[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

CERIC SULFATE AS A VOLUMETRIC OXIDIZING AGENT. IV. THE DETERMINATION OF ARSENIC. V. THE DETERMINATION OF ANTIMONY

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Introduction

The action of cerium dioxide, either pure or impure, on arsenious acid in a hot sulfuric acid medium was investigated by Browning[2] who found that the oxide was only partially reduced. Job[3] in a paper on a method of induced oxidation of ceric carbonate stated that this compound did not oxidize potassium arsenite, but that in the presence of dextrose the latter was converted into arsenate. The direct titration of arsenious acid with a ceric salt, however, has not been tested, but such a reaction, if quantitative, would give another primary standard[4] with which to compare such oxidizing solutions.

Experimental

IV. THE DETERMINATION OF ARSENIC

A 0.1 *N* solution of sodium arsenite was prepared by dissolving pure arsenious oxide in sodium hydroxide, diluting and adding sulfuric acid until the solution was slightly acid, followed by 10 g. of potassium bicarbonate. The ceric sulfate solution was that prepared for earlier work[4] and was 1 *M* in sulfuric acid. Preliminary experiments showed that the direct titration of arsenious acid with ceric sulfate in hydrochloric acid solution at room temperature was impossible. The reaction was too slow. If the reaction was carried out at 75–85°, the equilibrium was rapid and the end-point break amounted to 100–130 mv. per 0.03 cc. of 0.1 *N* oxidizing agent. At 70° or below, or with less than 15 cc. of concd. hydrochloric acid per 100 cc. of solution, the equilibrium was too slow to be satisfactory.

Lang[5] found that chloride, bromide and iodide ions catalyzed the action between arsenious and permanganic acids in sulfuric acid solution, stating that this titration with permanganate went smoothly if 0.5 cc. of 0.005 *N* potassium bromide was added to the boiling hot arsenious acid solution containing at least 25% sulfuric acid. He attributed the action of the bromide to the following reactions

$$MnO_4^- + 5Br^- + 8H^+ = Mn^{++} + 5Br + 4H_2O$$
$$As^{+++} + 2Br = As^{+++++} + 2Br^-$$

Further work by this same author showed that the action of chloride alone as a catalyst was not satisfactory but that it served as a medium for the iodide catalysis at room temperature. Also, rather narrow experimental conditions had to be maintained when

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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] Browning, *Z. anorg. Chem.*, **22**, 297 (1899).

[3] Job, *Compt. rend.*, **134**, 1052 (1902).

[4] Willard and Young, THIS JOURNAL, **50**, 1322 (1928).

[5] Lang, *Z. anorg. Chem.*, **152**, 197 (1926).

bromide was the catalyst. Iodine, iodide or iodate proved to be the most satisfactory. If the titration were carried out in a warm sulfuric acid solution, the presence of iodide would introduce a positive error, that of iodate, no error. In a hydrochloric acid solution iodide would cause a positive error and iodate a negative one, as the final form of the catalyst in either case is iodine monochloride. The amount of these catalysts required was so small, however, never more than 1 drop of 0.005 *N* solution, that any error caused by their presence was negligible. An explanation of the catalytic action of iodine in any of these three forms in the above reaction is given in Lang's paper.

A similar catalytic action with these materials in the arsenious acid–ceric salt titration might be expected. Potassium bromide was the first substance tested.

A 0.1 *N* sodium arsenite, prepared as directed above, was diluted with water and the stated amount of hydrochloric acid, sp. gr. 1.18, to a volume of 100 cc. This solution, to which potassium bromide was added, was titrated electrometrically at the indicated temperature with approximately 0.1 *N* ceric sulfate. The results are shown in Table I.

TABLE I

CATALYTIC ACTION OF BROMIDE

$NaAsO_2$, 0.1 *N*, cc.	HCl, cc.	KBr, g.	Temp., °C.	$Ce(SO_4)_2$, 0.1 *N*, cc.	Rate of the reaction
10	25	1.25	25	9.55	Too slow to be practical
10	25	2.50	25	9.55	More rapid—only fairly satisfactory
10	25	5.00	25	9.56	Rapid—satisfactory
10	35	2.50	25	9.56	Rapid—satisfactory
10	35	5.00	25	9.55	Rapid—very satisfactory
10	50	1.25	25	9.52	Rapid—very satisfactory
10	50	0.00	25	9.57	*Very* slow—not practical
40	35	5.00	25	38.26	Very satisfactory
10	25	1.25	70–75	9.50	Rapid
10	25	0.50	70–75	9.52	Rapid
10	25	0.25	70–75	9.56	Rapid
10	25	0.12	70–75	9.58	Rapid
10	25	0.00	70–75	9.58	*Very* slow—not practical
10	15	0.25	70–75	9.57	Rapid
10	15	.50	70–75	9.55	Rapid
10	15	1.25	70–75	9.52	Rapid
10	35	0,12	70–75	9.58	Rapid
10	35	.50	70–75	9.53	Rapid
40	35	.25	70–75	38.30	Rapid
10	25	1,25	50–55	9.54	Quite rapid
10	25	2.50	50–55	9.53	Rapid
10	35	0.50	50–55	9.55	Rapid

The break at the end-point was 60–80 mv. per 0.03 cc. of 0.1 *N* ceric sulfate when the titration was made at room temperature and 100–150 mv. for temperatures of 50–75°. The data show that the amount of bromide necessary for a rapid reaction decreases as the temperature or the hydrochloric acid content is increased, but it is always much greater than that required to catalyze the arsenite–permanganate reaction. The quantity of arsenite may be varied through wide limits, and results were identical whether the ceric sulfate was added slowly or the greater portion of it rapidly from a pipet.

Ten cc. of 0.1 *N* sodium arsenite, a different solution from that used in the experiments in Table I, was taken and diluted with water, the stated amount of hydrochloric acid (sp. gr. 1.18) and catalyst to a volume of 100 cc. The titration was made electrometrically with approximately 0.1 *N* ceric sulfate at room temperature. The results are shown in Table II.

TABLE II

CATALYTIC ACTION OF IODINE OR IODINE CHLORIDE

HCl, cc.	Catalyst, cc.	$Ce(SO_4)_2$, 0.1 *N*, cc.	Actual blank, cc.	Theoretical blank, cc.	Rate of the reaction
35	5 g. KBr	10.18	....	....	A standardization
	KI, 0.0025 *M*				
30	1	10.25	+0.07	+0.05	Rather slow
30	2	10.30	+ .12	+ .10	Fairly rapid
30	5	10.47	+ .29	+ .25	Rapid
30	7	10.57	+ .39	+ .35	Rapid
30	10	10.72	+ .54	+ .50	Very rapid
30[a]	2	10.31	+ .13	+ .10	As rapid as preceding one
40	5	10.43	+ .25	+ .25	No more rapid than with 30 cc. of acid
	ICl, 0.005 *M*				
30	5	10.17	− .01	....	Rapid
30	2.5	10.17	− .01	....	Quite slow
30	15	10.16	− .02	....	Rapid
30	20	10.17	− .01	....	Rapid
30[b]	5	10.16	− .02	....	Rapid

[a] The temperature of the solution was 50–55° during the titration.

[b] Ten cc. of concd. sulfuric acid was added before the titration.

Titrations were not made with potassium iodate as catalyst, because obviously iodine chloride, causing no blank correction, is the most convenient catalyst. The break at the end-point amounted to 150–250 mv. per 0.03 cc. 0.1 *N* ceric sulfate.

The iodine chloride solution was prepared by dissolving 0.279 g. of potassium iodide and 0.178 g. of potassium iodate in 250 cc. of water and adding at once 250 cc. of concd. hydrochloric acid.[6] The solution thus obtained was 0.005 *M* in iodine chloride. It was adjusted electrometrically by adding dilute potassium iodide or iodate.

In a titration in which either iodide or iodine chloride is used as catalyst the solution is somewhat yellow. When near the end-point, the color becomes deeper, due to the presence of considerable iodine, and during the addition of the last 0.5 cc. of ceric salt the color slowly bleaches as iodine chloride is formed. At the end-point the solution is still a pale yellow when the conditions are such that equilibrium is reached rapidly, or a slightly deeper yellow if less favorable conditions have been used. In the former case it is possible, after some experience, to determine the end-point visually, as the slightest excess of ceric salt causes the solution

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[6] G. S. Jamieson, "Volumetric Iodate Methods," The Chemical Catalog Company, New York, **1926**, pp. 8, 9.

to become a deeper yellow again, but the method cannot be recommended as a sharp one.

A number of indicators were tested in the titration of arsenite with ceric sulfate in hydrochloric acid solution: methyl orange which is used in the arsenite–bromate reaction was not satisfactory, nor were indigo, diphenylamine or diphenylbenzidine. Methylene blue was the only indicator which appeared promising. A description of its use in the oxalate-ceric salt titration has been given[4] and the conditions for satisfactory results in the arsenite–ceric sulfate titration are the same: iodine chloride as catalyst, rapid equilibrium in the region of the end-point so that the yellow color bleaches quickly and addition of the indicator, 2 drops of 0.1% solution in water for each 100 cc. of solution, within 0.2–0.3 cc. of the end-point. In a series of experiments the amount of indicator was varied from 1 to 5 drops with excellent results and no blank correction in any case. The indicator works well also when the arsenic content of a solution is varied widely. The solution turns green when the indicator is added, and with each succeeding drop of ceric sulfate becomes more blue until a final drop or two of the oxidizing agent causes the whole liquid to turn a deep pink color, which in five to ten seconds changes to a permanent blue shade.

It has been shown in earlier work[4] that the values of the factor obtained by standardizing ceric sulfate against (1) electrolytic iron, (2) sodium oxalate in hot solution, or (3) sodium oxalate at room temperature with iodine chloride as a catalyst were in very close agreement. At this time the conditions for the arsenite–ceric sulfate titration had also been worked out so that it was possible to include these standardizations. A weight buret was used for the ceric sulfate. The experimental conditions for the three methods mentioned above have been given in detail.[4] For the arsenite–ceric salt titration, 0.25–0.30-g. samples of arsenious oxide of very accurately known purity were treated with 1 g. of sodium carbonate and 15 cc. of water and heated gently until solution was complete. The liquid was cooled, diluted with water to about 80 cc., 20 cc. of hydrochloric acid, sp. gr. 1.18, and 5 cc. of iodine chloride were added and the titration was made electrometrically with ceric sulfate. The results are shown in Table III.

TABLE III

WEIGHT NORMALITY FACTOR OF CERIC SULFATE BY DIFFERENT METHODS

	Against (1) Electrolytic Fe, 99.97% Fe, *N*	(2) $Na_2C_2O_4$ in hot soln., *N*	(3) $Na_2C_2O_4$ at room temp. ICl as catalyst, *N*	(4) As_2O_3, 99.985%, *N*
	0.09410	0.09410	0.09406	0.09381
	.09414	.09416	.09409	.09380
	.09408	.09407	.09409	.09379
	.09408	.09406	.09404	.09381
Average	.09410	.09410	.09407	.09380

The normality factor from the standardization against arsenious oxide is about three parts in a thousand lower than that against electrolytic iron or oxalate, that is, more ceric salt has been required per equivalent weight of reducing agent in the former than in either of the latter cases. Two titrations were made in which the volumes of iodine chloride used were 10 and 15 cc., and the factors obtained were 0.09379 *N* and 0.09375 *N*. It would not be expected that the iodine chloride was responsible for the discrepancy as its use in the oxalate–ceric salt titration did not alter the results in the slightest degree. Since oxalate cannot be titrated with ceric sulfate in the presence of either phosphate or fluoride, because of the formation of insoluble salts, possibly double salts, it was thought that arsenate ion might behave in a similar way but the product is so soluble that only a slight error could be introduced. However, the addition of arsenate to either an oxalate solution or an arsenite solution at the beginning of a titration did not alter the volume of ceric salt required. There is as yet no explanation for this result, but from certain observations it seems possible that it may involve formation of double salts with cerium. In using this titration as a method for determining arsenic, accurate results may be obtained either by standardizing the ceric sulfate against arsenious oxide of known purity, or by multiplying the normality factor obtained from an oxalate titration by the correction factor 941/938, that is, 1.003.

V. THE DETERMINATION OF ANTIMONY

In the determination of antimony by an electrometric titration of antimonous chloride with ceric salt, samples of the metal which had been analyzed carefully in connection with atomic weight work[7] were dissolved in hot, concd. sulfuric acid, the cool material diluted with water and concd. hydrochloric acid and solid sodium sulfite added, the excess of sulfur dioxide being removed by boiling. To be certain that a solution thus prepared contained all of the antimony in the trivalent form, a few titrations of such solutions were made electrometrically with potassium bromate, a method shown by Zintl and Wattenberg[8] to be accurate. The potassium bromate solution was made up directly by weight as its oxidizing strength had been accurately determined by comparing it against arsenious oxide of known purity. Zintl and Wattenberg[8] call attention to the fact that it is necessary to make the titration quickly when working with a hot antimonous chloride solution because of oxidation by the air. To eliminate this error, carbon dioxide was used, and the greater part of the ceric sulfate added rapidly from a calibrated pipet and the last few cc. from a 10cc. buret.

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[7] Willard and McAlpine, **This Journal, 43, 797** (1921).

[8] Zintl and Wattenberg, *Ber.*, **56, 472** (1923).

From 0.35–0.45 g. of antimony (99.985%) was dissolved in 5 cc. of hot sulfuric acid, sp. gr. 1.83. To this, when cool, 20 cc. of water, 25 cc. of hydrochloric acid, sp. gr. 1.18, and 1 g. of sodium sulfite were added. The liquid was left on a low temperature hot-plate for ten minutes, then boiled for the stated time, the evaporated liquid being replaced at intervals by 1:1 hydrochloric acid, then diluted to 100 cc. and titrated electrometrically at 70–80° with 0.1083 *N* potassium bromate. The results are shown in Table IV.

TABLE IV

TITRATION OF ANTIMONOUS CHLORIDE WITH POTASSIUM BROMATE

Time and conditions of boiling to remove excess sulfite	Factor obtained for $KBrO_3$ soln., *N*
5 minutes while CO_2 bubbled through solution	0.1081
10 minutes while CO_2 bubbled through solution	.1083
20 minutes while CO_2 bubbled through solution	.1084
30 minutes while CO_2 bubbled through solution	.1084
5 minutes no CO_2	.1075
10 minutes no CO_2	.1082
20 minutes no CO_2	.1082
30 minutes no CO_2	.1082

Thus it is seen that theoretical results are obtained by boiling the solution for ten to thirty minutes in a stream of carbon dioxide, and the error is very small if carbon dioxide is not used.

Antimonous chloride solutions, similarly prepared, were cooled to room temperature, iodine monochloride added and titration made electrometrically with ceric sulfate. This titration at room temperature without a catalyst is too slow to be practical. Satisfactory results were not obtained at a higher temperature. Experiments with antimonous chloride solutions containing iodine chloride showed that methylene blue could be used as internal indicator in the titration with ceric salt.

Procedure for Antimony

From 0.35–0.45 g. of antimony was dissolved in 5 cc. of hot sulfuric acid, sp. gr. 1.83. To this, when cool, the stated amounts of water and hydrochloric acid, sp. gr. 1.18, and 1 g. of sodium sulfite were added. The liquid was left on a low temperature hot-plate for ten minutes, then boiled for fifteen minutes while carbon dioxide was bubbled through the solution and the evaporated liquid was replaced at intervals by 1:1 hydrochloric acid, cooled and diluted to 100 cc.; 10 cc. of iodine chloride was added and titration made electrometrically with ceric sulfate, 0.1042 *N* against sodium oxalate. The results are shown in Table V.

The break at the end-point varied considerably in magnitude, amounting in some cases to 40–50 mv. and in other instances, where the same experimental conditions had been maintained, to as much as 150–180 mv.

TABLE V

TITRATION OF ANTIMONOUS CHLORIDE WITH CERIC SULFATE

H_2O, cc.	HCl, cc.	Sb taken	Sb found
20	25	0.3617	0.3620
		.3708	.3708
		.3804	.3808
30	15	.3778	.3773
		.3362	.3362
		.3709	.3710

per 0.03 cc. of 0.1 *N* ceric sulfate. The end-point was, however, never difficult to locate.

Summary

1. Arsenious acid may be titrated accurately at 75–85° in hydrochloric acid solution with ceric sulfate, the end-point being determined electrometrically.

2. Potassium bromide may be used as a catalyst in this reaction and the titration made electrometrically either at room temperature or in hot solution. The amount of potassium bromide required for a rapid reaction decreases as the temperature or the hydrochloric acid content of the solution is increased.

3. Iodine has a greater catalytic effect, iodine monochloride being the most convenient form in which to use it, as its presence in a hydrochloric acid solution necessitates no blank correction. With this catalyst, the titration is made at room temperature, the end-point being determined either electrometrically or with methylene blue as an indicator.

4. The normality factor of ceric sulfate obtained by comparison against arsenious oxide is about three parts in a thousand lower than that against oxalate. Therefore, in determining arsenic, the ceric sulfate should be standardized against arsenious oxide of known purity, or a correction be applied to the factor obtained from an oxalate titration.

5. Antimony may be accurately determined by electrometric titration of antimonous chloride with ceric sulfate at room temperature, iodine monochloride being present as catalyst, and the theoretical factor being used.

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