solution in sulfuric acid, addition of solid potassium bromate and completion of the titration with 0.01 *N* potassium bromate solution. The purity of potassium bromate was established by comparison with silver and arsenious acid. The atomic weights of antimony thus obtained are as follows: stibnite from Hungary, 121.14; from Borneo, 121.56; from Peru, 121.72; from Bolivia, 122.37.

CAMBRIDGE, ENGLAND

[CONTRIBUTION FROM THE LABORATORY OF GRINNELL COLLEGE]

ELECTROMETRIC TITRATION OF IODATE, BROMATE, CHLORATE, FERRICYANIDE WITH TITANOUS SULFATE

BY W. S. HENDRIXSON

Received May 22, 1923

In a recent paper from this Laboratory[1] it was stated that work was in progress on the titration of oxidizing substances with titanous ion.

In the work described in the present paper the same general methods and the same apparatus as mentioned in the former paper were used. The stirrer was provided with a mercury seal and all titrations were carried out in an atmosphere of carbon dioxide. All solutions affected by light were kept in bottles coated with a black enamel paint, provided with siphons and never unstoppered. Titanium solutions were standardized with permanganate and dichromate. The latter and the solutions of pure potassium iodate, bromate and chlorate were made up by weight and the contents of calibrated flasks at 20°.

Titration of Iodate with Titanous Ion

A 0.05 *N* solution of iodate was made up by weight and also standardized with pure iodide and thiosulfate. The volume of the solution at the end of the titrations was about 300 cc. and its acidity was between *N* and 2 *N* with sulfuric acid. Hydrochloric acid was unsatisfactory. A sharp drop of about 0.3 volt occurred when the iodate was all decomposed, as shown in Fig. 1. The iodine set free reacted slowly on further addition of titanium and an excess was required to drive the reaction to completion. Possibly the sharp rise in voltage at first shows the effect of hypo-iodous acid, the first fall the decomposition of all the iodate, and the final fall the completed reduction of the iodine. The

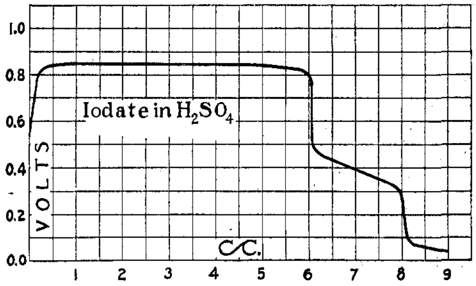

Fig. 1

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[1] Hendrixson and Verbeck, THIS JOURNAL, 44, 2382 (1922).

second fall is fairly sharp but irregularly delayed by about 1 cc., the average for the determinations of Table I being 29.92 cc., while that calculated is 28.95. The correct end-point is found by multiplying the volume of titanium at the first fall by 1.2, which is in accord with the following equations representing the stages in the reduction:

$$5Ti_2(SO_4)_3 + 2HIO_3 + 5H_2SO_4 = 10Ti(SO_4)_2 + 6H_2O + I_2 \qquad (1)$$

$$Ti_2(SO_4)_3 + I_2 + H_2SO_4 = 2Ti(SO_4)_2 + 2HI \qquad (2)$$

Table I gives the results thus obtained. The concentration of the titanous solution was 0.05 $N \times 1.727$; 50 cc. of iodate solution was used in each experiment.

Table I

Titration with Titanous Ion

$Ti_2(SO_4)_3$, cc.	24.05	24.05	24.20	24.12	24.10
Iodate factor	0.997	0.997	1.003	1.000	0.999
				Av., 0.05 $N \times$	0.999

Titration of Bromate with Titanous Ion

After the first draft of this paper had been written there came to the notice of the author the work of Zintl and Wattenberg, in which they used bromate as one of the substances for back-titration in the determination of copper,[2] and of arsenic and antimony with titanium.[2b] In their first paper the work was carried out at 80° and no adequate description is given of the details of the titration of bromate against titanium. Their work does not seem to interfere with the main purposes of this study, which have been to ascertain whether these halogen acids could be accurately and quickly determined directly and at room temperature with titanous salts, and by the electrometric method.

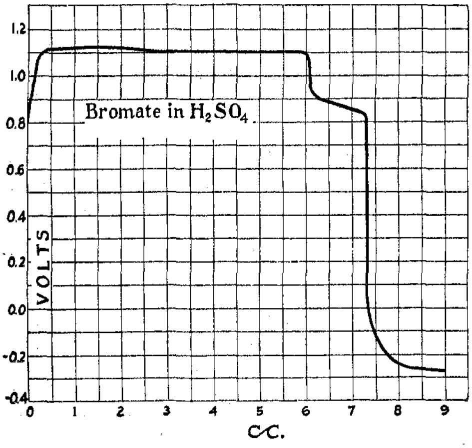

Fig. 2

Pure potassium bromate free from bromide, iron and other impurities likely to occur, was used in making a 0.05 N solution. In the first series, the titration vessel containing 50 cc. of bromate solution, 200 cc. of boiled water and 10 cc. of 10 N sulfuric acid, was filled with carbon dioxide after which the vessel[3] was closed air-tight except for the exit through the mercury seal. The

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[2] Zintl and Wattenberg, (a) *Ber.*, **55**, 3366 (1922); (b) **56**, 472 (1923).

[3] Knecht and Hibbert, "New Reduction Methods in Volumetric Analysis," **1918**, p. 65.

curve obtained on adding titanium in excess strikingly resembles that for iodate and is shown in Fig. 2. The sudden rise at first and the two falls in potential have the same meaning. Apparently either fall may be used for determining the end-point, by calculation, of course, if the earlier fall is used. In this work the long, abrupt fall marking the disappearance of the bromine was preferred. In some experiments free way was provided for the escape of bromine from the titration vessel and its passage over potassium iodide solution, but only a trace of free iodine was obtained. When the vessel was tightly stoppered, therefore, the escape of bromine must have been negligible.

Five experiments carried out as described gave the concentration of the bromate solution $0.05\ N \times 1.002$, with the average deviations from this factor $+0.0007$ and -0.004.

Hydrochloric acid can be used to advantage instead of sulfuric, if not in concentration sufficient to set bromine free before the titration vessel can be filled with carbon dioxide. Apparently, it should not greatly exceed $0.5\ N$ at the end of the titration. In the presence of this acid a smaller amount of bromine seems to be set free, the two reactions running more or less simultaneously, and the end-point is more quickly reached. The first fall in potential, found when sulfuric acid is used, is nearly obliterated in the presence of hydrochloric. In Table II the acid varied from $0.5\ N$ to N, and the concentration of the titanium solution was $0.05\ N \times 1.4663$; 50 cc. of bromate solution was used in each experiment.

TABLE II

TITRATION OF BROMATE WITH TITANOUS ION IN HYDROCHLORIC ACID

50 cc. of Bromate Solution Used

$Ti_2(SO_4)_3$, cc....	34.05	34.00	34.07	34.15	34.20	33.95	34.20
Bromate factor..	0.999	0.997	0.999	1.001	1.003	0.996	1.003
						Av., $0.05\ N$ ×	0.9997

The literature shows increasing use of bromate as an analytical reagent, making greater the need of methods for its rapid and accurate determination under various conditions. It is hoped to give this matter further and more detailed study.

Titration of Chlorate with Titanous Ion

Knecht and Hibbert[3] and Kikuchi[4] have titrated chlorate with excess of titanous salt, titrating back with ferric iron and thiocyanate as indicator. Kikuchi titrated iodate and bromate also, working in all cases at 60°. The results here obtained show that chlorate may be accurately determined at room temperature by the addition of titanous salt at the end-point.

Apparently, chlorate may be titrated with titanium in either sulfuric or hydrochloric acid solution from less than N to more than $4\ N$. Expts.

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[4] Kikuchi, *J. Chem. Soc. Japan*, **43**, 173 (1922); *C. A.*, **16**, 1716 (1922).

3 and 4, Table III, were carried out in sulfuric, and others in hydrochloric acid. Fig. 3 shows a very great rise in potential, due to hypochlorous acid, when a little titanium solution is added, then nearly constant voltage, then a very sharp curve to the nearly vertical drop of about 0.8 volt.

Table III

Titration of Chlorate with Titanous Ion

$Ti_2(SO_4)_3$, cc.....	35.52	35.60	35.45	35.60	35.75	35.57
Chlorate factor..	0.9990	1.0025	0.9920	1.0025	1.0060	1.0010
					Av., 0.05 N ×	1.0013

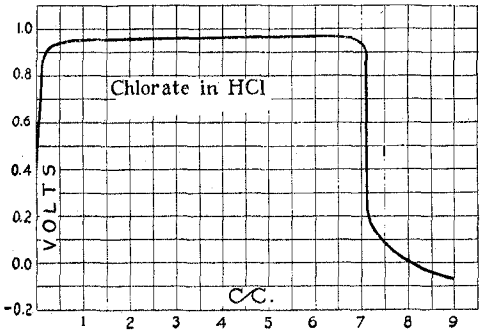

Fig. 3

The titanous solution was 0.05 N × 1.407; 50 cc. of chlorate solution was used in all experiments.

Experiments similar to those with bromate showed, by titration of the iodine set free with thiosulfate, that with the free exit thus provided, not more than 1 part in 600 of the chlorine escaped oxidation in the titration vessel and, hence, when the vessel was closed the chlorine that escaped must have been negligible.

Titration of Ferricyanide with Titanous Ion

The determination of ferricyanide by the potential method seems as simple and accurate as the determination of ferric iron in other compounds. When the solution is concentrated and sulfuric acid is used, a brown precipitate forms near the end of the titration with titanium, but this does not interfere with the end-point.

A solution of pure potassium ferricyanide, determined by the iodine method showed a concentration of 0.05 N × 0.7200. Six titrations with titanium gave a mean for the factor of 0.7201, and the average departures from the mean were +0.0005 and —0.0004.

The author wishes to express his hearty appreciation to Mr. Paul W. Hush and Mr. Neil L. Crone for assistance in this work.

Summary

1. Iodate, bromate and chlorate have been determined electrometrically at room temperature by the addition of titanous salt to the solution to the end-point; that is, without adding an excess and titrating back with an oxidizing agent.

2. Iodate is best determined in sulfuric acid by the addition of titanium to the solution until the first drop in potential is reached, which marks the

disappearance of the iodate; bromate and chlorate may be determined in either sulfuric or hydrochloric acid by adding titanium to the solution until the final drop which marks complete reduction, is reached.

3. Ferricyanide also may thus be determined electrometrically with titanium as accurately as any other form of ferric iron.

GRINNELL, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY, I, 28]

THE CONDUCTANCE OF DILUTE AQUEOUS SOLUTIONS OF HYDROGEN CHLORIDE

BY HENRY C. PARKER[1]

Received June 4, 1923

Introduction

In a recent investigation,[2] Kraus and Parker determined the conductance of iodic acid, using water of various degrees of specific conductance and both glass and quartz cells. If it is assumed that the measurements made in quartz cells with water having a specific conductance of $0.09–0.12 \times 10^{-6}$ are correct, the presence of an error was demonstrated in the measurements made with water of higher specific conductance and with glass cells. The use of glass cells was shown to influence the results to a somewhat greater extent than the impurities that are present in ordinary "conductivity water." The limiting value for the equivalent conductance of iodic acid, found from the measurements in the quartz cells, was about 0.9% higher than the value found from the measurements in glass cells.

It appeared of interest to confirm the results of Kraus and Parker by carrying out a series of measurements with a typical strong acid in a quartz cell. Hydrochloric acid was chosen, since the equivalent conductance of the chloride ion is known with considerable certainty, and since solutions of this acid may be made by weighing the constituents involved.

Preparation of Materials

The hydrochloric acid was prepared by means of the apparatus shown in Fig. 1.

In this figure, A is the generating flask; B is a wash bottle, containing "special" sulfuric acid, and C is a trap, introduced to prevent the water in the absorption flask from being drawn back into the generating flask. This trap is likewise filled with "special" sulfuric acid. The absorption flask E is constructed of clear quartz and has a capacity of approximately 1500 cc. D is the drying tube containing phosphorus pentoxide. With the exception of a short piece of rubber tubing, connecting the absorption flask to the drying tube, all connections are of glass. In order to avoid contamination,

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[1] National Research Fellow in Chemistry.

[2] Kraus and Parker, THIS JOURNAL, **44**, 2429 (1922).