

THE FORMAL POTENTIAL  
OF THE ANTIMONOUS-ANTIMONIC COUPLE  
IN HYDROCHLORIC ACID  
AND  
A METHOD FOR THE DETERMINATION  
OF TRIPOSITIVE ANTIMONY

Thesis By

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## ACKNOWLEDGMENTS

I wish to thank Dr. Swift for proposing the problem and for his many helpful suggestions.

## SUMMARY

1. The antimonous-antimonic half cell formal potential has been found to be -0.746 in 3.5 weight formal HCl, -0.784 in 4.5 weight formal HCl, and -0.818 in 6.0 weight formal HCl when the total antimony concentration is  $3.20 \times 10^{-2}$  weight formal.
2. The dependence of the formal potential upon total antimony concentration and the ratio  $Sb^{+III}/Sb^{+V}$  has been studied.
3. Tripositive antimony has been determined in quantities ranging from 10 to 1,500 micrograms by coulometric titration in hydrochloric acid solutions containing bromide with electrolytically generated bromine using an amperometric end point.

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PART I

THE COULOMETRIC TITRATION OF TRIPOSITIVE ANTIMONY  
WITH ELECTROLYTICALLY GENERATED BROMINE  
USING AN AMPEROMETRIC END POINT

## Introduction:

In the course of an investigation made to measure the values of the antimonous-antimonic potential in hydrochloric acid solutions, the necessity arose of determining quantities of antimony from 10 to 1,000 micrograms. The method and apparatus described by Myers and Swift<sup>1</sup> for the determination of arsenic which involved the titration with electrolytically generated bromine and an amperometric end point seemed to offer distinct advantages. Therefore, an investigation of its application to the titration of antimonous solutions in hydrochloric acid was undertaken. Since iodine was present in the solutions on which potential measurements were being made, the study was extended to determine the effect of its presence.

## Experimental Part:

### Chemicals:

A standard antimony solution was prepared by dissolving in hydrochloric acid the appropriate weight of antimony trioxide which had been prepared according to the procedure described by Schumann.<sup>2</sup> The solution was standardized by titration with permanganate according to the procedure of Hillebrand and Lundell.<sup>3</sup>

The iodide solution was prepared gravimetrically from dried reagent grade potassium iodide which had been tested for carbonate and iodate.

For reasons discussed below, most of the titrations were made in solutions 2 F in hydrochloric acid and 0.2 F in sodium bromide. Reagent grade concentrated hydrochloric acid was found to give a titer corresponding to approximately  $4 \times 10^{-7}$  equivalents of reducing material per 10ml. This was eliminated by the addition of a calculated amount of diluted 30 per cent hydrogen peroxide and then boiling the solution. At times the distilled water contained as much as  $2 \times 10^{-7}$  equivalents of an oxidizing agent, believed to be chlorine. This was eliminated by bubbling air through the water while it boiled.

#### Titration Procedure:

The apparatus and the procedure used were essentially the same as those described by Myers and Swift.<sup>1</sup> As shown in Figure I, a simplified schematic diagram of the apparatus, there are two sets of electrodes. One set is used for the electrolytic generation of bromine. The other set has a much larger area, and a potential of about 200 MV impressed across them. If the solution is stirred at a constant high rate, the current flowing between them is determined by the concentrations of

the reversible couples present; this is called the indicator current. Since antimony does not form a reversible couple in 2 F hydrochloric acid at low concentrations, there will be a negligible current flowing between the indicator electrodes until all the antimony is oxidized and there is an excess of bromine. A variable speed motor stroboscopically controlled was used for the stirrer. Preliminary experiments showed that antimony was deposited on the generator cathode and therefore it was necessary to isolate this electrode from the solution being titrated. This was done by enclosing the generator cathode in a tube with a sintered glass plug in the bottom as shown in Figure I. 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.

The desired quantities of antimony taken as  $\text{Sb}_2\text{O}_3$  dissolved in 2 F hydrochloric acid were pipetted into the titration vessel and the appropriate volumes of HCl, NaBr and water were then added to give the concentrations indicated. The titration procedure was then carried out as described by Myers and Swift.<sup>1</sup> The end point correction was determined by interpolation after generating bromine in solutions of the same acid



and bromide concentration as those of the titration for fixed intervals until an indicator current greater than that at the end of the titration was obtained. This procedure was modified when iodide was present. The value of the current at the minimum point was subtracted from that found at the end point in order to obtain the current value to use in the interpolation for the end point correction. The titration in the presence of iodide is discussed below.

#### Discussion of the Method:

The data obtained from titrations made under various conditions are collected in Table I. Experiments were made to determine the optimum hydrochloric acid concentration. At concentrations of 1.5 formal there is a slight tendency towards negative errors, and at lower concentrations hydrolysis of the antimony became pronounced. When 4.0 formal hydrochloric acid was used, the indicator current gradually increased as the titration proceeded in the neighborhood of the end point with the result that the change in current in the vicinity of the equivalence point was not adequate to give a clearly defined end point. Measurements have shown that for the purpose of calculation of potentials in 3.5 formal HCl solutions where rapid oxidation is desired, the

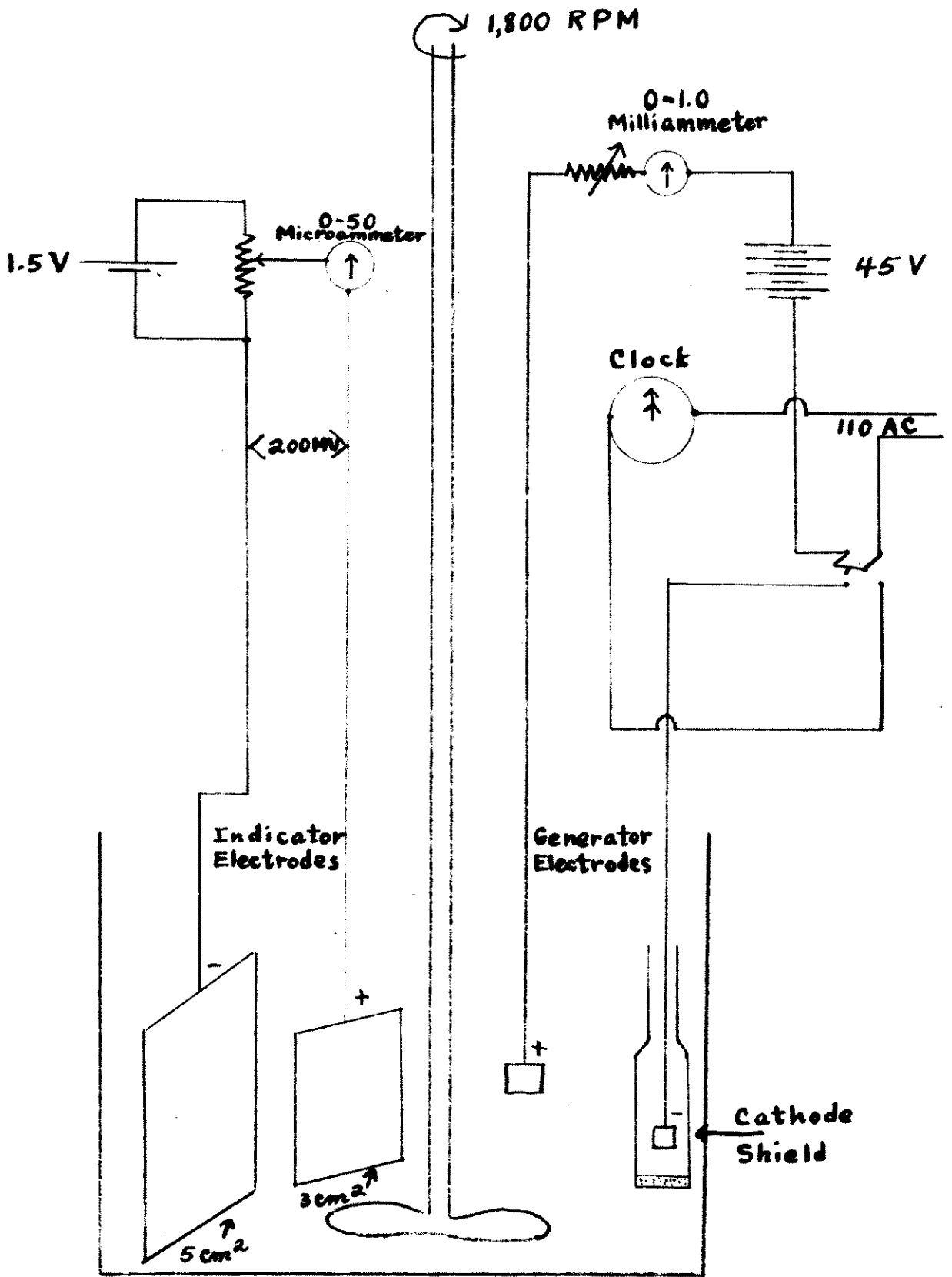


Figure I

antimonous-antimonic potential is -0.84 volts. The potential increases with the acid concentration. (See Part II for further details.) Use of this potential and the bromine potential in a calculation of the equilibrium,  $\text{Sb}^{+III} + \text{Br}_2 = 2\text{Br}^- + \text{Sb}^{+V}$ , shows that there is appreciable equilibrium concentration of bromine and tripositive antimony at the equivalence point. Because of these facts, 2.0 formal acid was used for most of the work.

Because certain of the solutions employed in the potential measurements being made might have iodine present in amounts ranging up to 20 atomic weight per cent of the tripositive antimony, 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. Figure II shows a titration of  $1.43 \times 10^{-5}$  formula weights of tripositive antimony in a solution 2.0 formal in HCl and 0.2 formal in bromide and another with the same amount of antimony plus  $6 \times 10^{-7}$  formula weights of potassium iodide. The minimum was taken as the end point and the assumption was made that the iodine was unipositive at this point. A detailed study of the titration

of iodide and the phenomena at the end point is being made by another investigator.

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 was about 1 microgram; with iodine present in 20 atomic weight per cent an average error of plus 8 micrograms was obtained.

Summary:

Tripositive antimony can be determined in quantities ranging from 10 to 1,500 micrograms by coulometric titration in hydrochloric acid solutions containing bromide with electrolytically generated bromine; the end point is determined amperometrically. Iodide may be present in relatively small amounts.

TABLE I

2N Hcl-0.2N KBr

Time(sec)	End Point Correction(sec)	Current Milliamperes	Sb (Micrograms)		
			Taken	Found	Error
266.5	-0.8	9.463 <sub>5</sub>	1585	1586	+1
267.0	-0.9	"	"	1589	+3
266.7	-1.4	"	"	1584	-1
			"Average	1586	+1
134.8	-1.4	9.467 <sub>5</sub>	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	"	"	50.52	+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

TABLE I (Continued)

1.5N HCl-0.2N KBr

Time(sec)	End Point Correction(sec)	Current Milliamperes	Sb (Micrograms)		
			Taken	Found	Error
261.4	-2.9	9.717 <sub>5</sub>	1585	1585	0
259.6	-1.5	"	"	1582	-3
259.5	-1.2	"	"	1584	-1
			"Average	1584	-1

4N HCl-0.2N KBr

Time(sec)	End Point Correction(sec)	Current Milliamperes	Sb (Micrograms)		
			Taken	Found	Error
259.9	-2.3	9.7160	1585	1579	-6
259.2	-1.5	"	"	1580	-5
259.4	-1.4	"	"	1582	-3
			"Average	1580	-5

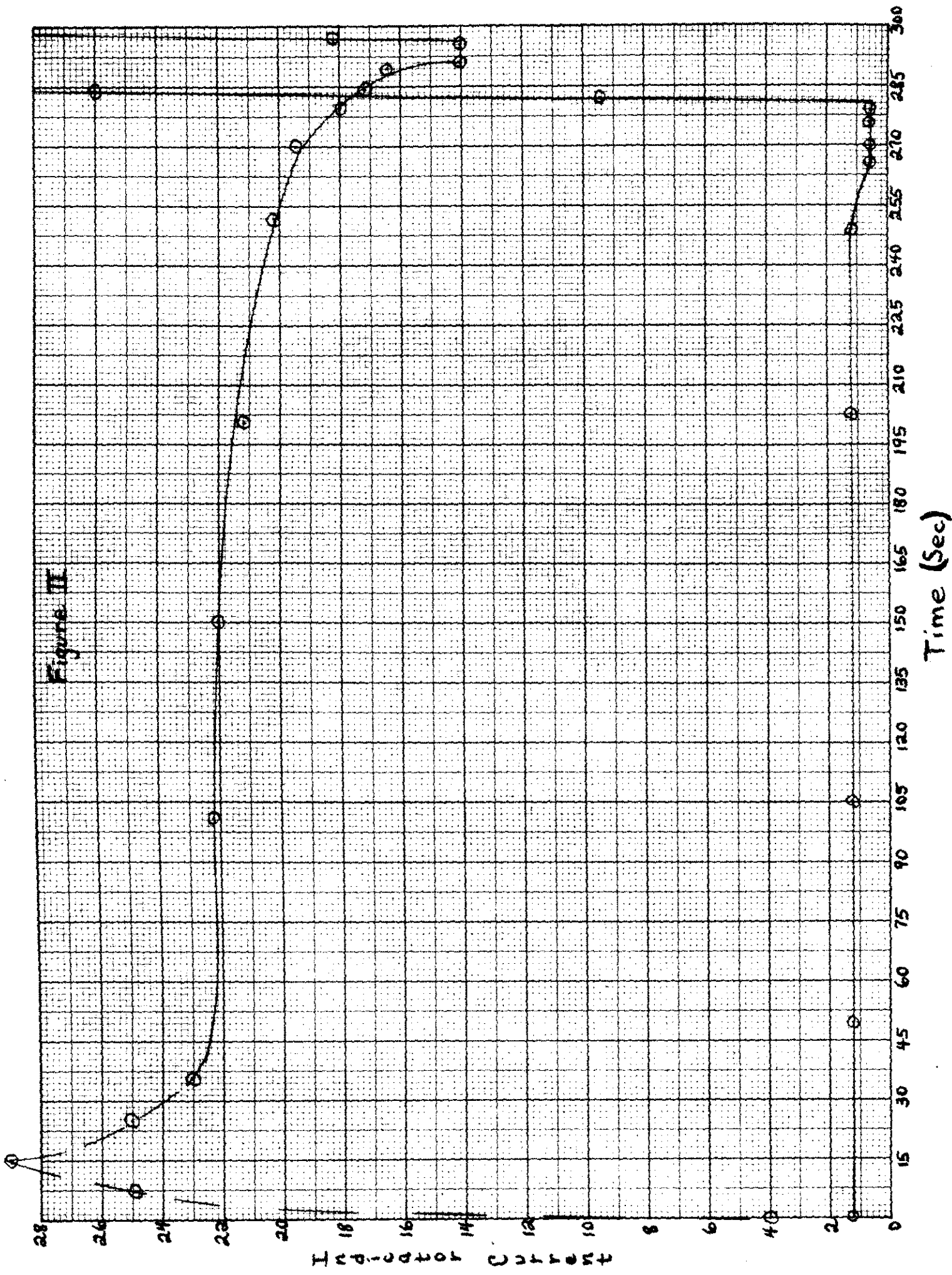
2N HCl-0.2N KBr-2.405X10<sup>-7</sup>fw KI

Time(sec)	End Point Correction(sec)	KI Correction (sec)	Current(MA)	Sb (Micrograms)		
				Taken	Found	Error
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

2N HCl-0.2N KBr-2.409X10<sup>-6</sup>fw KI

Time(sec)	End Point Correction(sec)	KI Correction (sec)	Current(MA)	Sb (Micrograms)		
				Taken	Found	Error
309.4	-1.1	-47.9	9.707 <sub>5</sub>	1585	1595	+10
308.5	-0.9	"	"	"	1591	+6
309.3	-1.3	"	"	"	1593	+8
				"Average	1593	+8

Figure II



References:

1. Myers and Swift, Paper to Be Published
2. Schumann, Journal American Chem Soc 46, 52, 1924.
3. Hillebrand and Lundell, Applied Inorganic Analysis,  
New York: John Wiley and Sons, 1929.



**PART II**

**THE FORMAL POTENTIAL  
OF THE ANTIMONOUS-ANTIMONIC HALF CELL  
IN HYDROCHLORIC ACID**

## Introduction:

A formal potential is the potential of a half cell containing one formula weight total concentration of each oxidation state measured against the standard hydrogen electrode. There is no estimate in the literature of the formal potential of the antimonous-antimonic half cell in hydrochloric acid. Since this value is of considerable interest and use in analytical and inorganic work, it was decided to investigate the possibility of determining it. The medium most commonly used for work with antimony is hydrochloric acid. Consequently, the investigation was carried out in hydrochloric acid solutions.

## Experimental Details:

### Apparatus:

Randall and Young<sup>1</sup> have determined the molal potential for the calomel half cell with hydrochloric acid in the presence of air to be  $-0.2689$ . Since it is readily reproducible and would eliminate junction potential when working with hydrochloric acid solutions of the same concentration, it was chosen as the reference electrode. The values for the half cell in different acid concentrations were calculated using Randall and Young's<sup>1</sup> activity coefficients. The cells were made up with Merck's "reagent" grade

calomel and distilled mercury. With one exception, mentioned later, the cells checked within 0.1 MV against each other.

A student type potentiometer with a Leeds 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 carried out in a constant temperature bath at  $25.02 \pm 0.02^\circ \text{C}$ .

Solutions:

All concentrations are in formula weights per 1,000 grams of solvent. An antimony stock solution was made from  $\text{Sb}_2\text{O}_3$  purified according to a procedure outlined by Schumann.<sup>2</sup> A known amount of  $\text{Sb}_2\text{O}_3$  was added to a definite quantity of approximately 6 weight formal standardized hydrochloric acid. The amount of HCl consumed in dissolving the  $\text{Sb}_2\text{O}_3$  was calculated and corrected for assuming the solution reaction to be:  $\text{Sb}_2\text{O}_3 + 6\text{HCl} = 2\text{SbCl}_3 + 3\text{H}_2\text{O}$ . The stock solution was checked with permanganate. A stock solution of HCl was standardized against potassium acid phthalate by means of sodium hydroxide. All solutions were made up from these stock solutions.

Several methods were used for the analysis of the antimony concentrations. In the potentiometric

titration method for determining the antimonous-antimonic potential, tripositive antimony was titrated using a hydrochloric acid solution of chlorine as the oxidizing agent. Stock solutions were standardized with  $\text{KMnO}_4$  using the procedure of Hillebrand and Lundell.<sup>3</sup> For determining the ratio of tripositive to pentapositive antimony,  $\text{KMnO}_4$  was in general used for large concentrations of tripositive antimony and the coulometric method, outlined in Part I, was used for dilute solutions. Those figures marked with an asterisk in the tables were determined coulometrically.

#### Electrodes:

Platinum electrodes in antimony solutions gave erratic values which changed with stirring. It was found that gold electrodes gave more reproducible results although 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) increased the reversibility of the cells markedly. The iodine was added in the form of  $\text{ICl}$ . The latter was made by passing chlorine into 6 weight formal  $\text{HCl}$  containing iodine. Carbon tetrachloride was used as an end point indicator.

#### Potential Measurements:

An attempt was made to measure the potentials in 2.0 weight formal  $\text{HCl}$  by means of a potentiometric

titration using 2.0 weight formal HCl partially saturated with chlorine as the oxidizing agent. It was found impossible to maintain a constant  $\text{Cl}_2$  concentration even in a closed system. Although tripositive antimony is stable in 2.0 weight formal HCl, it was found that a precipitate formed after several days in these solutions when the antimony was half oxidized to the pentapositive state. The precipitate was not of constant composition but corresponded approximately to the formula  $\text{Sb}_5\text{O}_8\text{Cl}_6$ . The results of one titration are given in Table I and Graph I. They should give an indication of the potential in 2.0 weight formal HCl.

A different technique was used for the determinations in higher acid concentrations. Stopped 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.

To the antimony half cell container was added an antimony solution which had been partially oxidized with a 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 pentapositive by difference. In the calculations all iodine was assumed to be in the form of  $I_2$ .

Table I and Graph I give the results of the potential measurements in various acid concentrations. The values obtained in 6.0 weight formal HCl are not very consistent. It is believed that the calomel cells were responsible. There was disagreement by as much as 2.5 MV between the various cells. It may be that the oxygen present prevents equilibrium from being obtained.

In the tables E represents voltage measured,  $E^{o'}$  voltage corrected for the ratio of tripositive to pentapositive antimony and  $E^{o''}$  the formal potential.

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

The measurements shown in Table I were done with total antimony concentration equal to  $3.2 \times 10^{-2}$  weight formal because the cells were found to be reversible and came to equilibrium in a relatively short time at

this concentration. Upon going to lower antimony concentrations, the cells became less reversible and took longer to come to equilibrium. It took six days for the cells with  $3 \times 10^{-4}$  weight formal total antimony concentration to come to equilibrium. The potential became more positive with time. It was found that the formal potential depended on the total antimony concentration. Table II and graph II show the dependence of the potentials upon total antimony concentration. The vertical lines in the graph represent the average deviation of the formal potential in the respective total concentrations.

The change of potential with total concentration suggested the possibility that the formal potential might change with very large or very small values of the ratio  $\text{Sb}^{+III} / \text{Sb}^{*V}$ . Table III gives the results of some measurements in which this ratio was changed over a ten fold range. In these

experiments the iodine concentration was decreased to one tenth that used in the experiments of Table I and II in order to increase the precision of the determination of small quantities of tripositive antimony. It is to be noted that at this low concentration of iodine the formal potential with the  $\text{Sb}^{+III}/\text{Sb}^{+V}$  ratio roughly equivalent to one is 1.2 MV lower than that in the determination with ten times as much iodine present. When both the iodine and the antimony are reduced by a factor of ten, the difference was 6.0 MV.

The coulometric titration method of Part I with both antimony and iodide present suggests a second method of obtaining the antimonous-antimonic potential. Work by Mr. Wooster in these laboratories has shown that the indicator current in an iodide titration is approximately proportional to the iodine concentration. As outlined in Part I, it is believed that iodide is



first oxidized to iodine and then iodine to iodine monobromide in an antimony titration with iodide and bromide present. The iodine monobromide has been observed to give a relatively large indicator current while the current with iodine monochloride under the same conditions is not significant. Therefore if one takes a definite amount of KI in hydrochloric acid, oxidizes it all to iodine and observes the indicator current, he may, by observing the indicator current, calculate the amount of iodine and iodine monochloride in any partially oxidized antimony solution with the same concentration of acid and of KI. It must be assumed that there is no contribution to the indicator current by the antimony, that there is no association of the iodine with the antimony, and that the iodine and antimony reach equilibrium during the measurement. From the concentrations of the iodine and iodine monochloride one may calculate the iodine-iodine monochloride potential and, assuming equilibrium, the antimonous-antimonic potential.

The concentrations used were: total antimony equals  $3.67 \times 10^{-4}$ , potassium iodide  $2.57 \times 10^{-5}$ , and hydrochloric acid 3.5. The indicator current was 17.8 microamperes for the potassium iodide titration at the mid-point and 10.1 microamperes for the antimony titration at the point where the tripositive

and pentapositive antimony are equal and the iodide has all been converted to iodine. The above values are the result of two titrations which gave only slightly different results. Using these figures and Latimer's<sup>4</sup> value for the iodine monochloride potential,  $E^{\circ} = -1.06$ , one finds  $-0.84$  for the antimonous-antimonic formal potential. This is about 0.1 volt more negative than that obtained with the cells of corresponding acid concentration. The discrepancy between the value obtained by this measurement and that obtained from the cell measurement indicates that one or more of the assumptions is not correct. It is believed that they are all reasonably true with the exception that in antimony solutions of these concentrations the antimonous-antimonic half cell does not come to an equilibrium. Experience with the cells has shown this to be true. The disagreement will be discussed later.

#### Sensitivity of Electrodes:

In an attempt to explain the lower electrode sensitivity of cells with low antimony concentration, an experiment was carried out as follows. In the titration apparatus described in Part I was placed various antimony solutions in 3.5 formal HCl and the indicator current was observed. For concentrations less than 0.01 weight formal in total antimony no appreciable indicator current was observed regardless

of the oxidation state. In more concentrated solutions experiments have shown that there is no indicator current when the antimony is all in either the tripositive or pentapositive state; but that there is considerable current when both are in approximately equal amounts. Graph III shows that the indicator current plotted against the square of the total concentration for solutions made up of equal amounts of tripositive and pentapositive antimony is a straight line. Since the two concentrations are equal, the same result would have been achieved if the indicator current had been plotted against the product of the tripositive and pentapositive 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 show the characteristic color which has been observed for such complexes. Preliminary experiments by Mr. Whitney in these laboratories on the absorption spectra of the plus four complex indicate that the amount of association of tripositive and pentapositive antimony<sup>in</sup> all normal HCl into the plus four complex is proportional to the product of the two concentrations which is in agreement with the above results. As was pointed out in Part I, the indicator current is dependent upon the presence of reversible couples. Therefore the reversibility of the antimony half cell electrode should decrease as some function

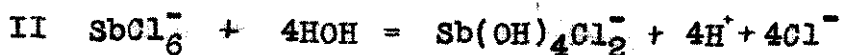
of the square of the total concentration to agree with the results of the experiment described above. This checks qualitatively with the facts.

Discussion of results:

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

Lingane and Nishida<sup>5</sup> in some polarographic experiments have found that pentapositive antimony is not reversibly reduced in dilute HCl concentrations but does give a good half-wave potential in 6 normal HCl. They believe that pentapositive antimony exists in solution in two forms:  $\text{SbCl}_6^-$  and an inert compound probably an oxychloride. Only in strong HCl is there sufficient  $\text{SbCl}_6^-$  to give a reversible reaction. The oxychlorides of antimony are in general insoluble and a better assumption might be that the second species is of the form  $\text{Sb}(\text{OH})_4\text{Cl}_2^-$ . Experimental evidence is that tripositive antimony is reversibly oxidized in moderate concentrations of HCl.

In moderate HCl concentrations probably all the tripositive antimony is substantially in the form of  $\text{SbCl}_4^-$ . If one assumes that  $\text{SbCl}_6^-$  and  $\text{Sb}(\text{OH})_4\text{Cl}_2^-$  are the two pentapositive species present, the reactions taking place when tripositive antimony is oxidized in HCl 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:

$$E = E^\circ - \frac{RT}{2F} \ln \frac{\text{SbCl}_6^-}{\text{SbCl}_4^-(\text{Cl}^-)^2}$$

Since by equation II the  $\text{SbCl}_6^-$  should increase with the acid concentration, the solution potential should become more negative with increasing HCl strength.

The slope of the plot of EMF against the logarithm of the HCl activity should be approximately  $-6 \times 0.02957$  or  $-0.177$  assuming that the  $\text{Sb(OH)}_4\text{Cl}_2^-$  concentration remains constant. Using the EMF found for solutions in 3.5 formal and 6.0 formal HCl and the respective activities, the experimental slope is found to be  $-0.129$  in agreement within the error of the assumptions. At low concentrations of HCl the  $\text{SbCl}_4^-$  should begin to hydrolyze and the slope become less negative. This is observed at around 2.0 formal HCl.

It is believed that reaction II, the hydrolysis of  $\text{SbCl}_6^-$ , proceeds at a rather slow rate and that when tripositive antimony in hydrochloric acid solutions is oxidized, equation I represents the reaction; and consequently  $\text{SbCl}_6^-$  is the predominate species. 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 potentials found under equilibrium conditions from the cells 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 titration value  $-0.84$  should be used for potential calculations.

In support of the above assumptions, it has been observed that in 3.5 formal hydrochloric acid a solution of partially oxidized antimony which has been freshly oxidized has the deep yellow color which has been found to be characteristic of the plus four complex and that this color fades upon standing. In 12 formal hydrochloric acid where there is little tendency towards hydrolysis the color does not fade. The concentration of the plus four complex decreases as the  $\text{SbCl}_6^-$  hydrolyzes as shown in equations II and III.

The variation of the formal potential with total antimony concentration and the ratio  $\text{Sb}^{+III}/\text{Sb}^{+V}$  is undoubtedly in part due to the hydrolysis of the antimony with the consequent change in acid concentration. The change in  $\text{Sb}_2\text{Cl}_{10}^{--}$  concentration with total antimony concentration and the ratio  $\text{Sb}^{+III}/\text{Sb}^{+V}$  may also be a factor.

Summary:

The antimonous-antimonic half cell formal potential in hydrochloric acid has been found to be -0.746 in 3.5 weight formal HCl, -0.784 in 4.5 weight formal HCl, and -0.818 in 6.0 weight formal HCl when the total antimony concentration is  $3.20 \times 10^{-2}$  weight formal. The dependence of the formal potential upon total antimony concentration and the ratio  $Sb^{+III}/Sb^{+V}$  has been studied.

TABLE I - EFFECT OF ACID CONCENTRATION

Total Sb conc wt.f.f.	ICl Conc wt.f.f.	HCl Conc wt.f.f.	E	Sb <sup>3+</sup> /Sb <sup>5+</sup>	E <sup>0'</sup>	E <sup>0</sup>	E <sup>0'</sup>
3.57x10 <sup>-2</sup>	3.57x10 <sup>-4</sup>	2.0	0.4058	3.000	0.4199	0.4199	-0.6705
2.78x10 <sup>-2</sup>	2.78x10 <sup>-4</sup>	"	0.4210	1.000	0.4210	0.4210	-0.6716
1.82x10 <sup>-2</sup>	1.82x10 <sup>-4</sup>	"	0.4363	0.333	0.4222	0.4222	-0.6728
					Average	Average	-0.6716
3.20x10 <sup>-2</sup>	3.20x10 <sup>-4</sup>	3.5	0.5202	0.9846	0.5200	0.5200	-0.7460
"	"	"	0.5196	0.9804	0.5193	0.5193	-0.7453
"	"	"	0.5196	1.038	0.5201	0.5201	-0.7461
"	"	"	0.5200	0.9146	0.5192	0.5192	-0.7452
					Average	Average	-0.7456±0.4mV
3.20x10 <sup>-2</sup>	3.20x10 <sup>-4</sup>	4.5	0.5711	#1.086	0.5721	0.5721	-0.7839
"	"	"	0.5708	#1.023	0.5714	0.5714	-0.7832
"	"	"	0.5711	#1.073	0.5720	0.5720	-0.7838
"	"	"	0.5708	#1.077	0.5718	0.5718	-0.7836
					Average	Average	-0.7836±0.2mV
3.20x10 <sup>-2</sup>	3.20x10 <sup>-4</sup>	6.0	0.6170	1.728	0.6240	0.6240	-0.8168
"	"	"	0.6218	1.594	0.6278	0.6278	-0.8206
"	"	"	0.6172	1.879	0.6253	0.6253	-0.8181
"	"	"	0.6155	1.680	0.6222	0.6222	-0.8150
					Average	Average	-0.8176±1.7mV

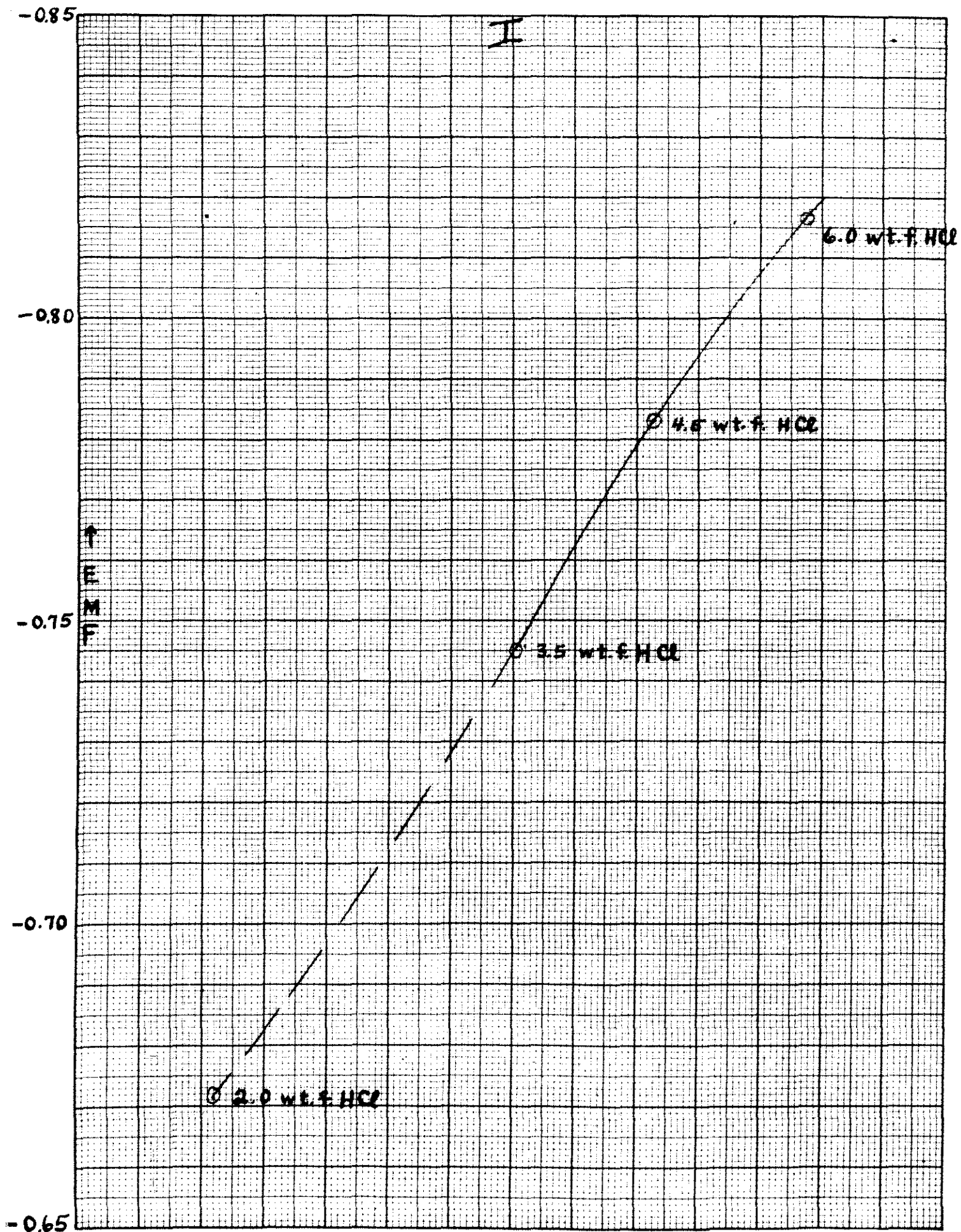


TABLE II - EFFECT OF TOTAL ANTIMONY CONCENTRATION

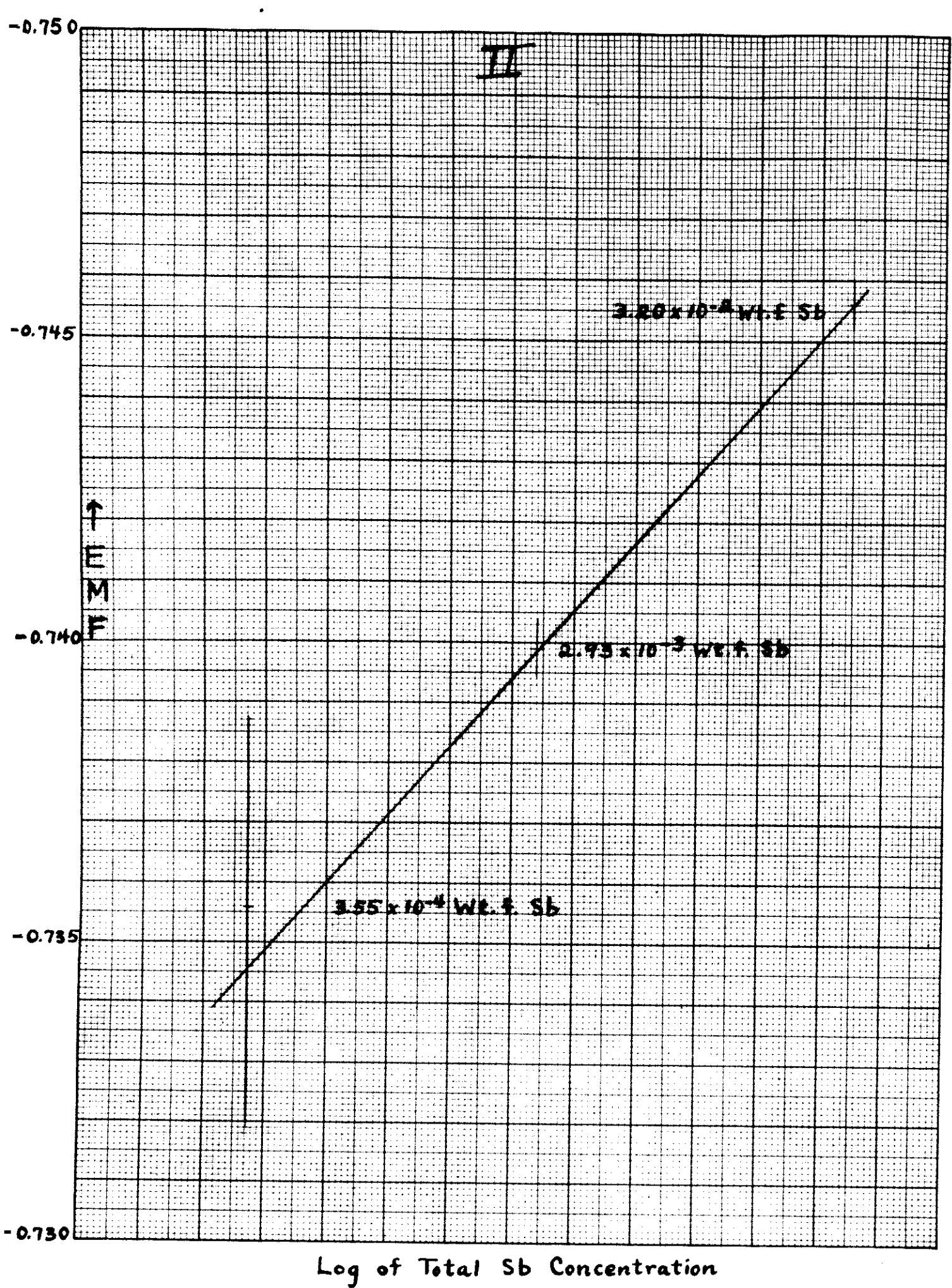
Total Sb Conc wt.f.	ICl Conc wt.f.	HCl Conc wt.f.	E	Sb <sup>+</sup> III/Sb <sup>+</sup> V	E <sup>01</sup>	E <sup>02</sup>
3.20x10 <sup>-2</sup>	3.20x10 <sup>-4</sup>	3.5	0.5202	0.9846	0.5200	-0.7460
"	"	"	0.5196	0.9804	0.5193	-0.7453
"	"	"	0.5196	1.038	0.5201	-0.7461
"	"	"	0.5200	0.9146	0.5192	-0.7452
					Average	-0.7456±0.4mV
2.93x10 <sup>-3</sup>	2.93x10 <sup>-5</sup>	3.5	0.5236	*0.4757	0.5137	-0.7397
"	"	"	0.5268	*0.4161	0.5137	-0.7397
"	"	"	0.5120	*1.186	0.5142	-0.7402
"	"	"	0.5106	*1.216	0.5131	-0.7391
"	"	"	0.5119	*1.251	0.5148	-0.7408
"	"	"	0.5078	*1.253	0.5137	-0.7397
					Average	-0.7399±0.5mV
3.55x10 <sup>-4</sup>	3.55x10 <sup>-6</sup>	3.5	0.5006	*1.985	0.5094	-0.7354
"	"	"	0.5036	*2.193	0.5137	-0.7397
"	"	"	0.4953	*2.276	0.5059	-0.7319
"	"	"	0.4961	*2.094	0.5048	-0.7308
"	"	"	0.5120	*1.161	0.5139	-0.7399
"	"	"	0.5152	*0.8933	0.5139	-0.7399
"	"	"	0.5099	*0.7877	0.5060	-0.7320
"	"	"	0.5111	*0.8673	0.5093	-0.7353
					Average	-0.7356±3.2mV

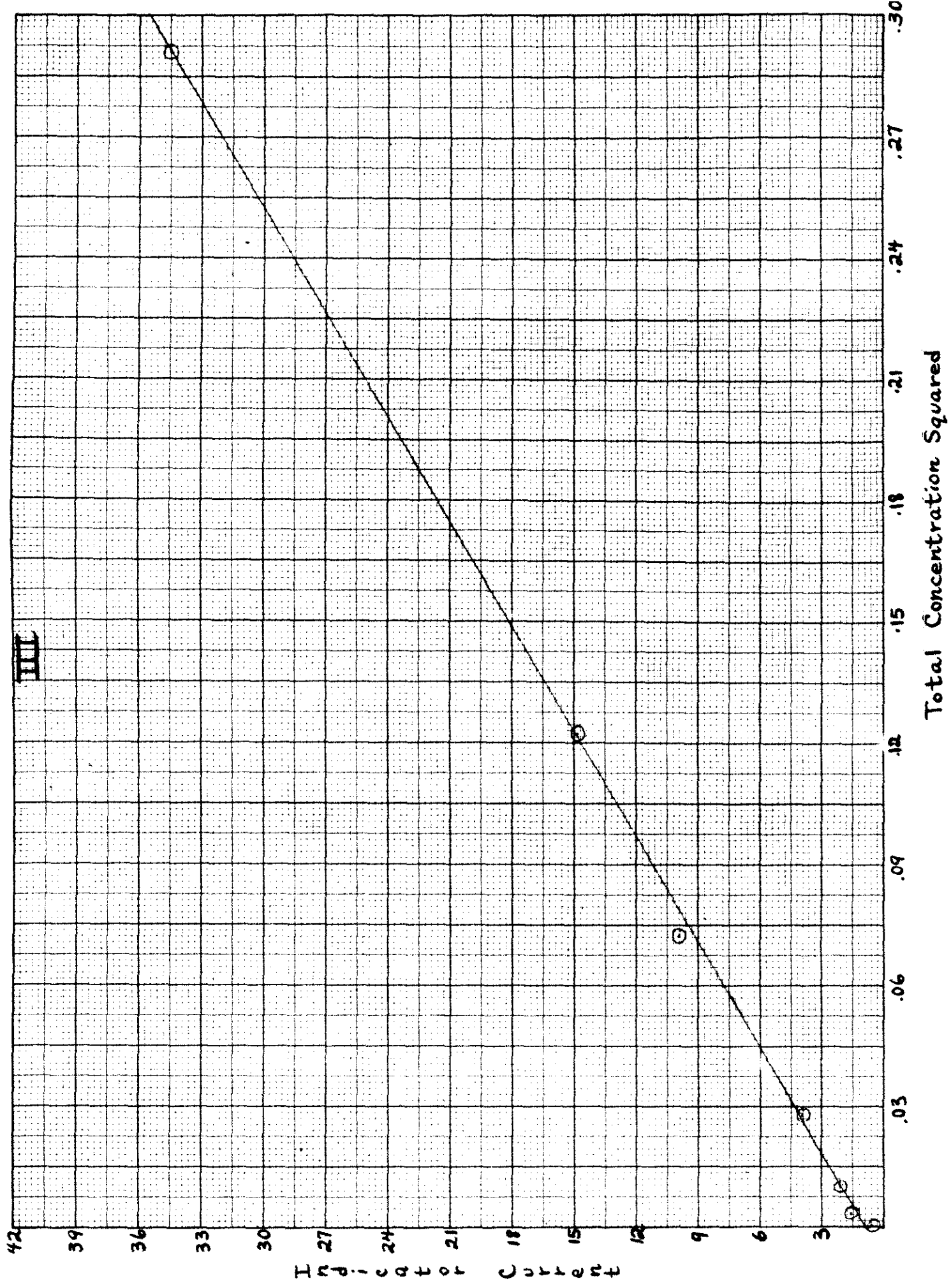
TABLE III - EFFECT OF THE RATIO  $Sb^{+III}/Sb^{+V}$

Total Sb Conc Wt.f.f.	ICl Conc wt.f.f.	HCl Conc wt.f.f.	E	$Sb^{+III}/Sb^{+V}$	$E^{\prime\prime}$	$E^{\prime}$
$3.20 \times 10^{-2}$	$3.20 \times 10^{-5}$	3.5	0.5348	*0.2477	0.5168	-0.7428
"	"	"	0.5313	*0.2528	0.5136	-0.7396
"	"	"	0.5328	*0.2339	0.5141	-0.7401
			Average	*0.245		-0.7408 ± 1.4MV
$3.20 \times 10^{-2}$	$3.20 \times 10^{-5}$	3.5	0.5171	1.139	0.5188	-0.7448
"	"	"	0.5165	1.158	0.5184	-0.7444
"	"	"	0.5154	1.167	0.5174	-0.7434
"	"	"	0.5172	1.139	0.5189	-0.7449
			Average	1.151		-0.7444 ± 0.5MV
$3.20 \times 10^{-2}$	$3.20 \times 10^{-5}$	3.5	0.5055	2.629	0.5179	-0.7439
"	"	"	0.5065	2.494	0.5182	-0.7442
"	"	"	0.5059	2.568	0.5180	-0.7440
"	"	"	0.5061	2.573	0.5182	-0.7442
			Average	2.57		-0.7441 ± 0.1MV



Log of HCl Concentration





III

References:

1. Randall and Young, Journal American Chem Soc 50, 989, 1928.
2. Schumann, Journal American Chem Soc 46, 52, 1924.
3. Hillebrand and Lundell, Applied Inorganic Analysis, New York: John Wiley and Sons, 1929.
4. Latimer, Oxidation Potentials, New York: Prentice Hall, 1938.
5. Lingane and Nishida, Journal American Chem Soc 69, 530, 1947.