

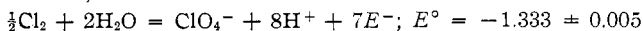
Combining this value with the free energy of solution of potassium perchlorate, +2688, and of potassium chloride,⁸ -936, gives



Using -20,430, the average of the two methods, and the Lewis and Randall⁴ value for the free energy of chloride ion, -31,367, we obtain for the free energy of perchlorate ion, $F_{298.1}^\circ = -10,937$ cal.

The error in this value is determined very largely by the accuracy of the heat of decomposition of potassium perchlorate measured by Berthelot. Although this is difficult to estimate, we judge it is within ± 500 cal.

For many purposes it is more convenient to express the free energy of perchlorate ion in terms of the reduction potential referred to the $\text{H}_2\text{-H}^+$ couple as zero. Using the Lewis and Randall⁴ value for the free energy of water, we find



Summary

The specific heat-temperature curve and the heat of solution of potassium perchlorate have been determined. These values have been used in the calculation of the entropy and free energy of perchlorate ion.

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CERIC SULFATE AS A VOLUMETRIC OXIDIZING AGENT. XII. THE DETERMINATION OF TELLUROUS ACID

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Introduction

An excellent survey of the volumetric methods proposed for tellurium up to the year 1926 has been given by Lenher.¹ The electrometric titration of tellurate with titanous chloride either in a hydrochloric or a sulfuric acid solution has been described recently.² The volumetric method based upon the oxidation of tellurous acid by dichromate, proposed first by Brauner³ and modified by Moser and Miksch,⁴ Lenher and Wakefield,⁵ and Schrenk and Browning,⁶ appears to be the most satisfactory and is applicable in the presence of selenious acid. The oxidation, if carried out at room temperature in hydrochloric acid solution,⁵ is rather slow and

⁸ Rodebush, *ibid.*, **40**, 1204 (1918).

¹ Lenher, *Proc. Am. Phil. Soc.*, **65**, 33 (1926).

² Tomiček, *Bull. soc. chim.*, **41**, 1389 (1927).

³ Brauner, *Monatsh.*, **11**, 526 (1890).

⁴ Moser and Miksch, *ibid.*, **44**, 349 (1923).

⁵ Lenher and Wakefield, *This Journal*, **45**, 1423 (1923).

⁶ Schrenk and Browning, *ibid.*, **48**, 139 (1926).

the concentration of hydrochloric acid must be carefully controlled. If too low, the speed of the reaction is retarded; if too high, hydrochloric acid and telluric acid react to give free chlorine. Schrenk and Browning⁶ carried out the oxidation at room temperature in a sulfuric acid solution, forty-five to sixty minutes being required for complete oxidation. They did not study the reaction in hot solution.

This paper describes a rapid and accurate volumetric procedure for tellurium, based upon the oxidation of tellurous acid by excess standard ceric sulfate in the presence of chromic sulfate as catalyst, and electrometric titration of the excess ceric sulfate with standard ferrous sulfate.

Experimental

The potassium tellurite solution was prepared by dissolving pure basic tellurium nitrate in dilute potassium hydroxide, and was approximately 0.09 *N*. It was standardized by the method of Lenher and Wakefield⁵ against dichromate of known purity, the excess of dichromate being titrated electrometrically with ferrous sulfate. A 0.1 *N* selenious acid solution was prepared from high grade selenious acid. The ceric sulfate solution was a part of a large supply made by the method described by the authors⁷ from high-grade ceric oxide and was 0.5 *M* in sulfuric acid. It was standardized against sodium oxalate.⁸ The ferrous sulfate solution was standardized electrometrically against standard ceric sulfate.⁸

The oxidizing action of ceric sulfate on selenious acid and tellurous acid was first tested. Measured portions of 0.1 *N* selenious acid were diluted with water, 25 cc. of 0.09611 *N* ceric sulfate and sulfuric acid (sp. gr. 1.5) to 200 cc., heated to boiling, held just below the boiling point

TABLE I

THE OXIDIZING ACTION OF CERIC SULFATE ON SELENIOS ACID

In each experiment 25 cc. of 0.09611 *N* ceric sulfate was added

0.1 <i>N</i> H ₂ SeO ₃ cc.	H ₂ SO ₄ (sp. gr. 1.5) before ox., cc.	Time at b. p., min.	0.1 <i>N</i> Ce(SO ₄) ₂ reduced cc.
10	10	30	0.16
10	30	30	.04
10	50	30	.01
10	10	60	.42
10	30	60	.05
10	50	60	.03
25	10	30	.17
25	30	30	.03
25	50	30	.03

TABLE II

THE OXIDIZING ACTION OF CERIC SULFATE ON TELLUROUS ACID

In each experiment 25 cc. of 0.09611 *N* ceric sulfate was added

0.09 <i>N</i> K ₂ TeO ₃ cc.	H ₂ SO ₄ (sp. gr. 1.5) before ox., cc.	Time at b. p., min.	0.1 <i>N</i> Ce(SO ₄) ₂ reduced, cc.
10	10	30	0.62
10	30	30	.44
10	50	30	.28
10	10	60	.74
10	30	60	.81
10	50	60	.50
25	10	30	1.00
25	30	30	0.93
25	50	30	.58

⁷ Willard and Young, *THIS JOURNAL*, **51**, 149 (1929).

⁸ Willard and Young, *ibid.*, **50**, 1322 (1928); see also Furman, *ibid.*, **50**, 755 (1928).

over a small flame for the time indicated, then cooled to 30–35°, and the excess of ceric sulfate titrated electrometrically with standard ferrous sulfate. The results are shown in Table I.

These results indicate that selenious acid is not oxidized by ceric sulfate in a hot solution of moderate acid concentration and only very slightly oxidized in a solution of low acidity.

Measured portions of a 0.9 *N* tellurite solution were diluted with water, acid and 25 cc. of 0.09611 *N* ceric sulfate to 200 cc., and treated in the same way as the solutions for the experiments in Table I. The results obtained are shown in Table II.

Thus tellurous acid is only slightly oxidized under the conditions used in these experiments.

Since dichromate may be used, either in a hydrochloric or a sulfuric acid solution, to determine tellurous acid in the presence of selenious acid,^{4,5,6} and since ceric sulfate may be used to oxidize chromic salt quantitatively to chromic acid in sulfuric acid solution,⁹ it seemed obvious that

TABLE III

OXIDATION OF TELLUROUS ACID BY CERIC SULFATE USING CHROMIC SALT AS CATALYST

Expt.	H ₂ SO ₄ (sp. gr. 1.5) before ox., cc.	Time at b. p., min.	Vol. dur- ing ox., cc.	0.08 <i>N</i> Cr ₂ (SO ₄) ₃ added, cc.	0.09611 <i>N</i> Ce(SO ₄) ₂ added, cc.	0.1 <i>N</i> Ce(SO ₄) ₂ used, cc.	Te taken, g.	Te found, g.
1 ^a	10	5	200	10	50	22.43	0.1434	0.1430
2	10	10	200	10	50	22.47	.1434	.1432
3	10	30	200	10	50	22.49	.1434	.1434
4	10	10	200	5	50	22.47	.1434	.1432
5	10	30	200	5	50	22.49	.1434	.1434
6 ^a	10	30	200	2	50	21.82	.1434	.1391
7	30	10	200	5	50	22.47	.1434	.1432
8	50	10	200	5	50	22.51	.1434	.1435
9 ^a	10	20	200	5	35	22.41	.1434	.1429
10	10	10	200	5	75	22.46	.1434	.1432
11	10	10	100	5	50	22.47	.1434	.1432
12	20	20	300	5	50	22.46	.1434	.1432
13	10	10	200	5	50	8.99	.0574	.0573
14	30	10	200	5	50	9.00	.0574	.0574
15	10	20	200	5	75	44.98	.2868	.2867
16	20	20	200	10	100	67.49	.4302	.4302
17 ^b	10	10	200	5	50	22.50	.1434	.1434
18 ^b	30	10	200	5	50	22.55	.1434	.1437
19 ^{a, b}	50	10	200	5	50	22.65	.1434	.1444
20 ^c	10	10	200	5	50	22.54	.1434	.1437
21 ^d	10	10	200	5	50	22.52	.1434	.1436
22 ^e	10	10	200	5	50	22.55	.1434	.1437

^a In these experiments the conditions were not correct for quantitative results.

^b 0.15 g. of Se added. ^c 0.30 g. of Se added. ^d 0.15 g. of Se + 0.30 g. of Cu added.

^e 0.30 g. of Se + 0.30 g. of Cu added.

⁹ Willard and Young, *THIS JOURNAL*, 51, 139 (1929).

chromic salt should catalyze the reaction between ceric sulfate and tellurous acid. Ceric sulfate oxidizes the small amount of chromic salt to chromic acid, which, after oxidizing tellurous acid, would be reoxidized by the ceric sulfate. To test this point, solutions were prepared as for the experiments in Table II, except that additions were made of chromic sulfate, and in some cases of selenious acid and copper sulfate, and the volume of the solution at the time of oxidation was varied. The treatment of the solutions was the same as for the experiments in Table II. Results are shown in Table III.

The above data show that the oxidation of tellurous acid by ceric sulfate in the presence of chromic salt as catalyst is quantitative over wide variations in acid concentration, excess of oxidizing agent and time of its action, volume of solution in which the oxidation is carried out, amount of chromic salt as catalyst and tellurous acid content. Selenious acid does not interfere if the sulfuric acid concentration at the time of oxidation is not too high. Cupric salts are without effect. The method offers a much wider possibility of variation in conditions than does the oxidation of tellurous acid by dichromate in hydrochloric acid solution, and is more rapid. The same is true in comparing it with the oxidation of tellurous acid by dichromate in sulfuric acid solution, though the experiments in Table III show that a much wider range of conditions could be developed for this latter method than those described by Schrenk and Browning.⁶

Also, preliminary experiments have shown the possibility of using chromic salt as catalyst in many oxidation reactions in which ceric sulfate alone is not effective, for example, in the oxidation of certain organic substances.

Summary

1. Selenious acid is not oxidized by ceric sulfate in hot sulfuric acid solution. Tellurous acid is oxidized only to a very slight extent under the same conditions.
2. A rapid quantitative method for tellurous acid has been developed, based upon its oxidation in hot sulfuric acid solution by ceric sulfate in the presence of chromic sulfate as catalyst. Selenious acid and cupric salts do not interfere.
3. Attention is called to the possibility of using chromic sulfate as catalyst in other oxidation reactions in which ceric sulfate alone is not effective, especially in the oxidation of certain organic substances.