or a stronger solution of the dye is employed, the sensitiveness is decreased considerably.

Summary

An experimental study of the reaction of Alizarin Red S with aluminum under various conditions has been made, and quantitative measurements on the following effects were obtained: (1) time, (2) temperature, (3) volume, (4) concentration of reagents and (5) the presence of other ions. The range and the sensitiveness of the test have been determined.

UNIVERSITY, VIRGINIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

APPLICATIONS OF CERIC SULFATE IN VOLUMETRIC ANALYSIS. I. THE PREPARATION AND STABILITY OF SOLUTIONS OF CERIC SULFATE (CONTAINING FREE SULFURIC ACID). II. POTENTIOMETRIC STUDY OF THE REACTIONS BETWEEN CERIC AND FERROUS OR OXALATE ION. APPLICATION TO THE STANDARDIZATION OF CERIC SOLUTIONS. III. THE POTENTIOMETRIC DETERMINATION OF CERIUM

BY N. HOWELL FURMAN

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Introduction

Barbieri[1] was apparently the first to propose the use of a solution of ceric sulfate in volumetric analysis. He described the direct titration of nitrite with ceric sulfate. The end-point was determined by the disappearance of the yellow color of the ceric ion (the nitrite solution was placed in the buret). He found that more exact results could be obtained by adding an excess of ceric solution. The excess of ceric salt was then determined iodimetrically. It was stated that the nitrite solution could contain nitrates and that the ceric solution need not be free from other rare earths. No experimental data were given.

A solution of ceric sulfate, or of other ceric salts, was found by Sommer and Pincas[2] "to be ideal" for the quantitative oxidation of hydrazoic acid. The volume of nitrogen that was evolved was measured.

Quite recently Martin[3] has used ceric sulfate for the oxidation of hydra-

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[3] Horn, *Am. Chem. J.*, **36**, 195 (1906).

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

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

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

zine. The reagent was added in excess and an iodimetric back-titration was then made.

Hitherto, perhaps because of a lack of satisfactory indicators, no systematic study of the *direct* and indirect applications of ceric sulfate in volumetric analysis has been made. The author has found that ceric sulfate solutions that contain a moderate excess of sulfuric acid are quite stable, and he therefore proposes to make such a study. The familiar methods of potentiometric titration will be shown to be especially suitable for the determination of end-points.

Mention should be made of the fact that Van Name and Fenwick[4] have published graphs that represent the potentiometric titration of ceric with titanous sulfate. No data were given with regard to the accuracy, since these titrations were incidental to a study of bimetallic electrode systems. Recently Someya[5] has made a study of the potentiometric adaptation of Metzger's[6] bismuthate procedure for the oxidation of cerium. Someya titrates the quadrivalent cerium directly with standardized ferrous sulfate.

Preliminary qualitative orientation studies make it appear probable that a number of the titrations with ceric solution as reagent will be of both theoretical and practical interest.

Experimental

Preparation of Solutions of Ceric Sulfate in Dilute Sulfuric Acid.—The raw material was in some cases commercial cerous oxalate and in others mixed oxides of the rare earths.[7] In some instances (see Table I for details) no attempt was made to separate the cerium from the other rare earths. In other cases the details of James' method of basic bromate-nitrate separation were carefully followed.[8] The author found that this method was relatively easy to use and that it made possible the preparation of large quantities (30–50 g.) of pure, ignited ceric oxide in a few hours.[9] The purification was not found to be necessary in order to obtain a "stable" ceric solution. A much higher percentage of the oxide is, however, converted into the sulfate if the oxide is pure. The ceric oxide, whether obtained from the impure oxalate, basic bromate-nitrate or commercial mixed oxides, was heated with a large excess of sulfuric acid (sp. gr. 1.84) as directed by Meyer and Aufrecht.[10] Most of the excess of sulfuric acid was removed

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[4] Van Name and Fenwick, THIS JOURNAL, **47**, 9, 19 (1925).

[5] Someya, *Z. anorg. allgem. Chem.*, **168**, 56 (1927).

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

[7] The oxides were supplied through the courtesy of Dr. H. S. Miner of the Welsbach Co., Gloucester, N. J.

[8] James, THIS JOURNAL, **34**, 757 (1912); also James and Pratt, *ibid.*, **33**, 1326 (1911).

[9] Commercial specimens of cerous oxalate are far from pure. In two instances 22.25 and 22.8% of CeO_2 were found, respectively, whereas $Ce_2(C_2O_4)_3 \cdot 10H_2O$ contains 47.5%.

[10] Meyer and Aufrecht, *Ber.*, **37** (1), 140 (1904); it is interesting to note that H. Rose, "Handbuch d. analyt. Chemie," Vol. II, **1871**, p. 70, states that ceric oxide is soluble in sulfuric acid without the evolution of oxygen. Spencer, *J. Chem. Soc.*, [2] **107**, 1265 (1915), carries out the heating at water-bath temperature. Cuttica and Bonamici *Gazz. chim. ital.*, **53**, 761 (1923), state that the CeO_2 should be boiled with the acid.

from the practically insoluble ceric sulfate by decantation. The remaining paste of ceric sulfate and sulfuric acid was treated with cold water little by little. There is usually an insoluble residue of unattacked oxide that must be removed by filtration (asbestos). The author confirmed the finding of other investigators[7,10] that the unattacked residue is much greater when the oxide is impure.

The Stability of Ceric Sulfate Solutions (Containing Sulfuric Acid).—Ceric sulfate solutions are reported in the literature to be unstable.[11] No data are given as to the extent of the instability. There is no *a priori* reason to expect that such solutions should be less stable than equivalent solutions of potassium permanganate.

Data regarding the stability of ceric sulfate solutions that have been accumulated, in part incidentally (Solutions I–IV), in the study of various bimetallic electrode systems, are presented in Table I.

TABLE I

THE STABILITY OF CERIC SULFATE SOLUTIONS (WITH FREE SULFURIC ACID PRESENT)

Time, weeks	Normalities of ceric sulfate solutions I	II	III	IV	V	VI
0	0.02000	0.03334	0.04292	0.04828	0.1093	0.07830
1	.02001	....	....	.04822	.1090	.07830
2	....	.03323	....	....	....	.07832
4	.02001	.03321	....	.04821	.1090	.07832
6	.02004	....	.04274	.04813	....	.07833
12	....	.03306	.04268	.04788	.1094	....

Solutions I and II were prepared from impure CeO_2 that was obtained by the ignition of commercial oxalate; No. III from impure commercial oxide; nos. IV–VI from nearly pure oxide that was prepared by James' method.

Between 10 and 40 cc. of free sulfuric acid (sp. gr. 1.84) were present per liter of ceric solution. The normalities of the solutions were determined by adding a measured excessive quantity of freshly standardized ferrous sulfate solution and titrating the excess of ferrous salt with permanganate solution (0.05 or 0.1N) that had been standardized against pure sodium oxalate. The volumetric apparatus that was used had been carefully calibrated. The normalities that are given in the table are averages of two (in a few instances more) concordant determinations. Solutions I–IV were kept in clear glass bottles and were exposed to diffuse but not direct sunlight; their temperature was not as carefully controlled as was the case for solutions V and VI. The two latter solutions were kept in the dark.

From the data already in hand it appears that dilute sulfuric acid solutions of ceric sulfate possess at least a moderate degree of stability. Further observations regarding the stability of ceric solutions will be included in future communications regarding the applications of such solutions. The method of Meyer and Aufrecht[10] insures the preparation of ceric solutions that are perhaps more nearly free of halogen than those that are prepared by many other methods (oxidation of precipitated ceric hydroxide with halogens, etc.).

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[11] Brauner, *Z. anorg. allgem. Chem.*, 39, 286 (1904); Bauer and Glaessner, *Z. Elektrochem.*, 9, 534 (1903); see also handbooks, for example, Abegg, Mellor, etc.

II. Potentiometric Study of the Reaction between Ceric and Ferrous or Oxalate Ion. Application to the Standardization of Ceric Solutions

In the preceding section it has been shown that ceric solutions acidified with sulfuric acid are quite stable. The reaction between such a solution and a standardized ferrous sulfate solution has many obvious applications; it serves as a convenient means of checking the normality of ceric solutions. A thorough study of the reaction was therefore made.

Experimental

The Ceric-Ferrous Reaction.—The majority of the determinations were made with the same apparatus that has been described elsewhere.[12] The indicator electrodes were spirals of bright platinum wire of 6–8 cm. length (No. 28 B. and S. gage). In all titrations that involve ceric ion it is well to exclude chloride, and hence a bridge of approximately N potassium sulfate solution was inserted between the N calomel electrode (N. C. E.) and the titration beaker. A simple slide-wire potentiometer was used in that portion of the work which was done at the analytical chemical laboratory of the Eidgenössche Technische Hochschule at Zürich, Switzerland.

The potentiometric titration of ceric sulfate with freshly standardized ferrous sulfate in dilute sulfuric acid solution gives accurate results. The jump in potential at the end-point is very large, and under the conditions that were employed (50–100 cc. of solution containing 3–5 cc. of sulfuric acid of sp. gr. 1.84), 0.05 cc. of 0.05 N ferrous sulfate produces a change of 0.3–0.37 volt, at the end-point. The potential readings are steady except within a short range (2–5 drops, depending on the dilution) about the end-point. It is necessary to wait a few minutes for the reaction to complete itself (1–4 minutes) after the addition of each drop of reagent. The potentials tend up if the end-point has not been reached. The data in the following table indicate the accuracy of the determination.

TABLE II

TITRATION OF CERIC SOLUTIONS WITH FERROUS SULFATE

A. Ceric solution 0.0200 N

$FeSO_4$, calcd., cc.	13.66	27.36	13.66	19.68	19.88
$FeSO_4$, found, cc.	13.63	27.41	13.70	19.65	19.87
Error, cc.	− 0.03	+ 0.05	+ 0.04	− 0.03	− 0.01

B. Ceric solution 0.0429 N

$FeSO_4$, calcd., cc.	21.33	21.33	21.50	21.50
$FeSO_4$, found, cc.	21.31	21.37	21.52	21.46
Error, cc.	− 0.02	+ 0.04	+ 0.02	− 0.04

C. Ceric solution 0.1093 N

$FeSO_4$, calcd., cc.	22.65	32.46	32.46	24.44	24.44
$FeSO_4$, found, cc.	22.68	32.41	32.41	24.48	24.50
Error, cc.	+ 0.03	− 0.05	− 0.05	+ 0.04	+ 0.06

The ferrous sulfate solutions that were used were all approximately 0.05 N. The calculated values are based upon averages of two or more concordant determinations that were made by adding standard ferrous sulfate in excess, followed by back-titration with permanganate; the end-points were determined potentiometrically. The results that are given are representative of a much larger number of observations. The

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[12] Furman, *J. Chem. Education*, **3**, 932 (1926).

determination is accurate over a wide range of dilutions. The general nature of the titration graph is indicated by Curve 1, Fig. 1. The disappearance of the ceric color cannot be observed accurately enough to serve as end-point indication in 0.05 *N* solution. The yellow color disappears from 1–3 drops before the potentiometric end-point and serves as a convenient warning of the approach of the end-point. These observations were made before the work of Someya[5] appeared. The observations of the author are in complete accord with Someya's description of the potentiometric titration of ceric with ferrous ion. He did not, however, study the titration of ceric solutions of known content; the results that are here presented extend the range of dilutions over which the reaction is known to be accurate. Someya states that a calomel half cell was used, but makes no mention of the use of a salt bridge.

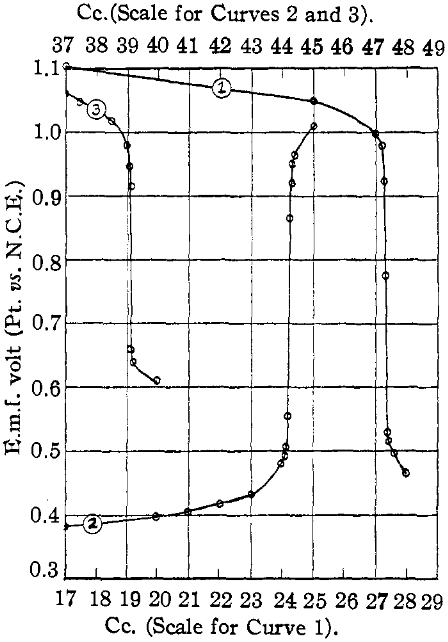

Fig. 1.—Curve 1, titration of 50 cc. of 0.0200 *N* ceric sulfate with 0.03654 *N* ferrous sulfate (abscissas at bottom of figure). Curve 2, titration of 50 cc. of 0.0691 *N* ferrous sulfate with 0.0783 *N* ceric sulfate. Curve 3, titration of 50 cc. of 0.0783 *N* ceric sulfate with 0.1000 *N* oxalic acid (abscissas for Curves 2 and 3 are above the figure).

The reverse titration, which has not hitherto been described, was found to be accurate. Here again the potentials are not established immediately, in the neighborhood of the equivalence point. The same effect is noticeable in the potentiometric titration of ferrous ion with permanganate under like conditions. If the end-point has not been reached, the potentials tend down. A few representative results follow.

The accuracy is, therefore, of the same order as in the reverse titration. Additional observations were made with more dilute and more concentrated solutions; the accuracy was of the same order as for the data that have been presented. Curve 2, Fig. 1, is a representative titration graph.

Table III

Titration of Approximately 0.05 *N* Ferrous Sulfate with Ceric Sulfate (0.04822 or 0.0546 *N*)

Ceric, soln. calc., cc.	25.55	25.55	26.28	26.28	22.59
Ceric, soln. found, cc.	25.57	25.50	26.30	26.25	22.56
Error, cc.	+ 0.02	− 0.05	+ 0.02	− 0.03	− 0.03

It seems obvious that ceric sulfate solutions may be used for the determination of iron or, conversely, may be standardized against ferrous solutions of known strength. Titrations of separate specimens of Mohr's salt, that contained 14.29 and 14.23% of Fe by permanganate analysis (theory, 14.24%), yielded an average normality of 0.07820 for a ceric solution that was found to be 0.07830 *N* ($FeSO_4$-$KMnO_4$) and 0.07832 *N* iodimetrically.

Other Electrode Systems.—It was found possible to use the Pt-gold amalgam electrode system that the author has described[13] for ceric-ferrous titrations. The titration errors found were −0.01, +0.04 cc. (titration with ferrous) and +0.03, −0.03, +0.00 cc. in the reverse titration. The Pt-W "galvanometric" method that Furman and Wilson have described[14] gave errors of −0.03, −0.01, +0.03 cc. (titration with ferrous), and +0.03, +0.05, and −0.01 cc. (titration with ceric). The resistance was 150,000 ohms and end-point deflections of 10–14 galvanometer divisions were found. The rated sensitivity of the galvanometer was 0.15 micro-ampere (per division) (Leeds and Northrup Co., No. 2310-D).

The Reaction between Ceric and Oxalate Ions. Application to the Standardization of Ceric Solutions.—This reaction seems to afford a convenient method of standardizing ceric solutions. When a ceric solution is titrated with oxalic acid satisfactory results are obtained if the ceric solution is at 50–60°. At room temperature the reaction is very slow near the end-point, as one would expect from the work of Benrath and Ruland,[15] who studied the kinetics of the reaction. At the higher temperature the reaction is rapid and the ceric color is enhanced, probably because of increasing dissociation of the ceric complexes, and the disappearance of the yellow color gives a sharp end-point with good illumination. Observations that were made during the course of potentiometric studies showed that the color end-point is on the average 0.03 cc. before the potentiometric for approximately 0.1 *N* solutions.

An exactly 0.1 *N* solution of oxalic acid was prepared by dissolving 6.700 g. of pure sodium oxalate in water that contained 10 cc. of sulfuric acid of sp. gr. 1.84, and diluting to a liter. Such a solution has been shown to be stable when shielded from light, whereas oxalic acid alone is unstable in solution.[16] The ceric solution had been found to be 0.07833 *N* (av. of four concordant determinations with ferrous sulfate in excess, followed by titration with permanganate that had been standardized against the same sodium oxalate). By direct titration with 0.1 *N* oxalic acid the ceric solution was found to be 0.07828, 0.07836, 0.07826, 0.07820, 0.07840, average 0.07830. Expressed in terms of cc. of error on the assumption that the permanganate values are correct, the deviations are −0.01, +0.01, +0.03, −0.03, +0.05. The buret delivered 0.025 cc. per drop; either 25 or 50 cc. of ceric solution was titrated. The potential values are imme-

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[13] Furman, This Journal, **50**, 268 (1928).

[14] Furman and Wilson, *ibid.*, **50**, 277 (1928).

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

[16] Beckurts, "Massanalyse," Vieweg and Son, Braunschweig, **1913**, or Treadwell-Hall, "Analytical Chemistry," Vol. II, John Wiley and Sons, Inc., New York, for details.

diately steady to within 0.1–0.2 cc. of the end-point. No precipitate of cerous oxalate is formed until several cc. of oxalic acid have been added beyond the end-point. The character of the titration graph is shown by Curve 3, Fig. 1.

The reverse titration is apparently accurate, but is not practicable because of the slow rate of reaction, even at points remote from the equivalence point. Pure sodium oxalate was dissolved in 50 cc. of solution that contained 5 cc. of concd. sulfuric acid. The solutions were at 50°. The average of two titrations yielded a normality of 0.07820 for the ceric solution. No precipitate of cerous oxalate is formed under these conditions.

III. The Potentiometric Determination of Cerium

The work that is here presented has in part been anticipated by the appearance of an investigation by Someya,[5] who studied the application of potentiometric titration with ferrous sulfate to the determination of cerium that had been oxidized with sodium bismuthate.[17]

The author had commenced a comparative study of the potentiometric determination of cerium with ferrous sulfate, after oxidation to the ceric condition by Metzger's[6] method or von Knorre's persulfate method,[18] with a potentiometric method that is very different in principle, namely, the oxidation of cerous salt in potassium carbonate solution by potassium ferricyanide[19] that has been proposed by Tomiček.

The results that had been obtained at the time of the appearance of Someya's work will be presented briefly because they confirm his experience, and in addition show that the bismuthate, persulfate and ferricyanide methods are in substantial agreement.

In studying the potentiometric application of the ferrous titration to solutions of cerium that had been oxidized by persulfate it was necessary to consider the recent work of Lindeman and Hafstad,[20] who have found that the best range of sulfuric acid concentration for complete oxidation with ammonium persulfate is between 2.7 and 9.5 g. of acid per 100 cc. of solution. For quantities of the cerium metals between 0.05 and 0.75 g., they find an optimum acid concentration of about 3.2 g. per 100 cc. They report that constant values are obtained under these conditions, but that if a large quantity of magnesium sulfate is added (at least 5 g. of magnesium per 1 g. of cerium metals) constant results are again obtained that are appreciably higher than the former ones. They found **43.5%** of Ce in a given substance when no magnesium was added, and under like conditions **47.5%** of Ce with the presence of magnesium, and in another material **31.46%** of Ce without magnesium, and **34.50%** after the addition.

The author was unable to confirm these latter findings; the excess of cerium that was found was never as large as that reported by Linde-

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[17] Metzger's method, ref. 6; see also Metzger and Heidelberger, *ibid.*, **32,** 642 (1910).

[18] Von Knorre, *Z. angew. Chem.*, **1897,** 685, 717.

[19] Method of Browning and Palmer, *Am. J. Sci.*, **26,** 83 (1908); Tomiček, *Rec. trav. chim.*, **44,** 410 (1925).

[20] Lindeman and Hafstad, *Z. anal. Chem.*, **70,** 433 (1927).

man and Hafstad, nor was the excess constant with variable duration of boiling of the solutions in order to decompose the excess of persulfate. The addition of magnesium sulfate appears to be undesirable because it alters the acid concentration and also seems to prevent the decomposition of the last traces of persulfate. If two solutions are oxidized under like conditions with 5 g. of magnesium present per g. of cerium metals, then boiling for fifteen minutes to decompose the excess of persulfate gives results that check. If the boiling is continued for thirty minutes, the results again check, but at a lower titer than before. Even one hour's boiling does not bring the titer down to the value that is found when no magnesium is added. The titration graphs show an ill-defined inflection that lies high in the oxidizing region within a few drops of the end-point when magnesium is present in excess; this is apparently due to undecomposed persulfate.

The results of a number of comparative determinations are assembled in the following table.

TABLE IV

COMPARISON OF POTENTIOMETRIC METHODS FOR THE DETERMINATION OF CERIUM

	Method employed							
	Titr. with Fe^{++} after persulfate oxidation usual meth.		mod. method[a]		Bismuthate oxidation titr. with Fe^{++}		Ferricyanide (Tomiček)	
Oxalate "A," % CeO$_2$	22.89	22.81	23.00	22.90	22.85	22.85	22.76	22.70
			23.07		22.90			
Cc. of 0.1N soln. per 1.3666 g. of oxalate	18.16	18.10	18.25	18.18	18.13	18.13	18.07	18.02
			18.30		18.18			
Oxalate "B," % CeO$_2$	22.25	22.37	22.55	22.21	22.28		...	...
	22.29		22.49					
			22.30					
			22.37					
Cc. of 0.1N soln. per 1.4279 g. of oxalate	18.96	19.07	19.22	18.93	18.99			
	19.00		19.18					
			19.00					
			19.07					
Ceric oxide (partially purified), % CeO$_2$	93.50	93.50	94.44	93.52	93.85		93.52	93.84
			94.92					
			93.91					
			94.06					
Cc. of 0.1N soln. per 0.3319 g. of oxide	18.03	18.03	18.20	18.04	18.09		18.04	18.08
			18.29					
			18.10					
			18.13					

[a] Method of Lindeman and Hafstad that involves addition of at least 5 g. of magnesium as sulfate per g. of Ce metals before the oxidation.

The customary persulfate, the bismuthate and the ferricyanide methods are in fair agreement. Tomiček's method is convenient when the apparatus has been assembled. The necessity of rigid exclusion of air and of employing large quantities of potassium carbonate militate against the method. In point of time required, the bismuthate and persulfate methods are approximately equivalent, provided the excess of bismuthate must be filtered off. According to Someya[5] this filtration is not necessary if the bismuthate is pure.

The data show that the modification that was suggested by Lindeman and Hafstad[20] does not give results that are mutually consistent or that check with other methods. The determinations that are bracketed together were made at the same time and under as nearly as possible the same conditions. The time of boiling was not accurately recorded for the first sample of oxalate. In the other two instances the first pair of determinations was made after 25–30 minutes of boiling, and the second pair after 50–60 minutes of boiling. In all cases where the customary conditions are used, from 20 to 30 minutes' boiling after the end of the oxidation is sufficient to destroy the excess of persulfate, provided the conditions that von Knorre[18] first established are carefully followed.

The determinations that are given for the per cent. of CeO_2 in the oxalates were in part made upon small separate samples, and in part upon solutions of large quantities of the oxalate. In case of the ceric oxide all of the determinations were made upon a uniform solution that was prepared by transposing the oxide to the sulfate. After dilution, reduction was effected by excess of hydrochloric acid, which was removed by heating. A small quantity of ceric salt escaped reduction and was decolorized with a slight excess of hydrogen peroxide in strongly acid solution followed by boiling to destroy the excess. For convenience in comparison the quantity of exactly 0.1 N reagent per constant weight of substance is given in each case.

Work is now in progress upon direct applications of ceric sulfate in the potentiometric titration of various reducing substances.

Acknowledgment

A portion of the experimental work that is here presented was done in the analytical chemical laboratory of the Eidgenössche Technische Hochschule, Zürich, Switzerland. The author wishes to make grateful acknowledgment of the privilege of working as guest in this Laboratory, and to thank the authorities of the Technische Hochschule, and especially Professor W. D. Treadwell, for making this arrangement possible.

Summary

Solutions of ceric sulfate in diluted sulfuric acid are sufficiently stable to be used in volumetric analysis. It is advisable to use pure ceric oxide in their preparation and to shield the solutions from direct sunlight.

The reaction between ceric and ferrous solutions is suitable for the potentiometric determination of either ion with a high order of accuracy. The reaction is sluggish near the equivalence point but this fact does not cause serious inconvenience. The reaction may be applied in the standardization of ceric solutions and in the potentiometric determination of cerium.

Ceric solutions may be standardized or determined by titration with standard oxalic acid. The ceric solution must be heated. The reverse titration is impractical because of the slow rate of reaction, even when the oxalic acid solution is heated.

A potentiometric study of the determination of cerium has been made. Oxidation by bismuthate or persulfate followed by potentiometric titration with ferrous sulfate is a very rapid and satisfactory mode of procedure.

PRINCETON, NEW JERSEY, and
ZÜRICH, SWITZERLAND

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 163]

THE CRYSTAL STRUCTURES OF BETA BENZENE HEXABROMIDE AND HEXACHLORIDE

BY ROSCOE G. DICKINSON AND CONSTANT BILICKE

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Introduction

In a previous investigation[1] β-benzene hexabromide,[2] $C_6H_6Br_6$, and β-benzene hexachloride, $C_6H_6Cl_6$, both crystallizing in the cubic system, were found to possess the space group symmetry T_h^6 with four molecules in the cubic unit of structure. The $C_6H_6X_6$ molecule was found to possess a three-fold rotation axis and a center of symmetry. Since all atoms of any one element are in equivalent positions, and since all atoms are in the general positions,[3] a completion of the structure determination requires the evaluation of three parameters for each element in each compound. In the case of the bromide, where the great majority of all electrons are in the bromine atoms, at least the predominant features of the intensities of x-ray reflection must be determined by the positions of the halogen atoms. Consequently a determination of the bromine

[1] Hendricks and Bilicke, THIS JOURNAL, **48**, 3007 (1926).

[2] Since this paper confines itself to the beta isomers, the Greek prefix will be omitted.

[3] The coördinates of the general positions in T_h^6 are:

$$(xyz)(\tfrac{1}{2}+x, \tfrac{1}{2}-y, \bar{z})\ (\bar{x}, \tfrac{1}{2}+y, \tfrac{1}{2}-z)(\tfrac{1}{2}-x, \bar{y}, \tfrac{1}{2}+z)$$
$$(zxy)(\bar{z}, \tfrac{1}{2}+x, \tfrac{1}{2}-y)(\tfrac{1}{2}-z, \bar{x}, \tfrac{1}{2}+y)\ (\tfrac{1}{2}+z, \tfrac{1}{2}-x, \bar{y})$$
$$(yzx)(\tfrac{1}{2}-y, \bar{z}, \tfrac{1}{2}+x)(\tfrac{1}{2}+y, \tfrac{1}{2}-z, \bar{x})(\bar{y}, \tfrac{1}{2}+z, \tfrac{1}{2}-x)$$
$$(\overline{xyz})(\tfrac{1}{2}-x, \tfrac{1}{2}+y, z)(x, \tfrac{1}{2}-y, \tfrac{1}{2}+z)(\tfrac{1}{2}+x, y, \tfrac{1}{2}-z)$$
$$(\overline{zxy})(z, \tfrac{1}{2}-x, \tfrac{1}{2}+y)\ (\tfrac{1}{2}+z, x, \tfrac{1}{2}-y)(\tfrac{1}{2}-z, \tfrac{1}{2}+x, y)$$
$$(\overline{yzx})(\tfrac{1}{2}+y, z, \tfrac{1}{2}-x)(\tfrac{1}{2}-y, \tfrac{1}{2}+z, x)\ (y, \tfrac{1}{2}-z, \tfrac{1}{2}+x).$$