10–27°. A comparison of values found by other investigators is included. It is shown that the concentration of the volatile component in the water, phase can be determined by means of the vapor pressure measurements and the concentration of water in the sulfur dioxide phase, approximately calculated by using Raoult's Law.

A method was designed for separating a portion of one liquid phase from any three phase system (liquid–liquid–gas) which is in equilibrium at pressures which are so great that there is difficulty in obtaining accurate analysis of the equilibrium concentration. This method was employed for measuring the concentration of sulfur dioxide in the aqueous phase and the values deduced from the vapor pressure measurements for the range 10–27° were confirmed at the temperature where measurements were made.

A method was devised by means of which the concentration of water in the sulfur dioxide phase can be more exactly determined. This method consisted in the measurement of vapor pressures of solutions of water in sulfur dioxide, and gave values agreeing very closely with those calculated.

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CERIC SULFATE AS A VOLUMETRIC OXIDIZING AGENT. III. THE TITRATION OF IODIDE

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Introduction

Previous work with ceric sulfate as a volumetric oxidizing agent[2] suggested the importance of investigating potentiometrically the iodide-ceric salt reaction. Lange[3] stated that since ceric sulfate, even in the most dilute solutions, set free iodine from potassium iodide, it might be used as an oxidizing agent in volumetric analysis. Numerous investigators have made use of this reaction[4] as an iodimetric method for ceric cerium, their procedure being to treat the ceric salt with excess iodide in acid solution and to titrate the iodine liberated with thiosulfate. The direct titration of iodide with ceric sulfate, however, or the reverse reaction appears not

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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, 1334 (1928).

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

[4] Bunsen, *Ann. Chem.*, **86**, 285 (1853); Hartley, *J. Chem. Soc.*, **41**, 202 (1882); Browning, Hanford and Hall, *Z. anorg. Chem.*, **22**, 297 (1899); Browning, *Am. J. Sci.*, **158**, 451 (1899); Power and Shedden, *J. Soc. Chem. Ind.*, **19**, 636 (1900); Meyer and Koss, *Ber.*, **35**, 3740 (1902); Brauner, *Z. anorg. Chem.*, **34**, 207 (1903).

to have been worked out. The present paper describes the results obtained for these reactions in a hydrochloric or a sulfuric acid medium.

Experimental

The 0.05 *N* potassium iodide, prepared from especially pure material, was standardized against potassium permanganate[5] the normality of which had been determined with sodium oxalate. From two analyses the same factor, 0.05325 *N*, was obtained. The 0.1 *N* ceric sulfate was that prepared for earlier work[2] and was 0.5 *M* in sulfuric acid. It was standardized against sodium oxalate. Measured portions of potassium iodide were taken, diluted with water and sulfuric acid to definite volumes and titrated electrometrically with 0.1 *N* ceric sulfate. The results are shown in Table I.

TABLE I

TITRATION OF IODIDE WITH CERIC SULFATE IN SULFURIC ACID SOLUTION

KI, 0.05 *M*, cc.	H_2SO_4 (sp. gr. 1.25) at beginning, cc	Vol. at beginning, cc.	KI, normality
25	0	100	0.05324
25	10	100	.05320
25	50	100	.05324
25	20	200	.05324
50	0	100	.05320
50	15	100	.05318
50	15	200	.05320

The potential break at the end-point amounted to 175–200 mv. per 0.03 cc. of 0.1 *N* ceric sulfate. In the presence of bromide the break was decreased. With a ratio of I : Br = 5 : 1, it became 45 mv. per 0.03 cc. of 0.1 *N* solution. The iodide factor obtained above corresponds to the reaction

$$2Ce(SO_4)_2 + 2KI = Ce_2(SO_4)_3 + K_2SO_4 + I_2$$

Thus, the titration of iodide in sulfuric acid solution with ceric sulfate or potassium permanganate, both of which have been standardized against the same primary standard, gives values which agree within less than 1 part in a thousand.

Measured portions of 0.1 *N* ceric sulfate were taken, diluted with water and sulfuric acid to 100 cc., and titrated electrometrically with 0.05 *M* potassium iodide. The results are shown in Table II.

TABLE II

TITRATION OF CERIC SULFATE WITH IODIDE IN SULFURIC ACID SOLUTION

$Ce(SO_4)_2$, 0.1 *N*, cc.	H_2SO_4 (sp. gr. 1.83) at beginning, cc.	KI, actual vol., cc.	KI, theoretical vol., cc.
25	5	25.40	25.36
25	10	25.38	25.36
15	5	15.24	15.22
50	5	50.75	50.72

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[5] Müller and Möllering, *Z. anorg. Chem.*, 141, 111 (1924), have shown that this titration is a very accurate one.

The potential break at the end-point amounted to 250–300 mv. per 0.03 cc. of 0.05 *M* iodide solution. The theoretical volumes were obtained by calculations from the data from two reverse titrations in which 25 cc. of potassium iodide required 24.66 and 24.64 cc. of ceric sulfate.

It was found possible to use this iodide titration after the bismuthate oxidation[6] of a cerous salt as a method for cerium. An approximately 0.05 *N* cerous sulfate solution was prepared from C. P. material. Fifty cc. portions of this solution, after oxidation with bismuthate and electrometric titration with ferrous sulfate which had been standardized electrometrically against standard ceric sulfate, were found from three analyses which agreed closely to contain 0.1745 g. of cerium. Table III gives the corresponding data for analyses in which the ceric sulfate formed was titrated with potassium iodide which had been standardized electrometrically against a ceric sulfate solution of known strength.

TABLE III

DETERMINATION OF CERIUM

$Ce_2(SO_4)_3$, 0.05 *N*, cc.	Ce found	Ce present
25	0.0873, 0.0874	0.0873
50	0.1745, 0.1748, 0.1745	0.1745
100	0.3501, 0.3493, 0.3502	0.3490

Titration in Hydrochloric Acid Solution

Measured portions of 0.05 *M* potassium iodide were taken, diluted with water to a definite volume, treated with hydrochloric acid according to the procedures described below and titrated electrometrically with 0.1 *N* ceric sulfate, forming iodine chloride. The potassium iodide is the same solution as in Table I. Therefore its factor should be 2 × 0.05321 *N* or 0.1064 *N*, and was actually found to have this value by comparison with standard ceric sulfate. The results are given in Table IV.

TABLE IV

TITRATION OF IODIDE WITH CERIC SULFATE IN HYDROCHLORIC ACID SOLUTION

KI, 0.05 *M*, cc.	HCl (sp. gr. 1.18), cc.	Vol. at beginning, cc.	KI, normality
25	55	100	0.1060
25	45	100	.1060
25	35	100	.1061
25	25	100	.1062
25	45	300	.1060
15	45	100	.1058
50	45	100	.1057

Nearly all of the ceric sulfate was added rapidly to the iodide solution from a pipet before the hydrochloric acid was poured in. An odor of iodine was noticeable in the experiments and this loss was undoubtedly the cause

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

for the slightly low results. If the acid was added before the ceric sulfate, the average factor obtained for the iodide was 0.1057–0.1058 *N*. When all but 0.2 cc. of the ceric sulfate, followed by the hydrochloric acid, was added to the iodide in a glass stoppered flask, the closed flask shaken thoroughly and its contents transferred to a beaker for the completion of the titration, the average factor from two closely agreeing titrations was 0.1061 *N*. Using a ratio of Br : I = 2 : 3, and 25 cc. of the iodide solution, the end-point break amounted to 30 mv. per 0.03 cc. of 0.1 *N* solution instead of 125–150 mv. for the same volume, the value obtained for the experiments in the table above. With 25 cc. of concd. hydrochloric acid per 100 cc., the equilibrium at the end-point was very slow; with less than this amount of acid, not practical.

Willard and Fenwick's[7] method of titrating iodide electrometrically in the presence of cyanide with permanganate, in which the iodide was changed quantitatively into iodine cyanide, was tested, using standard ceric sulfate instead of permanganate as the oxidizing agent. The reaction was found to be quantitative and the end-point equilibrium rapid.

A few experiments similar to those in Table IV were made using standard potassium iodate instead of ceric sulfate. The factor of the iodide varied from 0.1056 *N* to 0.1061 *N* as the conditions were changed, indicating the same loss of iodine.

Summary

1. Iodide may be determined very accurately in a sulfuric acid solution by electrometric titration to iodine with standard ceric sulfate. Moderate amounts of bromide may be present.
2. The titration of ceric sulfate with iodide in sulfuric acid solution goes smoothly and may be used in determining cerium after a bismuthate oxidation.
3. When iodide is titrated in a hydrochloric acid solution to iodine chloride with ceric sulfate, a small loss of iodine occurs during the oxidation and causes the results to be low—five parts or less in a thousand.

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[7] Willard and Fenwick, THIS JOURNAL, **45**, 623 (1923).