

generated bromine and an amperometric end-point. 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.

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RECEIVED MARCH 9, 1949

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 1274]

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

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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 Young¹ 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 $25.02 \pm 0.02^\circ$.

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

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

A different technique was used for the potential

(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.

TABLE I
EFFECT OF HYDROCHLORIC ACID CONCENTRATION ON POTENTIAL VALUES

Expt.	Total Sb concn. (wt. f.)	ICl concn. (wt. f.)	HCl concn. (wt. f.)	E	Sb ^{III} /Sb ^V	E ⁰ "	E ⁰ '
1(a)	3.57×10^{-2}	3.57×10^{-4}	2.0	0.4058	3.000	0.4199	-0.6705
(b)	2.78×10^{-2}	2.78×10^{-4}	2.0	.4210	1.000	.4210	-.6716
(c)	1.82×10^{-2}	1.82×10^{-4}	2.0	.4363	0.333	.4222	-.6728
						Average	-.6716
2	3.20×10^{-2}	3.20×10^{-4}	3.5	0.5202	0.9846	0.5200	-0.7460
3	3.20×10^{-2}	3.20×10^{-4}	3.5	.5196	0.9804	.5193	-.7453
4	3.20×10^{-2}	3.20×10^{-4}	3.5	.5196	1.038	.5201	-.7461
5	3.20×10^{-2}	3.20×10^{-4}	3.5	.5200	0.9146	.5192	-.7452
						Average	-.7456 \pm 0.4 mv.
6	3.20×10^{-2}	3.20×10^{-4}	4.5	0.5711	*1.086	0.5721	-0.7839
7	3.20×10^{-2}	3.20×10^{-4}	4.5	.5708	*1.023	.5714	-.7832
8	3.20×10^{-2}	3.20×10^{-4}	4.5	.5711	*1.073	.5720	-.7838
9	3.20×10^{-2}	3.20×10^{-4}	4.5	.5708	*1.077	.5718	-.7836
						Average	-.7836 \pm 0.2 mv.
10	3.20×10^{-2}	3.20×10^{-4}	6.0	0.6170	1.728	0.6240	-0.8163
11	3.20×10^{-2}	3.20×10^{-4}	6.0	.6218	1.594	.6278	-.8206
12	3.20×10^{-2}	3.20×10^{-4}	6.0	.6172	1.879	.6253	-.8181
13	3.20×10^{-2}	3.20×10^{-4}	6.0	.6155	1.680	.6222	-.8150
						Average	-.8176 \pm 1.7 mv.

measurements in higher acid concentrations. Stoppered gas bottles connected by a capillary tube containing a stopcock were used as cell containers. The gold electrode used was made by fusing gold leaf to platinum wire and then sealing the wire into a glass tube containing the usual mercury connection. The calomel electrode consisted of a platinum wire sealed in glass and dipped into the mixture of mercury and calomel.

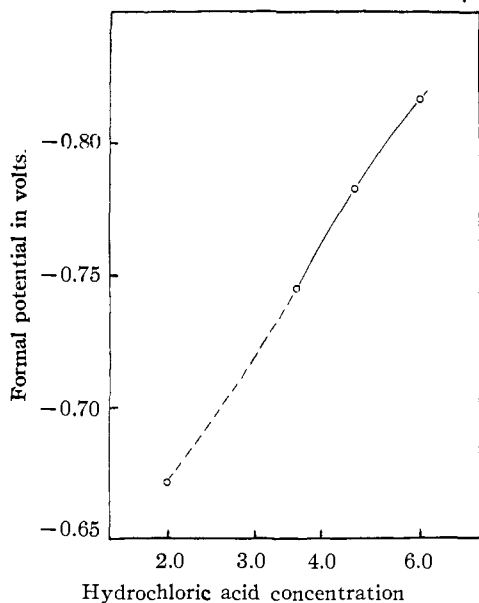


Fig. 1.—Formal potential of the antimonous-antimonic half-cell plotted against the logarithm of the hydrochloric acid concentration.

To the antimony half-cell container was added an antimony solution which had been partially oxidized by means of an hydrochloric acid solution saturated with chlorine. In all cases the acid concentrations in the antimony half-cell and the calomel half-cell were the same. The stopcock between the two half-cells was kept closed except during readings. The cells were kept in the constant temperature bath until readings became constant.

The tripositive antimony was determined by titration and the quinquepositive by difference. In order to simplify calculations all of the iodine was assumed to be in the elementary state.

Experiments 2 to 13 of Table I show the results of the potential measurements in acid concentrations 3.5 to 6.0 weight formal. Figure 1 is a plot of the formal potentials listed in Table I against the logarithms of the acid concentrations. The values obtained in 6.0 weight formal hydrochloric acid were not very consistent. It is believed that the calomel cells were responsible since at this acid concentration there was disagreement by as much as 2.5 mv. between the various cells.

Experiments 2-13, inclusive, shown in Table I were made with total antimony concentration equal to 3.2×10^{-2} weight formal because the cells were found to be reversible and to come to equilibrium in a relatively short time at this concentration. When lower antimony concentrations were used, the cells became less reversible and took longer to come to equilibrium. For example it took six days for the cells which were 3×10^{-4} weight formal in total antimony to come to equilibrium and the potential became more positive with time.

TABLE II
 EFFECT OF TOTAL ANTIMONY CONCENTRATION ON POTENTIAL VALUES

Expt.	Total Sb concn. (wt. f.)	ICl concn. (wt. f.)	HCl concn. (wt. f.)	<i>E</i>	Sb ^{III} /Sb ^V	<i>E</i> ⁰	<i>E</i> ⁰ '
1	3.20×10^{-2}	3.20×10^{-4}	3.5	0.5202	0.9846	0.5200	-0.7460
2	3.20×10^{-2}	3.20×10^{-4}	3.5	.5196	0.9804	.5193	-.7453
3	3.20×10^{-2}	3.20×10^{-4}	3.5	.5196	1.038	.5201	-.7461
4	3.20×10^{-2}	3.20×10^{-4}	3.5	.5200	0.9146	.5192	-.7452
						Average	-.7456 \pm 0.4 mv
5	2.93×10^{-3}	2.93×10^{-5}	3.5	0.5236	*0.4757	0.5137	-0.7397
6	2.93×10^{-3}	2.93×10^{-5}	3.5	.5268	*0.4161	.5137	-.7397
7	2.93×10^{-3}	2.93×10^{-5}	3.5	.5120	*1.186	.5142	-.7402
8	2.93×10^{-3}	2.93×10^{-5}	3.5	.5106	*1.216	.5131	-.7391
9	2.93×10^{-3}	2.93×10^{-5}	3.5	.5119	*1.251	.5148	-.7408
10	2.93×10^{-3}	2.93×10^{-5}	3.5	.5078	*1.253	.5137	-.7397
						Average	-.7399 \pm 0.5 mv.
11	3.55×10^{-4}	3.55×10^{-6}	3.5	0.5006	*1.985	0.5094	-0.7354
12	3.55×10^{-4}	3.55×10^{-6}	3.5	.5036	*2.193	.5137	-.7397
13	3.55×10^{-4}	3.55×10^{-6}	3.5	.4953	*2.276	.5059	-.7319
14	3.55×10^{-4}	3.55×10^{-6}	3.5	.4961	*2.094	.5048	-.7308
15	3.55×10^{-4}	3.55×10^{-6}	3.5	.5120	*1.161	.5139	-.7399
16	3.55×10^{-4}	3.55×10^{-6}	3.5	.5152	*0.8933	.5139	-.7399
17	3.55×10^{-4}	3.55×10^{-6}	3.5	.5099	*0.7877	.5060	-.7320
18	3.55×10^{-4}	3.55×10^{-6}	3.5	.5111	*0.8673	.5093	-.7353
						Average	-.7356 \pm 3.2 mv.

It was found that the formal potentials which were obtained were dependent upon the total antimony concentration and the data collected in Table II show this dependence. If the potential values are plotted against the total antimony concentration there is evidence of a linear relation.

The dependence of the formal potential upon the ratio Sb^{III}/Sb^V was investigated by making potential measurements on cells in which this ratio was varied over a ten-fold range. The results listed in Table III show the formal potential to be slightly dependent upon the ratio Sb^{III}/Sb^V. In these experiments the iodine concentration was decreased to one tenth that used in the experiments of Tables I and II in order to increase the precision of the determination of small quantities of tripositive antimony.

A consideration of the principles involved in the coulometric method for the titration of tripositive antimony solutions, described in the previous paper, suggested that they might be utilized for an approximate determination of the formal potential of the antimonous-antimonic half-cell in hydrochloric acid solutions. Work done in these laboratories⁴ has shown that iodide can be coulometrically titrated to iodine monochloride in hydrochloric acid solutions by electrolytically generated chlorine and that the curve obtained during the latter half of the titration by plotting indicator current *versus* generation time is quite linear. Therefore if one takes a known quantity of potassium iodide in hydrochloric acid of appropriate

concentration, and establishes the slope of this curve by titrating to an appropriate point and noting the indicator current, one may then calculate the amount of iodine and iodine monochloride in any partially oxidized antimony solution with the same initial concentrations of acid and potassium iodide. Since the equilibrium formal potential of the antimonous-antimonic half-cell is approximately -0.75 v. and that of the iodine-iodide half-cell is -0.54 v., the assumption is made that the concentration of iodide present in a solution containing equal amounts of tripositive and quinquepositive antimony will be very small and may be neglected. One must also assume (1) that there is no contribution to the indicator current by the antimony couple, (2) that there is no appreciable association of the iodine in any oxidation state with the antimony, and (3) that the iodine and antimony attain equilibrium during the measurement. From the concentrations of the iodine and iodine monochloride thus calculated one can calculate the value of the iodine-iodine monochloride potential in the solution. Assuming equilibrium, the formal antimonous-antimonic potential can be calculated since the ratio Sb^V/Sb^{III} can be obtained from the generation time.

Experiments were made in which the concentrations in formula weights per liter used for the titrations were: total antimony, 3.67×10^{-4} , potassium iodide, 2.57×10^{-5} , and hydrochloric acid, 3.5. In the titrations of the iodide solutions the value of the indicator current was read at the point where the generation equivalents were equal to the oxidation of the iodide to iodine.

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

TABLE III
 EFFECT OF THE RATIO Sb^{III}/Sb^V ON POTENTIAL VALUES

Expt.	Total Sb concn. (wt. f.)	ICl concn. (wt. f.)	HCl concn. (wt. f.)	E	Sb^{III}/Sb^V	E^0	E^0'
1	3.20×10^{-2}	3.20×10^{-5}	3.5	0.5348	*0.2477	0.5168	-0.7428
2	3.20×10^{-2}	3.20×10^{-5}	3.5	.5313	*0.2528	.5136	- .7396
3	3.20×10^{-2}	3.20×10^{-5}	3.5	.5328	*0.2339	.5141	- .7401
				Average	*0.245		- .7408 \pm 1.4 mv.
4	3.20×10^{-2}	3.20×10^{-5}	3.5	0.5171	1.139	0.5188	-0.7448
5	3.20×10^{-2}	3.20×10^{-5}	3.5	.5165	1.158	.5184	- .7444
6	3.20×10^{-2}	3.20×10^{-5}	3.5	.5154	1.167	.5174	- .7434
7	3.20×10^{-2}	3.20×10^{-5}	3.5	.5172	1.139	.5189	- .7449
				Average	1.151		- .7444 \pm 0.5 mv.
8	3.20×10^{-2}	3.20×10^{-5}	3.5	0.5055	2.629	0.5179	-0.7439
9	3.20×10^{-2}	3.20×10^{-5}	3.5	.5065	2.494	.5182	- .7442
10	3.20×10^{-2}	3.20×10^{-5}	3.5	.5059	2.568	.5180	- .7440
11	3.20×10^{-2}	3.20×10^{-5}	3.5	.5061	2.573	.5182	- .7442
				Average	2.57		- .7441 \pm 0.1 mv.

In the titration of tripositive antimony in the presence of iodide, indicator current readings were made after the generation equivalents were equal to oxidation of one half the antimony plus oxidation of iodide to iodine. In two sets of experiments the current readings were 17.6 and 18.0 microamperes for the iodide titrations and 10.0 and 10.2 for the titrations of antimony in the presence of iodide. The indicator current did not change more than 0.3 microampere over a one-minute period. Making use of these figures and the value given by Latimer⁵ for the iodine-iodine monochloride potential, $E^0 = -1.06$ v., one calculates the antimonous-antimonic formal potential, E_f , as follows

$$E_f = -1.06 - 0.02957 \ln \frac{(ICl_2^-)^2}{(I_2)(Cl^-)^4} = -0.84 \text{ v.}$$

$$(I_2) = 10.1/17.8(1.286 \times 10^{-7})$$

$$(ICl_2^-) = 7.7/17.8(1.286 \times 10^{-7})$$

The value of -0.84 v. is 0.1 volt more negative than that obtained under equilibrium conditions with the cells of corresponding acid and antimony concentration. The discrepancy between the value obtained from the titrations and the equilibrium value obtained from the cells indicates that one or more of the assumptions made above is not correct. The effectiveness of iodine in catalyzing the equilibrium cells leads one to believe that the iodine-iodine monochloride couple and the antimony couple are in equilibrium. We are inclined to believe that the disagreement between the equilibrium and non-equilibrium values is probably due to a slow equilibrium between two or more quinquepositive antimony species. This equilibrium is discussed below.

Equilibria in Antimony Solutions.—In an attempt to explain the relative inertness of the electrodes in cells with low antimony concentra-

tions, the following experiment was made. In the coulometric titration apparatus described in the previous paper were placed various antimony solutions containing approximately equal molal quantities of Sb^{III} and Sb^V in 3.5 formal hydrochloric acid and the indicator current was observed. Even for concentrations up to 0.01 weight formal in total antimony no appreciable indicator current was observed. It had been found that in more concentrated solutions there is no indicator current if the antimony is all in either the tripositive or quinquepositive state; but that there is considerable current when both are in approximately equal amounts. It has been found that for concentrations above 0.01 formal the indicator current plotted against the square of the total antimony concentration for solutions made up of equal amounts of tripositive and quinquepositive antimony is a straight line. Since the two concentrations are equal, the same result would be obtained by plotting the indicator current against the product of the tripositive and quinquepositive antimony. It is believed that this phenomenon is due to a complex made up of equal amounts of the two oxidation states. Solutions at these concentrations are light yellow in color. Whitney and Davidson⁶ have observed that the optical density of concentrated hydrochloric acid solutions containing antimony in mixed oxidation states is proportional to the product of the concentrations of tripositive and quinquepositive antimony. They attribute the color of such solutions to a complex in which the average oxidation number of the antimony is plus four. In the previous paper it was pointed out that the indicator current is dependent upon the presence of reversible half-cell reactions. Therefore the reversibility of the antimony half-cell electrode should decrease as some function of the square of the total concentration to agree with

(5) Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938, p. 53.

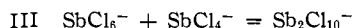
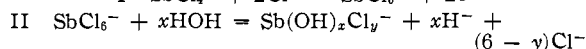
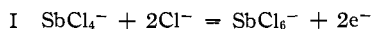
(6) James Whitney and Norman Davidson, THIS JOURNAL, **69**, 2076 (1947).

the results of the experiment above. This checks qualitatively with the facts.

Discussion

The dependence of the values of the formal potential upon acid concentration and time can be explained by several reasonable assumptions.

Lingane and Nishida⁷ have found as the result of polarographic measurements that quinquepositive antimony is not reversibly reduced in hydrochloric acid solutions less concentrated than 4 *N* but that a definite half-wave potential is obtained in 4 and 6 *N* hydrochloric acid. They suggest that quinquepositive antimony exists in solution in two forms: SbCl_6^- and "an ion containing both oxygen and chloride, such as $\text{SbO}_2\text{Cl}_2^-$ " and that only in hydrochloric acid solutions 4 *N* or greater is there sufficient SbCl_6^- to give a reversible reaction. It seems more probable that the quinquepositive antimony retains a coordination number of six and that the second species may be an ion of the type $\text{Sb}(\text{OH})_x\text{Cl}_y^-$. Evidence indicates that tripositive antimony is reversibly oxidized in 2 *N* hydrochloric acid. It seems reasonable to assume that tripositive antimony exists largely in the form of SbCl_4^- in hydrochloric acid solutions. If one assumes that SbCl_6^- and $\text{Sb}(\text{OH})_x\text{Cl}_y^-$ are the two quinquepositive species present, the reactions taking place when tripositive antimony is oxidized in hydrochloric acid solutions may be written as follows:



The above are type reactions and only represent reasonable formulas for the coordination complexes. The molal half-cell potential for I is

$$E = E^0 - \frac{RT}{2F} \ln \frac{[\text{SbCl}_6^-]}{[\text{SbCl}_4^-][\text{Cl}^-]^2}$$

Since by equation II the SbCl_6^- should increase with the acid concentration, the solution potential should become more negative with increasing hydrochloric acid concentration.

It is believed that reaction II, the hydrolysis of SbCl_6^- , proceeds at a rather slow rate; consequently when tripositive antimony in hydrochloric acid solutions is oxidized, equation I repre-

sents the reaction, and SbCl_6^- is initially predominant. Therefore a freshly oxidized antimony solution will have a more negative potential than one which has been allowed to come to equilibrium. This explains the discrepancy between the potential values found under equilibrium conditions from the cell measurements and that found by the coulometric titration method. This implies that in analytical work where one wants rapid and complete oxidation of the antimony, the value obtained by the titration method, -0.84 v., should be more useful. The above considerations are in agreement with the rate and equilibrium effects found by Hammock, Brown and Swift⁸ in titrations of tripositive antimony in hydrochloric acid solutions to the iodine monochloride end-point.

In support of the above assumptions, experiments have shown that if a solution of tripositive antimony in 3.5 formal hydrochloric acid is partially oxidized by chlorine a yellow color results which is characteristic of the plus four complex. This color fades upon standing. In 12 formal hydrochloric acid where there is little tendency toward hydrolysis the color does not fade. The concentration of the plus four complex decreases as the SbCl_6^- hydrolyzes as is shown by Equations II and III.

The change in $\text{Sb}_2\text{Cl}_{10}^{--}$ concentration with total antimony concentration and with the ratio $\text{Sb}^{\text{III}}/\text{Sb}^{\text{V}}$ may be factors in the dependence of the potential upon the total antimony concentration and upon the ratio $\text{Sb}^{\text{III}}/\text{Sb}^{\text{V}}$.

Summary

The formal potential of the antimonous-antimonic half-cell in hydrochloric acid solutions has been found to be -0.746 v. in 3.5 weight formal hydrochloric acid, -0.784 v. in 4.5 weight formal hydrochloric acid, and -0.818 v. in 6.0 weight formal hydrochloric acid when the total antimony concentration is 3.20×10^{-2} weight formal. Under the conditions studied the formal potential is dependent upon the total antimony concentration and upon the ratio $\text{Sb}^{\text{III}}/\text{Sb}^{\text{V}}$. The equilibria existing in hydrochloric acid solutions of tri- and quinquepositive antimony have been discussed.

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RECEIVED MARCH 9, 1949

(7) James J. Lingane and Fumio Nishida, *THIS JOURNAL*, **69**, 530 (1947).

(8) E. W. Hammock, Rupert A. Brown and Ernest H. Swift, *Anal. Chem.*, **20**, 1048 (1948).