The melting point was found to be 222.31 ± 0.05°K.; the boiling point, 237.75 ± 0.05°K.

The heat of fusion is 686.3 ± 0.8 cal. per mole. The heat of vaporization at the boiling point is 4724 ± 5 cal. per mole.

Two regions of high heat capacity were found in the solid state which appear to be internal transitions of the molecule; however, one of these, in particular, after progressing over a considerable temperature range, seems to develop into the ordinary or sharp transition type.

The entropy has been calculated from the experimental data and the third law of thermodynamics.

The entropy has also been calculated from spectroscopic data. The two methods lead to the same value within the limit of our experimental error, thus supporting the validity of each method.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

APPLICATIONS OF CERIC SULFATE IN VOLUMETRIC ANALYSIS. VI. OXIDATION OF HYDROGEN PEROXIDE BY CERIC SULFATE. INDIRECT DETERMINATION OF LEAD

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Introduction

Some of the uses of ceric sulfate in volumetric analysis have been described in other papers of this series[1] and in those of other investigators.[2] Von Knorre[3] made use of the reaction

$$2Ce(SO_4)_2 + H_2O_2 = Ce_2(SO_4)_3 + H_2SO_4 + O_2$$

in the determination of cerium. He added an excess of hydrogen peroxide (freshly standardized) to the ceric solution and determined the excess of the former with 0.1 *N* permanganate solution. Atanasiu and Stefanescu have published data for a single potentiometric titration of hydrogen peroxide with ceric sulfate in sulfuric acid solution. Our observations have been made with various acids and with a variety of different concentrations of acid.

Experimental

The apparatus was similar to that described in previous papers of this series; a bright platinum wire and a N calomel electrode made up the electrode system.

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[1] N. H. Furman, THIS JOURNAL, **50**, 755, 1675 (1928); Furman and Evans, *ibid.*, **51**, 1128 (1929).

[2] H. H. Willard and Philena Young, *ibid.*, **50**, 1322, 1334, 1368, 1372, 1379 (1928); **51**, 139, 149 (1929); *Ind. Eng. Chem.*, **20**, 972 (1928); I. A. Atanasiu, *Bull. soc. roum. chim.*, **30**, 1 (1928); Atanasiu and V. Stefanescu, *Ber.*, **61**, 1343 (1928); H. Rathsberg, *ibid.*, **61**, 1664 (1928).

[3] V. Knorre, *Z. angew. Chem.*, **10**, 685, 717 (1897); *Ber.*, **33**, 1924 (1900).

The ceric sulfate solutions were prepared in two ways: (1) by dissolving commercial rare earth oxides in enough dilute sulfuric acid to make the resulting solution about 2–3 *N* in sulfuric acid when 0.1 *N* in oxidizing power; (2) by heating purified oxide (basic nitrate method) with an excess of sulfuric acid at approximately 200°. An appreciable portion of the oxide was unattacked. The resulting solution was approximately 0.1 *N* in oxidizing power and from 1.0–1.5 *N* in sulfuric acid. Both solutions were stable.

The solutions were standardized potentiometrically against pure sodium oxalate in hydrochloric acid solution of the concentration suggested by Willard and Young.[4]

Hydrogen peroxide solutions approximately 0.1 *N* were prepared by diluting pure 30% hydrogen peroxide (Merck's "Superoxol"). The solutions were kept in a smooth bottle of amber-colored glass, and were found to be stable for at least four hours. The normality of the hydrogen peroxide was determined by titration with potassium permanganate solution which had been standardized against sodium oxalate. All of the end-points were determined potentiometrically.

Titration of Hydrogen Peroxide with Ceric Sulfate.—Ten or 25 cc. of hydrogen peroxide were pipetted out and were generally diluted to 100 cc. after addition of acid. The nature and concentration of acid were found to be important factors; variations in initial volume or in rate of addition of ceric sulfate were minor factors. The titrations were made at room temperature. The results are summarized in the following table.

TABLE I

TITRATION OF APPROXIMATELY 0.1 *N* HYDROGEN PEROXIDE WITH CERIC SULFATE

A. In Hydrochloric Acid Solution

		1	2	3	4	5	6	7
Init. acid concn., *N*		2.5	2.5	2.5	1.7	0.5	5	2.5
Hydrogen perox., cc.		25	25	25	25	10	10	25
$Ce(SO_4)_2$ soln.	Calcd., cc.	27.27	27.27	27.27	27.27	10.91	10.91	34.72
	Found, cc.	27.26	27.31	27.30	27.28	10.89	10.90	34.70
Error in cc.		−0.01	+0.04	+0.03	+0.01	−0.02	−0.01	−0.02

B. In Sulfuric Acid Solution

		8	9	10	11	12	13
Initial acid concn., *N*		0.5	1.0	2	2	2	9
Hydrogen peroxide, cc.		25	10	25	25	25	25
$Ce(SO_4)_2$ soln.	Calcd., cc.	35.58	10.91	35.58	35.58	34.72	34.72
	Found, cc.	35.57	10.89	35.60	35.60	34.75	34.71
Error in cc.		−0.01	−0.02	+0.02	+0.02	+0.03	−0.01

		C. Acetic Acid		D. Nitric Acid	
		14	15	16	17
Initial concn. of acid, *N*		1	3	0.5	2
Hydrogen peroxide, cc.		10	10	10	25
$Ce(SO_4)_2$ soln.	Calcd., cc.	10.91	10.91	10.91	27.27
	Found, cc.	10.86	10.91	10.88	27.21
Error in cc.		−0.05	±0.00	−0.03	−0.06

Determinations 1–6, 9 and 14–17 were made with 0.0991 *N* ceric sulfate which was prepared from commercial rare earth oxides. In the other instances the ceric solution, prepared from the purified oxide, was 0.0760 *N*.

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[4] Willard and Young, THIS JOURNAL, **50**, 1327 (1928).

The character of the titration graphs is indicated in Fig. 1. The downward trend just before the end-point that is shown in Curve 2 is usually a characteristic of titrations in hydrochloric acid solution.

When the initial concentration of sulfuric acid is below 1 *N*, the rate of reaction is very small, and the break in potential at the end-point is usually below 0.1 volt. The reaction was very sluggish at all of the concentrations of sulfuric acid that were used. From three to five minutes are required for the potential to become steady near the end-point. The voltage rise at the end varies from 0.15 to 0.25 volt per 0.05 cc. of ceric solution as the concentration of acid is increased.

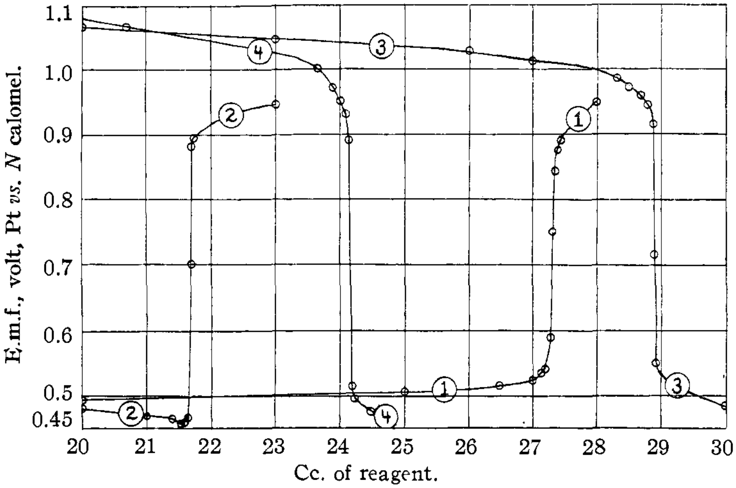

Fig. 1.—Curve 1. Titration of hydrogen peroxide in sulfuric acid solution (3.6 *N*). Curve 2. Titration of hydrogen peroxide in 1.2 *N* HCl solution. In 1 and 2 the ceric sulfate was 0.1051 *N*. Curve 3. Titration of 25 cc. (0.1051 *N*) ceric sulfate with peroxide. Initial acid concentration, 2.5 *N* (H_2SO_4). Curve 4. Titration of 25 cc. of 0.0991 *N* ceric sulfate with peroxide. Original acid concentration, 0.7 *N*.

The reaction proceeds very rapidly at all of the concentrations of hydrochloric acid that were tested. The rise in e.m.f. at the end-point is very sharp, and is of the order of 0.25–0.32 volt per 0.05 cc. of 0.1 *N* ceric solution. Acetic acid solutions give an equally rapid reaction rate and about the same rise in voltage at the end-point. When nitric acid is present the rise in voltage per drop of ceric solution is less, being of the order of 0.2–0.25 volt. The rate of reaction is somewhat slower than with hydrochloric acid.

The visual end-point was noted in a number of instances. In general it is 0.05 cc. beyond the potentiometric end-point. The presence of iron (about 1 mg. per 25 cc.) in the ceric solution obscures the end-point in solutions that contain high concentrations of hydrochloric acid.

The Reverse Titration.—The procedure was similar to that which has been described. The nature of the results is indicated in the following table.

TABLE II

TITRATION OF 0.0991 N CERIC SULFATE WITH 0.1027 N HYDROGEN PEROXIDE

Acid added		None	None	H_2SO_4	HNO_3	HNO_3	H_2SO_4
Initial concn., N		....	....	3	1.5	1.5	5
Ceric sulfate, cc.		25	25	25	25	25	10
H_2O_2, cc.	Calcd.	24.12	24.12	24.12	24.12	24.12	9.64
	Found	24.09	24.11	24.09	24.12	24.12	9.65
Error, cc.		−0.03	−0.01	−0.03	±0.00	±0.00	+0.01

When no acid was added the break in potential was about 0.4 volt per drop of hydrogen peroxide solution, and in the other instances it was about 0.2 volt per 0.05 cc. at the end-point. The nature of the graph is shown by Curves 3 and 4, Fig. 1.

Indirect Determination of Lead Peroxide

A determination of lead peroxide has been based upon the fact that an excess of hydrogen peroxide reacts with lead peroxide in nitric acid solution. The excess of hydrogen peroxide is then determined with permanganate.[5]

Our results showed that ceric sulfate could be employed to determine the excess of hydrogen peroxide.

Weighed samples of minium, ranging between 0.18 and 0.25 g., were transferred to a mixture of 25 cc. of approximately 0.1 N hydrogen peroxide (standardized against ceric sulfate) and 25 cc. of concentrated nitric acid of sp. gr. 1.42 (free from dissolved oxides of nitrogen). Solution of the lead oxide was complete after a few minutes' stirring. The excess of hydrogen peroxide was determined. The weight of PbO_2 was calculated from the amount of hydrogen peroxide that had been decomposed. The values which one of us (F) had obtained by Bunsen's iodometric method were unknown to the other (W) until after the determinations with ceric sulfate had been completed.

No. 1	Found, using $Ce(SO_4)_2$	33.71, 33.61, 33.95% of PbO_2
	Found, iodometrically	33.70, 33.89, 33.81, 33.65% of PbO_2
No. 2	Found, using $Ce(SO_4)_2$	25.68, 25.58, 25.61, 25.65, 25.81% of PbO_2
	Found, iodometrically	25.80, 25.73, 25.65% of PbO_2

After the end of a titration there was usually a slight precipitate of lead sulfate which did not interfere in any way with the convenience of the method.

The hydrogen peroxide–ceric sulfate procedure was not reliable in the determination of manganese dioxide in pyrolusite. The errors were in

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[5] Schlossberg, *Z. anal. Chem.*, **41**, 743 (1902).

the direction that would be expected on the basis of catalytic decomposition of hydrogen peroxide during the slow process of dissolving the mineral.

Summary

The direct potentiometric titration of hydrogen peroxide with ceric sulfate has been shown to be accurate in solutions moderately acidified with hydrochloric, sulfuric, nitric or acetic acid. The reverse titration is also accurate in sulfuric and nitric acid solutions.

The hydrogen peroxide–ceric sulfate reaction may be applied in the indirect determination of lead peroxide.

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REACTIONS IN LIQUID HYDROGEN SULFIDE. VI. REACTIONS WITH ORGANIC COMPOUNDS

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Hydrogen sulfide has been found by different workers to be a good solvent for organic substances[2] and for this reason it was thought important to study the reactions between liquid hydrogen sulfide and members of the different types of organic compounds.

Experimental

Several examples of each of the types of organic compounds were placed in glass tubes of 50-cc. capacity and, after cooling to $-77°$ with a mixture of ether and solid carbon dioxide, liquid hydrogen sulfide was added. The tubes were then sealed and allowed to come to room temperature. After standing for several weeks they were again cooled, opened, the excess of hydrogen sulfide was allowed to evaporate and the residues were examined for evidence of reaction.

The following types of organic compounds were studied: saturated hydrocarbons, unsaturated hydrocarbons, alcohols, phenols, ethers, aldehydes, ketones, alkyl and aryl halides, acids, acid anhydrides, esters, sugars, nitro compounds, Grignard reagent, amides, amines and acyl halides.

Hydrocarbons.—Benzene, toluene, naphthalene, anthracene, gasoline, kerosene and vaseline are all soluble and non-reactive in liquid hydrogen sulfide. The unsatu-

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[1] This paper is from a portion of the work presented to the Graduate Faculty of Iowa State College in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] McIntosh and Steele, *Proc. Roy. Soc. London*, **73**, 450 (1904); Archibald and McIntosh, *ibid.*, **73**, 454 (1904); Antony and Magri, *Gazz. chim. ital.*, **75**, 206 (1905); Steele, McIntosh and Archibald, *Phil. Trans. Roy. Soc.*, **205A**, 99 (1906); Magri, *Atti. accad. Lincei*, (V) **16**, 171 (1907); Quam, THIS JOURNAL, **47**, 103 (1925); Quam and Wilkinson, *ibid.*, **47**, 989 (1925); Ralston and Wilkinson, *ibid.*, **50**, 258 (1928).