13.45 $(4 \times 3.44 = 13.76)$ by 11.53 $(3 \times 3.97 = 11.91)$. The two pairs of comparable lengths differ by 2.3 and 3.3%, respectively. Our ignorance of the structure of this acid limits the comparison to mesh dimensions only.

Acknowledgment.—We have had the good fortune to be able to discuss this material with Prof. J. D. H. Donnay.

Summary

Glycine, pyridine betaine and β-alanine in aqueous sodium chloride solutions modify the crystal habit of growing sodium chloride; the first causes the formation of dodecahedra, the other two give octahedra. Glycine and β-alanine are themselves modified by sodium chloride. The largest or most unexpected (on the basis of the modified law of Bravais) new form developed on the amino acid is compared with the form developed on sodium chloride by the amino acid. A fairly good correspondence of mesh dimensions is found in both cases and a structural correspondence is found in the case of glycine.

RECEIVED APRIL 21, 1949

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 1273]

The Coulometric Titration of Tripositive Antimony by Means of Electrolytically Generated Bromine and an Amperometric End-point

BY RAYMOND A. BROWN AND ERNEST H. SWIFT

Introduction

In the course of the work on the formal potential of the antimonous–antimonic half-cell in hydrochloric acid solutions described in the following article, the necessity arose of determining quantities of antimony ranging from 10 to 1,000 micrograms. The method and apparatus described by Myers and Swift[1] for the determination of arsenic which involved a coulometric titration with electrolytically generated bromine and an amperometric end-point seemed to offer distinct advantages. Therefore, an investigation of the application of this method to the titration of antimonous solutions in hydrochloric acid was undertaken. Since iodine was present in the solutions on which the potential measurements were being made, the study was extended to determine the effect of its presence.

Experimental Part

Chemicals.—A standard solution of tripositive antimony was prepared by dissolving an appropriate weight of the oxide in hydrochloric acid. Antimony trioxide was prepared according to the procedure described by Schumann.[2] The solution was standardized by titration with permanganate according to the procedure of Hillebrand and Lundell.[3]

Iodide solutions were prepared gravimetrically from dried reagent grade potassium iodide which had been tested for carbonate and iodate.

Reagent grade potassium bromide, free of extraneous oxidizing or reducing material, was used.

For reasons discussed below, most of the coulometric titrations were made in solution 2 v. f. (volume formal) in hydrochloric acid and 0.2 v. f. in potassium bromide. The reagent grade of concd. hydrochloric acid was found to give a titer corresponding to approximately 4×10^{-7} equivalent of reducing material per 10 ml. This was eliminated by adding a calculated amount of diluted 30% hydrogen peroxide and boiling the solution. At times the distilled water used contained as much as 2×10^{-7} equivalent of an oxidizing agent, believed to be chlorine. This was eliminated by bubbling air through the water while it was being boiled.

Apparatus.—The apparatus and procedure used were essentially the same as those described by Myers and Swift.[1] Preliminary experiments showed that antimony was reduced and deposited on the generator cathode. Therefore, this electrode was enclosed in a glass tube open at the top and provided at the bottom with a sintered glass plug. To prevent diffusion of solution from the titration cell into the cathode compartment, the solution therein was kept at a higher level and greater ionic strength.

Procedure.—The desired quantities of antimony, taken as Sb_2O_3 dissolved in 2 v. f. hydrochloric acid, were pipetted into the titration vessel and the appropriate volumes of hydrochloric acid, sodium bromide and water were then added to give the concentrations indicated. The titration procedure was carried out as described by Myers and Swift.[1] The end-point correction was determined by interpolation using a curve obtained by generating bromine in solutions of the same acid and bromide concentration as those of the titration and recording the indicator current readings at short time intervals. In the titrations with iodide present, the end-point was calculated in the same manner. The assumption was made that iodine was unipositive at the end-point. The titration in the presence of iodide is discussed below.

Discussion of the Method.—The data obtained from confirmatory titrations made under various conditions are collected in Table I. Experiments made to determine the effect of the hydrochloric acid concentration showed that in 1.5 formal hydrochloric acid there is some indication of a tendency towards negative errors, and that hydrolysis of the antimony became pronounced at lower concentrations of acid. When 4.0 formal hydrochloric acid was used, the indicator current gradually increased as the titration proceeded with the result that in the neighborhood of the equivalence-point the change in current was not rapid enough to give a clearly defined end-point. Measurements presented in the following paper indicate that the equilibrium antimonous–antimonic formal potential in 3.5 formal

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[1] R. J. Myers and E. H. Swift, THIS JOURNAL, **70**, 1047 (1948).

[2] R. Schumann, *ibid.*, **46**, 52 (1924).

[3] Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, New York, N. Y., 1929.

hydrochloric acid solution is −0.75 volt, but that a non-equilibrium potential of −0.84 v. may exist in freshly oxidized antimony solutions in 3.5 formal hydrochloric acid. Use of this value and of the bromide–bromine potential in a calculation of the equilibrium, $Sb^{III} + Br_2 = 2Br^- + Sb^V$, indicates that in 3.5 formal acid there would be an appreciable concentration of bromine and of tripositive antimony at the equivalence point. Because of these facts, 2.0 formal acid was used for most of the work.

Certain of the solutions employed in the potential measurements being made had iodine present in amounts ranging up to 20 atomic weight per cent. of the tripositive antimony, therefore titrations were made of solutions containing both iodide and tripositive antimony. As these titrations proceeded, a rapidly increasing indicator current was obtained, followed by a relatively stable maximum, then a decrease to a sharp minimum. Curve A of Fig. 1 shows the indicator current behavior during a titration of 1.245×10^{-5} formula weight of tripositive antimony in a solution 2.0 formal in hydrochloric acid and 0.2 formal in bromide; curve B shows the titration of the same amount of antimony under the same conditions but with 5.33×10^{-7} formula weight of potassium iodide present. A detailed study of the titration of iodide has been made by another investigator.[4]

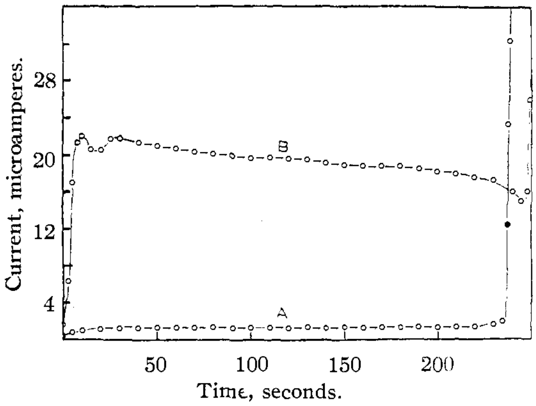

Fig. 1.—Effect of iodide on indicator current: indicator current plotted against generation time in titrations of: (A) 1.245×10^{-5} formula weight of tripositive antimony in a solution *2.0 formal in hydrochloric acid and 0.2 formal in bromide*; (B) same conditions as A but with 5.33×10^{-7} formula weight of potassium iodide present.

TABLE I

CONFIRMATORY TITRATIONS

The concentration of hydrochloric acid and the formula weight of potassium iodide in the solution being titrated are shown at the head of each series. The potassium bromide was 0.20 v. f. in all cases.

Time, sec.	End-point correction, sec.	Correction for KI, sec.	Gener. cur., milliamperes	Sb, micrograms Taken	Found	Error
Series I, Hydrochloric Acid 2.0 v. f.						
266.5	−0.8	....	9.463_5	1585	1586	−1
267.0	−0.9				1589	−3
266.7	−1.4				1584	−1
				Average	1586	−1
134.8	−1.4	....	9.467_5	796.1	796.8	−0.7
134.8	−1.2				798.0	−1.9
134.8	−1.3				797.4	−1.3
				Average	797.4	−1.3
141.8	−5.9	....	0.9325	79.45	79.95	−0.5
142.8	−5.6				80.72	−1.3
142.8	−5.4				80.84	−1.4
142.3	−5.5				81.07	−1.5
				Average	80.59	−1.1
74.68	−6.37	....	0.9325	39.90	40.19	−0.3
74.50	−5.62				40.52	−0.6
74.38	−3.34				41.79	−1.8
				Average	40.83	−0.9
20.60	−5.00	....	0.9325	7.96	9.18	−1.2
19.65	−4.34				9.01	−1.0
19.61	−4.00				9.18	−1.2
20.60	−5.50				8.29	−0.3
				Average	8.92	−1.0
Series II, Hydrochloric Acid, 1.5 v. f.						
261.4	−2.9	....	9.717_5	1585	1585	0
259.6	−1.5				1582	−3
259.5	−1.2				1584	−1
				Average	1584	−1
Series III, Hydrochloric Acid, 4.0 v. f.						
259.9	−2.3	....	9.716_0	1585	1579	−6
259.2	−1.5				1580	−5
259.4	−1.4				1582	−3
				Average	1580	−5
Series IV, Hydrochloric Acid, 2.0 v. f.; Potassium Iodide, 2.405×10^{-7} f. wt.						
264.3	−1.5	−4.8	9.715	1585	1585	0
264.2	−0.8	−4.8			1582	−3
264.7	−0.9	−4.8			1584	−1
				Average	1584	−1
Series V, Hydrochloric Acid 2.0 v. f.; Potassium Iodide, 2.409×10^{-6} f. wt.						
309.4	−1.1	−47.9	9.707_5	1585	1595	−10
308.5	−0.9				1591	− 6
309.3	−1.3				1593	− 8
				Average	1593	− 8

The data collected in Table I show that in solutions 2.0 formal in hydrochloric acid and 0.2 formal in bromide tripositive antimony can be titrated in quantities ranging from 10 to 1,500 micrograms with an average deviation of about 1 microgram. When iodide was present in quantities of about 2 atomic weight per cent. of the tripositive antimony, the average error in the determination of 1,500 micrograms of antimony was about 1 microgram; with iodide present in 20 atomic weight per cent., an average error of plus 8 micrograms was obtained.

Acknowledgment.—We are indebted to Mr. John J. Vrolyk for confirmatory titrations of antimonous solutions and for the data from which the curves shown in Fig. 1 were constructed.

Summary

A study has been made of the conditions under which a coulometric titration of tripositive antimony can be made by means of electrolytically

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(4) Warren Wooster, Master's Thesis, California Institute of Technology, 1947.

generated bromine and an amperometric endpoint. Quantities of antimony of from 10 to 1,500 micrograms have been titrated with an average error of about 1 microgram. Under the same conditions iodide is oxidized to the unipositive state and titrations can be corrected for known small quantities of iodide.

PASADENA, CALIFORNIA RECEIVED MARCH 9, 1949

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The Formal Potential of the Antimonous–Antimonic Half Cell in Hydrochloric Acid Solutions

BY RAYMOND A. BROWN AND ERNEST H. SWIFT

Introduction

A formal potential is defined as the potential of a half-cell, measured against the standard hydrogen electrode, when the total concentration of each oxidation state is one formal. Since the value of the formal potential of the antimonous–antimonic half-cell in hydrochloric acid solutions would be of considerable interest and use in analytical and inorganic work, and since no measurements of this potential were found in the literature, an investigation of the possibility of its determination was undertaken.

Experimental Details

Apparatus.—Randall and Young[1] have found the value of the molal potential of the calomel half-cell in hydrochloric acid solutions in the presence of air to be -0.2689 v. Since this half-cell is readily reproducible and could be used to eliminate junction potentials when working with hydrochloric acid solutions of the same concentration, it was chosen as the reference electrode. The values for this half-cell in various hydrochloric acid concentrations were calculated by making use of the activity coefficients of Randall and Young.[1] The reference cells were prepared with Merck "reagent" grade calomel and distilled mercury. With one exception, mentioned later, the cells agreed within 0.1 millivolt when checked against each other.

A student type potentiometer with a Leeds and Northrup type HS galvanometer number 2285-F was used to make all potential measurements. The standard cell was calibrated against another which had been checked by the Bureau of Standards within the past year. All measurements were made after equilibration in a constant temperature bath at 25.02 ± 0.02°.

Solutions.—All concentrations are expressed in formula weights per 1,000 g. of solvent. An antimony stock solution was made from Sb_2O_3 purified according to a procedure outlined by Schumann.[2] A known weight of Sb_2O_3 was added to a definite quantity of approximately 6 weight formal standardized acid. A correction for the hydrochloric acid consumed in dissolving the Sb_2O_3 was made based on the assumption that the solution reaction was: $Sb_2O_3 + 6HCl = 2SbCl_3 + 3H_2O$. The antimony concentration of the stock solution was checked by titration with permanganate according to the procedure of Hillebrand and Lundell.[3] A stock solution of hydrochloric acid was standardized against potassium acid phthalate by means of sodium hydroxide. All solutions were prepared from these stock solutions.

Several methods were used for the determination of the antimony concentrations. In the potentiometric titration method for determining the antimonous–antimonic potential, described below, tripositive antimony was titrated with a hydrochloric acid solution of chlorine as the oxidizing agent. For determining the ratio of tripositive to quinquepositive antimony, potassium permanganate was generally used for the titration of large concentrations of tripositive antimony and the coulometric method, described in the previous article, was used for more dilute solutions. In the tables which follow those values of this ratio marked with an asterisk were determined coulometrically.

Electrodes.—Platinum electrodes in antimony solutions gave erratic potential values which changed upon stirring the solutions. Gold electrodes gave more reproducible results although with time both electrodes seemed to approach the same potential. The presence of a small amount of iodine (about 0.5% by formula weight of the total antimony concentration) markedly increased the reversibility of the electrodes. The iodine was added in the form of ICl. The latter was made by passing chlorine into 6 weight formal hydrochloric acid containing iodine until carbon tetrachloride in equilibrium with the solution was colorless.

Potential Measurements.—An attempt was made to obtain preliminary values of the potential in 2.0 weight formal hydrochloric acid by means of a potentiometric titration of the tripositive antimony with a 2.0 weight formal hydrochloric acid solution partially saturated with chlorine. However, no satisfactory means were found for maintaining a constant chlorine concentration, even in a closed system. Although the tripositive antimony solutions were stable in 2.0 weight formal hydrochloric acid, precipitates formed after several days in these solutions when the antimony was half oxidized to the quinquepositive state. The precipitate was not of constant composition, but corresponded approximately to the formula $Sb_5O_8Cl_6$. The data from three determinations of the antimonous–antimonic formal potential made from one potentiometric titration in 2.0 weight formal hydrochloric acid are shown in Table I, Experiment 1a, b, c.

In the tables which follow E represents the cell potential as measured, $E^{0''}$ this cell potential corrected for the ratio of tripositive to quinquepositive antimony and $E^{0'}$ the formal potential of the antimonous–antimonic half-cell, that is

$$E^{0'} = E + E_{\text{calomel}} - \frac{RT}{2F}\ln\frac{[\text{Sb}^{\text{III}}]}{[\text{Sb}^{\text{V}}]}$$

A different technique was used for the potential

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(1) Randall and Young, THIS JOURNAL, **50**, 989 (1928).

(2) Reinhardt Schumann, *ibid.*, **46**, 52 (1924).

(3) Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, New York, N. Y., 1929.