COULOMETRIC AND AMPEROMETRIC STUDIES

Thesis by

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ABSTRACT

The coulometric titration of thiosulfate with iodine has been investigated at different hydrogen ion concentrations. The applicability of this titration to the determination of oxidizing agents has been demonstrated by determining microgram quantities of ferric iron, chromate, and selenious acid.

A modification of the Norris and Fay method for the volumetric determination of selenious acid has been compared to a proven, but less direct method.

It has been shown that tripositive antimony can be titrated in concentrated hydrochloric acid solutions more successfully with chlorine than with bromine. Evidence concerning the nature of the species of tripositive and pentapositive antimony existing hydrochloric acid solutions has been obtained amperometrically during the coulometric titrations in hydrochloric acid of tripositive antimony with bromine and chlorine, and of pentapositive antimony with cuprous copper.

The indicator currents obtained with an amperometric system during the reduction of iodate with cuprous copper and during the oxidation of iodide with both chlorine and ceric cerium have been investigated as functions of the hydrogen ion concentration, the chloride concentration, and the applied potential.

A quantitative study of the amperometric system used for above measurements has been made. An equation has been derived which relates the indicator current to the applied potential and to the concentrations of electrode-reactive species in the solution. Experimental tests have been made on the ferrocyanide-ferricyanide half-cell. The amperometric end point is discussed.

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PART I. THE COULOMETRIC TITRATION OF THIOSULFATE WITH IODINE AND ITS
APPLICATION TO THE DETERMINATION OF OXIDIZING AGENTS

Introduction

There is a need for reducing intermediates for secondary
coulometric titrations which will react completely, rapidly, and
stoichiometrically with a large number of oxidizing constituents. In
conventional volumetric titrations these requirements are frequently
met by the addition of excess iodide with subsequent titration of the
liberated iodine by thiosulfate. Therefore, it seemed possible that if
thiosulfate could be titrated with electrolytically generated iodine,
the coulometric process could be extended to many of the conventional
iodometric determinations of oxidizing agents. This investigation was
undertaken to determine the feasibility of the coulometric titration
of thiosulfate with iodine, and to establish the limiting conditions.
The results of three applications of this titration to the determination
of oxidizing agents are reported.

A. THE COULOMETRIC TITRATION OF THIOSULFATE

Although the titration of millinormal thiosulfate with millinormal
iodine, with use being made of either the starch end point (1, 2, 3)
or the amperometric end point (4, 5, 6), has found analytical applica-
tions the optimum conditions have not been studied thoroughly until
recently.

Since the completion of this experimental work, two papers
pertinent to this titration have been published. Tutzundic and

and Mladenovic (7) have titrated thiosulfate with electrolytically generated iodine and have used the starch end point. They did not extend their investigation to solutions as dilute as those in this investigation nor did they investigate the permissible pH limits for the titration. The effect of various pH values on the volumetric titration of millinormal thiosulfate solutions with millinormal iodine, with both the starch and the amperometric end points, has been studied by Bradbury and Hambly (8). The effect of still higher acid concentrations than those investigated by Bradbury and Hambly has been studied and is reported below.

Experimental

Chemicals. Reagent grade chemicals were used. A standard solution of 0.1 VF. (volume formal) sodium thiosulfate was prepared by dissolving 25 g. of sodium thiosulfate pentahydrate and 0.1 g. of sodium carbonate in one liter of freshly boiled distilled water. The resulting solution was standardized against a standard solution of potassium iodate. The millinormal thiosulfate solutions used in the titrations were prepared by appropriately diluting this standard solution with boiled distilled water. Since it was found that the iodine titer of a millinormal thiosulfate solution decreased significantly within two days, a fresh dilute thiosulfate solution was prepared each day that titrations were made.

A 1.0 VF. potassium iodide solution was prepared by dissolving reagent grade potassium iodide in boiled distilled water. The solution was made 0.001 VF. in sodium carbonate in order to retard air oxidation of the iodide.

The buffers listed by Ramsey, Farrington and Swift (9) were used to control the pH values of the solutions. Hydrochloric acid was used in order to obtain hydrogen ion concentrations 0.1 VF. or greater.

Boiled distilled water was used exclusively in making up all solutions; boiling removed a small amount of oxidizing agent from the distilled water and gave smaller blank corrections.

Apparatus, Adjustment, and Procedure. The apparatus used was that described by Meier, Myers, and Swift (10) with the modifications of Ramsey, Farrington, and Swift (9). The preliminary adjustments and the titration procedure were essentially those described by Ramsey, Farrington and Swift (9) with the following changes. In place of the 25 ml. of As(III) solution, 10 ml. of millinormal thiosulfate and 15 ml. of boiled distilled water were pipetted into the titration cell. The titrated solution was 0.1 VF. in potassium iodide and had a volume of 50 ml. When carbon dioxide was used for the titrations under oxygen-free conditions, the gas was bubbled through the water and the acid for five minutes in order to sweep out the dissolved oxygen. Then the thiosulfate and iodide solutions were pipetted into the titration cell, the cell was attached to the titration apparatus and the titration was conducted under a stream of carbon dioxide.

The methods of determining blank time and titration time, of adjusting the generator current, and of maintaining the sensitivity of the indicator electrodes were the same as those described by Ramsey, Farrington and Swift (9).

A potential difference of 135 millivolts was impressed across the indicator electrodes. The generation rates used were 1.037×10^{-7} equiv./sec. and 1.036×10^{-8} equiv./sec.

Discussion

The data obtained from coulometric titrations of 10 ml. of milli-normal thiosulfate (approximately 1 milligram of thiosulfate) with iodine at various pH values are presented in Table I, and show, in agreement with Bradbury and Hambly (8), that between a pH of 1 and 8 titrations can be made with errors of less than 2 parts per 1000 without exclusion of atmospheric oxygen. Titrations of 0.1 milligram quantities show the same absolute error, approximately 1 microgram. The trend from a small positive error at a pH of 8 to a small negative error at a pH of 1 is of doubtful experimental significance. At higher pH values positive errors are obtained. The data of Tables I to III show that in 0.6 to 1.2 VF. hydrochloric acid solutions values within 2 parts per 1000 can be obtained in the absence of oxygen; larger negative errors result in the presence of oxygen. These effects are discussed below.

Titrations at high pH values. At pH values of 9 and 9.7 too much iodine was required and the indicator currents were unstable. At these pH values the indicator current obtained with a blank solution in which iodine had been generated decreased slowly on continued stirring (without further generation of iodine) thus indicating that hydrolysis of iodine was becoming significant (9); however, the decrease of indicator current was so slow that reproducible blanks could be obtained. When a thiosulfate titration was made at these pH values an excess of iodine was required before an end point was obtained and the resultant indicator current then decreased much more rapidly than did those with the blanks. This indicates that during the titration some of the thio-sulfate is being oxidized to a higher oxidation state than tetrathionate,

TABLE I. Titrations of Thiosulfate at Various pH Values.

Oxygen Not Excluded.

pH	Number of Titrations	Thiosulfate ($S_2O_3^=$), Micrograms			
		Taken	Found	Error	Standard Deviation
9.7	2	1071	1192	+121	1.6
9.0	3	1138	1158	+ 20	1.7
8.0	5	1138	1138	0	1.4
7.0	6	1071	1071	0	0.7
	3	107.2	106.5	- 0.7	0.7
5.0	2	1071	1070	- 1	0.0
4.0	4	1138	1137	- 1	0.9
2.0	3	1071	1070	- 1	0.9
HCl, VF.					
0.1	5	1138	1136	- 2	0.6
	2	107.2	106.3	- 0.9	0.3
0.6	5	1138	1127	- 11	3.6

TABLE II. Titrations of Thiosulfate in Hydrochloric Acid Solutions.
All solution except thiosulfate oxygen-free, titrations made under CO_2.

HCl, VF.	Number of Titrations	Thiosulfate ($S_2O_3^=$), Micrograms			
		Taken	Found	Error	Standard Deviation
0.6	6	1071	1067	- 4	0.9
1.2	7	1071	1064	- 7	2.0
1.8	7	1071	1055	-16	2.9
2.4	2	1071	1054	-17	1.6
4.2	2	1071	985	-86	0.0

TABLE III. Titrations of Thiosulfate in Hydrochloric Acid Solutions.
All solutions oxygen-free, titrations made under CO_2.

HCl, VF.	Number of Titrations	Thiosulfate ($S_2O_3^=$), Micrograms			
		Taken	Found	Error	Standard Deviation
0.6	3	1073	1071	- 2	0.4
1.2	3	1073	1071	- 2	1.3
2.4	2	1073	1065	- 8	0.8

and that at least one of the products formed during the titration is being further oxidized by the excess of iodine. The formation of sulfate during the oxidation of thiosulfate by iodine in basic solutions is well-known (11), and could account for the excess iodine required at these high pH values (8).

Titrations at low pH values. Excess iodine was required when solutions 0.05 M. in thiosulfate and having a pH of 1 were titrated volumetrically, presumably because of the reactions:

$$S_2O_3^= + 2H^+ = S + H_2SO_3 \qquad (I-1)$$

$$H_2O + H_2SO_3 + I_2 = 2I^- + HSO_4^- + 3H^+. \qquad (I-2)$$
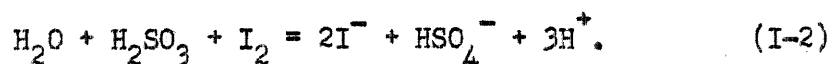
However, the kinetics of reaction (I-1) apparently is such as to cause smaller percentage errors in the titration of more dilute thiosulfate solutions (11a). Analytical procedures have been proposed (4, 6) involving the titration of an excess of millinormal thiosulfate in 0.1 N. acid solutions but it is doubtful if discrepancies of less than a few per cent could have been detected in the confirmatory work reported. We have found about 2 per cent excess of iodine required when 10 ml. of millinormal thiosulfate were added to 50 ml. of 0.5 VF. hydrochloric acid, the solution allowed to stand for 25 minutes under carbon dioxide, then buffered to a pH of 7, iodide added, and the solution titrated coulometrically. However, when the thiosulfate was added to the acid, iodide added at once, and the titration made immediately without buffering the solution, less than the equivalent quantity of iodine was required at the above and all other acid concentrations investigated.

With these dilute solutions the air oxidation of sulfite and/or of iodide in acid solutions apparently has a much greater effect than the acid decomposition of thiosulfate.

In obtaining the values shown in Tables I, II, and III for titrations in hydrochloric acid solutions the titration was made immediately after acidification. In 0.1 VF. hydrochloric acid titrations with errors of less than 2 parts per 1000 can be made without the use of carbon dioxide. When a solution which was 0.1 VF. in potassium iodide and 0.1 VF. in hydrochloric acid was placed in a titration cell on the apparatus and stirred, the indicator current rose very slowly due to air oxidation, but the magnitude of this effect was not such as to cause significant errors in the subsequent titrations made in this concentration of acid.

In 0.6 VF. hydrochloric acid the error is approximately - 1 per cent if oxygen is not excluded. If all of the solutions except the thiosulfate are swept with carbon dioxide for five minutes and the titration is done under carbon dioxide, the error decreases to 0.2-0.3 per cent. When all solutions, including the dilute thiosulfate solution, were made up with water through which nitrogen had been passed, the error decreased slightly to less than -0.2 per cent.

In 1.2 VF. hydrochloric acid, under the same conditions, the error was about the same, but rose to -0.8 per cent when the titration was done in 2.4 VF. hydrochloric acid. Loss of sulfur dioxide is a possible explanation of the consistently negative errors in these oxygen-free solutions.

B. THE DETERMINATION OF FERRIC IRON AND CHROMATE

The determinations on a macro scale of both Fe(III) and Cr(VI) by addition of an excess of potassium iodide to an acid solution and then titrating the liberated iodine with standard thiosulfate have long been standard analytical procedures; therefore these substances were selected as typical oxidizing agents with which to test the analytical application of the coulometric thiosulfate titration. The determinations were carried out by adding the solutions of Fe(III) or Cr(VI) to an iodide solution which was 0.1 VF. in hydrochloric acid, then adding an excess of standard thiosulfate solution and coulometrically titrating the excess with iodine.

Experimental

Chemicals. A solution of 0.1 VF. ferric chloride was prepared by dissolving the salt in 0.1 VF. hydrochloric acid. This solution was standardized iodometrically. A standard solution of 0.1 N potassium dichromate was prepared by diluting to a known volume a weighed quantity of the salt which had been dried for one hour at 150° C.

The more dilute standard solutions were prepared by making appropriate dilutions of these standard solutions. At first the dilute iron solutions were prepared with ordinary distilled water, but it was found necessary to use water through which carbon dioxide had been passed for 20 minutes and then to keep these solutions under carbon dioxide in order to avoid large oxygen errors.

Titration Procedure. Twenty ml. of distilled water, 5 ml. of 1 VF. hydrochloric acid, and 5 ml. of 1 VF. potassium iodide were placed in a titration cell and carbon dioxide was passed through this solution for 5 minutes. Then 10 ml. of the Fe(III) or Cr(VI) solution were added. Ten ml. of the dilute thiosulfate solution were added immediately, the solution was placed on the apparatus, and the excess thiosulfate was titrated at once under carbon dioxide in the same manner as described above.

Two methods were used to obtain a correction for reagent impurities, etc. In the first method, a blank was run with 5 ml. of 1 VF. potassium iodide, 5 ml. of 1 VF. hydrochloric acid and 40 ml. of water under the same conditions as was the titration.

In the second method, which gave results similar to those obtained by the first method, a thiosulfate titration was run as a blank. The blank solution was the same as the titration solution except that the Fe(III) or Cr(VI) solution was replaced by distilled water. The titration time was then subtracted from the blank time to give the net titration time. This method is to be preferred since, in addition to a correction for impurities, a standardization of the thiosulfate is also made under the conditions of the titration.

Discussion

Preliminary experiments showed that the titration of ferric iron is satisfactory only if oxygen is carefully removed from all solutions. Oxygen dissolved in the solutions caused positive errors of about

6 per cent in the titration of 500 mg. quantities of iron even though the titrations were done under carbon dioxide; a similar titration which was not done under carbon dioxide resulted in a positive error of 13 per cent. The dilute standard solutions used for the titrations shown in Table IV were prepared by diluting the stock standard solutions with distilled water through which carbon dioxide had been passed for 20 minutes. Carbon dioxide was also passed through the other solutions used in these titrations and the titrations were done under carbon dioxide. These titration values are slightly high, and show an absolute error of 3 micrograms with quantities of iron greater than 5000 micrograms and of less than 1 microgram with smaller quantities. The data from the dichromate titrations indicate that under the conditions of these titrations the errors are within those of the experimental measurements.

TABLE IV. Confirmatory Determinations of Fe(III) and Cr(VI).
Titrations done under carbon dioxide. Solutions oxygen-free.

| Number of Titrations	Iron, Micrograms			
	Taken	Found	Error	Standard Deviation
5	5755	5758	3	2.2
5	575.3	578.3	3.0	0.6
4	286.2	287.0	0.8	0.2
5	57.5	58.0	0.5	0.7
	Chromium, Micrograms			
5	158.3	158.5	0.2	0.1

C. THE DETERMINATION OF SELENIUM.

Introduction

The determination of microgram quantities of selenious acid is another possible application of the coulometric titration of thiosulfate. Several volumetric methods have been proposed which utilize thiosulfate and iodide for the determination of selenious acid (12, 13, 14, 15, 16, 17, 18). Each of these methods is based either on the reaction of selenious acid with thiosulfate to give selenopentathionate or on the reaction of selenious acid with iodide to give elemental selenium and iodine. The purpose of this investigation was to determine the feasibility of the coulometric determinations of microgram quantities of selenious acid based on these two reactions, and to study and compare the precision and accuracy of such determinations.

In preparation for the coulometric determinations, a stock solution of selenious acid was made up and standardized volumetrically by the Coleman and McCroskey modification (12) of the method of Norris and Fay (17). McNulty (19) has suggested a further modification which permits a direct volumetric titration with thiosulfate to the starch end point. Since McNulty did not investigate carefully the precision and accuracy attainable with his proposed method, the results of titrations of the stock selenious acid solution obtained with this method have been compared with the results obtained by the more complicated Coleman and McCroskey method. The precision and accuracy of this latter method have been carefully studied. The results of these volumetric titrations are given and discussed first.

1. The Volumetric Titration of Milligram Quantities of Selenium.

There are two methods for the determination of selenious acid which make use of standard thiosulfate solutions. In the first, excess iodide is added, and the iodine liberated by the reaction

$$4H^+ + 4I^- + H_2SeO_3 = Se + 2I_2 + 3H_2O \qquad (I-3)$$
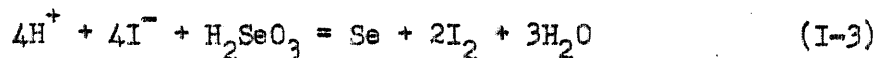
is titrated with standard thiosulfate (13, 16, 15). This method gives low results (20, 16), and the starch end point is obscured by the elemental selenium. In the second method, developed by Norris and Fay (17), an excess of standard thiosulfate is added which reacts with the selenious acid according to the reaction,

$$4H^+ + 4S_2O_3^= + H_2SeO_3 = Se(S_2O_3)_2^= + S_4O_6^= + 3H_2O \qquad (I-4)$$
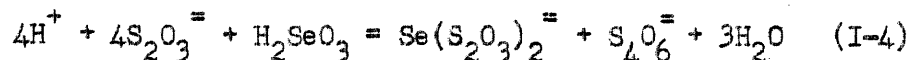
and the excess thiosulfate is back-titrated with a standard iodine solution. This method has been shown by Coleman and McCroskey (12) to give results accurate to within 0.2 per cent at room temperatures if a large excess of standard thiosulfate is avoided. In both of these methods one atom of selenium is equivalent to four moles of thiosulfate.

McNulty (19) has suggested a combination of these two methods in a direct titration. A small amount of potassium iodide is added to the selenious acid and a direct titration is made immediately to the starch end point with standard thiosulfate. The iodide reacts according to Reaction (I-3) above. Since, under the prevailing concentration conditions the reaction of thiosulfate with iodine is slower than the

reaction with selenious acid, Reaction (I-4) predominates when thio-sulfate is added. Any iodine which is reduced to iodide reacts again with selenious acid to give iodine again. If starch is present, the starch iodine color is visible throughout the titration. Only a small amount of elemental selenium is present at the end point, and the end point is not obscured. Although McNulty proposed the addition of only a small amount of iodide, he added more equivalents of iodide than the number of equivalents of selenium present. Thus, only Reaction (I-3) would take place, and his data prove nothing about his proposed method. Therefore, two modifications of McNulty's suggested method were studied. In one of these modifications, the selenious acid is titrated directly with thiosulfate to within a few per cent of the equivalence point before addition of iodide. In the second procedure, a smaller quantity of iodide is added before beginning the titration. These procedures are described below and a discussion is given of the data resulting from their use.

Experimental

Chemicals. A stock solution of selenium dioxide was prepared in the following manner. Eight grams of a technical grade of metallic selenium were dissolved in concentrated nitric acid and the nitric acid was fumed off. The resulting tetrapositive selenium was twice distilled as the tetrabromide from a concentrated hydrobromic acid solution (21) in order to separate the selenium from tellurium and other elements which are not volatile under these conditions. Sulfur dioxide was then passed through the distillate until there was no

further precipitation. The resulting elemental selenium was filtered off and again dissolved in concentrated nitric acid. The nitric acid was fumed off and the resulting selenium dioxide was twice sublimed. This purified selenium dioxide was dissolved in one liter of boiled distilled water and standardized according to the method of Coleman and McCroskey (12).

All other chemicals used were reagent grade.

A 0.1 VF. sodium thiosulfate solution was prepared and standardized against a standard potassium iodate solution.

A 0.1 N. iodine solution was prepared and standardized against the thiosulfate solution.

Titration Procedures. The two procedures described below were used. Procedure A should be used when the approximate amount of selenium present is known since it is subject to fewer uncertainties than Procedure B. Procedure B is useful when the approximate position of the end point is unknown.

Procedure A. The desired volume of selenious acid solution was pipetted into an Erlenmeyer flask, 5 ml. of 6 VF. hydrochloric acid were added, and the volume adjusted to approximately 30 ml. This solution was titrated with thiosulfate to within about a milliliter of the end point. Then 5 ml. of starch indicator solution and 0.5 to 1 ml. of 1.0 VF. potassium iodide were added, and the titration was continued to a starch end point.

When this procedure is followed, only a slight amount, if any, elemental selenium is apparent at the end point.

Procedure B. After pipetting the desired volume of selenious acid into the flask and adding the hydrochloric acid and water, 5 ml. of starch indicator solution and 2 drops (approximately 0.05 ml.) of 1.0 VF. potassium iodide were added. The solution was then titrated with thiosulfate. When the blue color of the starch iodine complex disappeared, two drops more 1.0 VF. potassium iodide were added, and, if the color re-appeared, the titration was continued until a permanent end point was reached.

Discussion of Results

The experimental results obtained with Procedures A and B are shown in Table V. The quantities of selenium taken are calculated on the basis of the standardization of the selenious acid solution by the method of Coleman and McCroskey (12). The agreement is within the volumetric error for both procedures.

In outlining Procedure B, it was stated that before the end point was reached, the starch-iodine color disappeared. If the solution was then allowed to stand, the color would gradually re-appear. More iodide was added in order to save time.

Although Procedures A and B yield comparable results, the statement was made that Procedure A was subject to fewer uncertainties than Procedure B because the most certain procedure is to add the iodide as close to the equivalence point as possible. The results become low as more iodide is added initially in Procedure B. When 1 milliequivalent of iodide was initially added to 2.9 milliequivalents of selenium, the error was -0.7 per cent. When 2 milliequivalents of iodide were added

TABLE V. The Direct Volumetric Titration of Selenious Acid With
Thiosulfate to the Starch End Point.

Procedure	Selenium, Milligrams			Per Cent Error
	Taken	Found	Error	
A	141.6	141.6	0.0	0.0
		141.6	0.0	0.0
	56.76	56.72	-0.04	-0.07
		56.67	-0.09	-0.16
	3.537	3.540	+0.003	+0.09
B	141.6	141.7	+0.1	+0.07
	56.76	56.72	-0.04	-0.07
	3.537	3.538	+0.001	+0.03

initially to the same quantity of selenium, the error increased to
-1.1 per cent. Thus, the amount of iodide added should be kept as
small as possible.

2. The Coulometric Determination of Microgram Quantities of Selenium.

It has been shown that millinormal thiosulfate solutions can be
titrated coulometrically with 0.1 per cent accuracy and precision in
0.1 VF. hydrochloric acid. It seemed possible that microgram quantities
of selenious acid might be determined by adding an excess of standard
millinormal thiosulfate solution and titrating the excess with
electrolytically generated iodine.

Two procedures which are based on volumetric procedures suggest
themselves. In both procedures selenious acid, hydrochloric acid,
sodium thiosulfate, and potassium iodide solutions are mixed, but
the order of mixing is different. If the thiosulfate is added to the
selenious acid solution before the iodide, selenious acid reacts
with thiosulfate to form selenopentathionate according to Reaction
(I-4). If the iodide is added before the thiosulfate, the selenious
acid is reduced to elemental selenium according to Reaction (I-3), and
the thiosulfate then reduces the liberated iodine.

Quantities of selenium ranging from 14 to 1400 micrograms have
been determined by both of these methods and the results are shown
below. The end point was determined amperometrically.

Experimental

Chemicals. Dilute standard solutions of sodium thiosulfate and selenious acid were prepared by appropriately diluting the stock standard solutions described earlier.

All other chemicals were reagent grade.

Apparatus. The coulometric and amperometric apparatus has been described previously (7, 10). The generation rates used were 1.037×10^{-7} and 1.036×10^{-8} equiv./sec. A galvanometer whose sensitivity was set to 0.5 microamperes per division by appropriate shunting was used in measuring the indicator currents. A potential of 200 millivolts was applied across the indicator electrodes.

Procedures. Two procedures, designated C and D, were used. In both of these procedures 10 ml. of selenious acid solution and 5 ml. of 1.0 VF. hydrochloric acid were pipetted into a titration cell, followed by 20 ml. of distilled water. The order of addition of the thiosulfate and the iodide differed in the two procedures.

In Procedure C 10 ml. of dilute standard thiosulfate solution were next pipetted into the titration cell followed by 5 ml. of 1.0 VF. potassium iodide, and the excess thiosulfate was titrated coulometrically with iodine immediately. Selenopentathionate is formed in this procedure.

In Procedure D the 5 ml. of 1.0 VF. potassium iodide were added to the titration cell first, followed by the thiosulfate solution, and the titration then made. Elemental selenium is formed in this procedure.

Blank thiosulfate titrations were run on solutions which were of similar composition except that the selenious acid was replaced with 10 ml. of distilled water.

Except for the determination of 1400 microgram quantities of selenium, these blank thiosulfate titrations agreed within 0.1 per cent with those calculated from the volume and normality of the dilute thiosulfate solution added and from a blank run on the potassium iodide and hydrochloric acid solutions alone.

As was to be expected from the previous work on the coulometric titration of thiosulfate, the thiosulfate concentration (0.002 VF. in the final solution) was large enough in the blank thiosulfate titrations for the 1400 microgram quantities of selenium that the thiosulfate was significantly decomposed by the acid, and as a result, iodine 1 per cent in excess of that calculated was required. Since, in the determination of selenium, the excess of thiosulfate was only about one-third of the total amount added, and since the generation time during a titration was only about one-third of that for the blank, the decomposition during a titration should be much less, and a blank titration run in this way can not be used. In this case a blank was run on the potassium iodide and hydrochloric acid, and the equivalents of thiosulfate added in a determination were calculated.

In all titrations and blanks the final volume was 50 ml., and the concentrations of hydrochloric acid and potassium iodide were each 0.1 VF.

Discussion of Results

The results of determinations by the above procedures are shown in Tables VI and VII. With the exception of the 14 microgram quantities, all errors are positive and are consistently higher when elemental selenium is formed. The per cent error is roughly constant for both procedures. There is a slight trend toward higher percentage errors for larger amounts of selenium when Procedure C is followed. Negative errors might have been expected for the titrations which require larger amounts of thiosulfate on the basis of the titration of thiosulfate alone in 0.1 VF. hydrochloric acid.

The consistency of the positive errors suggests either that some oxidizing impurity was still present in the selenious acid solution which was not reduced in the standardization of the solution, or, as seems more probable, that there is an induced oxygen error. This error is larger when elemental selenium is formed than when selenopentathionate is formed.

In order to check the possibility of an "oxygen error", titrations were made in which the 5 ml. of hydrochloric acid and the 20 ml. of distilled water were swept with carbon dioxide for 5 minutes, then the other solutions were added, and the titration was carried out under carbon dioxide. The results of these titrations are shown in Table VIII along with the results of similar titrations which were made on the same day in which no attempt was made to exclude oxygen. Although a smaller positive error was found in all titrations under carbon dioxide except those in Series IV, the evidence is not conclusive that the error is caused by oxygen.

TABLE VI. The Coulometric Determination of Selenious Acid Using
the Amperometric End Point.

Procedure C -- Selenopentathionate Formed.
Oxygen not Excluded.

Number of Titrations	Selenium, Micrograms				Per Cent Error
	Taken	Found	Error	Mean Deviation	
5	1416	1421	+5	0.59	+0.4
5	1415	1418	+3	0.55	+0.2
4	283.0	284.1	+1.1	0.14	+0.4
5	283.0	283.8	+0.8	0.14	+0.3
5	160.1	160.1	0.0	0.13	0.0
2	141.5	141.7	+0.2	0.08	+0.1
3	141.5	141.5	0.0	0.10	0.0
4	141.5	141.6	+0.1	0.08	+0.1
4	141.4	141.8	+0.4	0.14	+0.3
5	141.3	141.4	+0.1	0.10	+0.1
3	14.11	14.07	-0.04	0.04	-0.3

TABLE VII. The Coulometric Determination of Selenious Acid Using
the Amperometric End Point.

Procedure D — Elemental Selenium Formed.

Oxygen not Excluded.

Number of Titrations	Selenium, Micrograms				Per Cent Error
	Taken	Found	Error	Mean Deviation	
3	1416	1422	+6	0.63	+0.4
3	1415	1423	+8	0.88	+0.6
4	283.0	285.1	+2.1	0.09	+0.7
5	160.1	160.5	+0.4	0.07	+0.3
2	141.5	142.4	+0.9	0.04	+0.6
4	141.5	142.5	+1.0	0.06	+0.7
2	141.4	142.2	+0.8	0.10	+0.6
5	141.3	142.0	+0.7	0.08	+0.5
3	14.11	14.07	-0.04	0.02	-0.3

TABLE VIII. The Effect of Carbon Dioxide on the Coulometric Determination of Selenious Acid.

When carbon dioxide was used, the distilled water and hydrochloric acid were swept oxygen-free with carbon dioxide and the titration was made under carbon dioxide. The selenious acid, the thiosulfate, and the iodide solutions were not oxygen-free.

Series	Procedure	CO_2 Used	Number of Titrations	Selenium, Micrograms				Per Cent Error
				Taken	Found	Error	Mean Deviation	
I	C	No	4	141.4	141.8	+0.4	0.14	+0.3
	C	Yes	4	141.4	141.5	+0.1	0.08	+0.1
II	D	No	2	141.4	142.2	+0.8	0.10	+0.6
	D	Yes	3	141.4	141.9	+0.5	0.37	+0.4
III	C	No	4	141.5	141.6	+0.1	0.08	+0.1
	C	Yes	3	141.5	141.5	0.0	0.06	0.0
IV	D	No	4	141.5	142.5	+1.0	0.06	+0.7
	D	Yes	4	141.5	142.7	+1.2	0.08	+0.8

Experiments were also carried out in which the titration solutions with the iodide absent or present were allowed to stand without stirring and open to the air for 10 minutes before titration. The results are shown in Tables IX and X. When a solution 0.1 VF. in hydrochloric acid and 0.1 VF. in potassium iodide was allowed to stand for a similar length of time, atmospheric oxidation of iodide took place which would correspond to 0.5 micrograms of selenium. The positive error was greater with selenium present under similar conditions for both procedures. This error was much greater when the solutions were mixed in the order outlined under Procedure D than when they were mixed according to Procedure C. Although this evidence is also not conclusive, it offers strong support for the hypothesis that the errors are due to atmospheric oxidation.

In order to ascertain that the rate of solution of atmospheric oxygen was large enough to permit the observed errors, an attempt was made to measure this rate by measuring the rates of oxidation of a stirred solution of 0.1 VF. potassium iodide in various concentrations of hydrochloric acid. The greatest rate of oxidation obtained sets a lower limit on the rate of solution of atmospheric oxygen. The rate of oxidation was determined by measuring the indicator current as a function of time in iodide solutions of the specified acid concentrations which are open to the atmosphere. This indicator current is proportional to the iodine concentration. The results of the measurements are shown in Table XI.

TABLE IX. The Effect of Standing Before Titration With and Without Potassium Iodide Present on the Coulometric Determination of Selenious Acid.

Procedure C — Selenopentathionate Formed.

Time Solution Stood (minutes)	KI Present	Number of Titrations	Selenium, Micrograms				Per Cent Error
			Taken	Found	Error	Mean Deviation	
0		3	141.5	141.5	0.0	0.10	0.0
10	No	2	141.5	141.7	+0.2	0.03	+0.1
10	Yes	2	141.5	142.8	+1.3	0.08	+0.9

TABLE X. The Effect of Standing Before Titration With Potassium Iodide Present on the Coulometric Determination of Selenious Acid.

Procedure	Time Solution Stood (minutes)	Number of Titrations	Selenium, Micrograms				Per Cent Error
			Taken	Found	Error	Mean Deviation	
C	0	2	141.5	141.7	+0.2	0.08	+0.1
D	0	2	141.5	142.4	+0.9	0.04	+0.6
C	10	2	141.5	142.4	+0.9	0.04	+0.6
D	10	2	141.5	143.6	+2.1	0.10	+1.5

TABLE XI.

HCl, VF.	Rate of Air Oxidation (equiv./min.)
0.1	2.3×10^{-9}
2.0	1.9×10^{-8}
6	2.0×10^{-7}

The rates were constant over a ten minute period in the 0.1 VF. and 2.0 VF. hydrochloric acid solutions. The maximum rate of solution of atmospheric oxygen under stirring conditions identical with those under which a titration is made must be greater than 2.0×10^{-7} equiv./min. Thus, this rate is large enough that oxidation by atmospheric oxygen could easily account for the observed errors.

The somewhat inconsistent results obtained on different days could be due to the varying amounts of dissolved oxygen in the boiled distilled water which was used in making up all solutions; the amount of oxygen present is dependent on the length of time that the water or solution has stood between boiling and titration. In order to prove definitely that the observed errors are due to oxygen, all solutions should be made up oxygen-free and the titration should be carried out in an inert atmosphere. Unfortunately, time did not permit any further investigation of this effect.

The determination of selenium was attempted at only one other pH value. When the solution was buffered at a pH of 3, there was no indication of any reaction between the thiosulfate and the selenious

acid in the time required for a titration; the same number of reducing equivalents were found as were found in a titration of the thiosulfate alone.

Conclusions

A modification of the Norris and Fay method for the volumetric titration of selenious acid with thiosulfate has been shown to yield results which are within the accuracy of those obtained by the proven modification of Coleman and McCroskey.

Quantities of selenium varying from 14 to 280 micrograms have been determined coulometrically with an average error of less than +1 microgram and an average per cent error of less than +0.4 per cent when selenopentathionate was formed. The average errors obtained for the same quantities when elemental selenium was formed were larger, but were less than +2 micrograms. The average error for 1400 microgram quantities by both methods was larger than for the smaller quantities; it was less than +5 micrograms when selenopentathionate was formed and less than +8 micrograms when elemental selenium was formed. Contrary to the results of macro determinations, the errors obtained when elemental selenium was formed were all positive instead of negative. These errors are ascribed to atmospheric oxidation.

II. THE COULOMETRIC TITRATION OF ANTIMONY

A. OXIDATION OF TRIPOSITIVE ANTIMONY WITH BROMINE IN HYDROCHLORIC ACID SOLUTIONS.

Introduction

The oxidation of tripositive antimony to pentapositive antimony with electrolytically generated bromine was investigated by Brown and Swift (22), who found evidence that the equilibrium in approximately 3.5 VF. hydrochloric acid solutions was such that at the equivalence point of the titration significant amounts of tripositive antimony and bromine were present. Of all the chemical species present during the titration, only bromide and bromine were known to form a half-cell which would give an indicator current. Since an indicator current is observed which is proportional to the bromine concentration in a solution of bromine in the presence of large excess of bromide, it seemed possible to measure the bromine concentration during a titration by measuring the indicator current. If the bromide concentration, the bromine concentration, and the total bromine generated were known, the solution potential, and the concentrations of tripositive antimony and pentapositive antimony could be calculated. Thus, from measurements of the indicator current during the titration of tripositive antimony with bromine in hydrochloric acid solution, formal potentials of the antimonous-antimonic half-cell could be calculated. The attainment of stable indicator currents indicates either that a real equilibrium is attained in the solution, or that the rate of reaction is so slow that it can not be measured in this way. In either case, useful information

could be derived from calculated formal potentials.

The results of attempts to measure formal potentials in this way were not reproducible enough to make meaningful calculations. When the oxidation of tripositive antimony with electrolytically generated chlorine in hydrochloric acid solutions was investigated later, it was found that the antimonous-antimonic half-cell gives an indicator current in hydrochloric acid solutions. Thus, the assumption that the indicator current is proportional to the bromine concentration is not valid. For these reasons only a limited amount of qualitative information was obtained from the data.

The Effect of Hydrogen Ion and Chloride Concentrations.

The indicator currents observed during a titration depend on the hydrochloric acid concentration. In 2 VF. hydrochloric acid there is no significant indicator current until the equivalence point is reached, after which an indicator current proportional to the generation time is obtained. In 4 VF. hydrochloric acid indicator currents are observed throughout the titration and the sharp change in the slope of the graph of indicator current versus generation time near the equivalence point becomes less pronounced. In 6 VF. hydrochloric acid larger indicator currents are observed throughout the titration, and the change in slope near the equivalence point becomes still less pronounced.

When both the hydrogen ion and chloride concentrations were increased independently, the indicator currents observed during the titration also increased and changes in the current near the equivalence point became more gradual. Increasing the hydrogen ion concentration

had greater effect than increasing the chloride concentration. When
the chloride concentration was greater than 4 VF., the results were not
reproducible enough to determine if the indicator currents increased
or decreased as the chloride concentration was increased while holding
the hydrogen ion concentration constant.

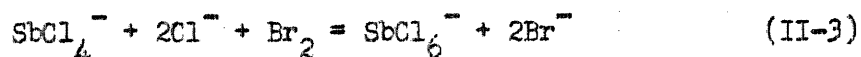### Equilibria of Tripositive and Pentapositive Antimony in Hydrochloric Acid.

In the ensuing discussion, only the chloro complexes of antimony
will be considered since the bromide concentration was constant in all
measurements. Because bromo complexes are not considered, however, it
should not be concluded that their effect is negligible.

The above observations can be explained by reactions of the type
suggested by Brown and Swift (23). Pentapositive antimony in con-
centrated hydrochloric acid solutions first forms a chloro complex,
$SbCl_6^-$, which slowly hydrolyzes to a complex of the type, $Sb(OH)_xCl_{6-x}^-$.
The extent and rate of hydrolysis depend on the acid and chloride con-
centrations. Thus, when tripositive antimony is oxidized, the reactions
are

$$SbCl_4^- + 2Cl^- = SbCl_6^- + 2e^- \qquad\qquad (II-1)$$

$$SbCl_6^- + xHOH = Sb(OH)_xCl_{6-x}^- + xH^+ + xCl^-$$

$$(II-2)$$
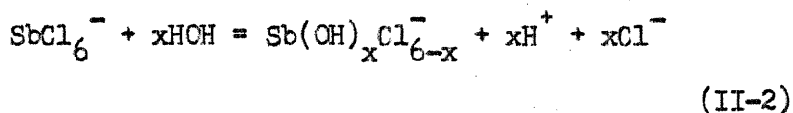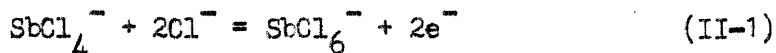
Polarographic evidence also suggests the existence of both $SbCl_4^-$ (24) and
$SbCl_6^-$ (25) in concentrated hydrochloric acid solutions. Increasing
the acid and chloride concentrations favors the formation of $SbCl_6^-$.

For the equilibrium

$$SbCl_4^- + 2Cl^- + Br_2 = SbCl_6^- + 2Br^- \qquad (II-3)$$

the concentration of bromine would decrease as the chloride concentration increases and we would expect the end point to become sharper. However, for the equilibrium involving the formation of hydrolyzed pentapositive antimony

$$2Cl^- + SbCl_4^- + x\ HOH + Br_2 = Sb(OH)_x Cl_{6-x}^- + x\ H^+ + x\ Cl^- + 2Br^-$$

$$(II-4)$$
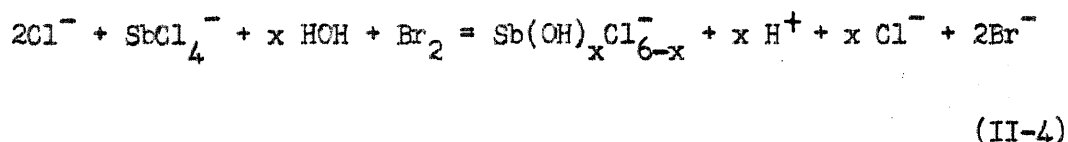
the concentration of bromine is increased by increasing the chloride concentration if $x \geq 3$. In both cases the concentration of bromine is increased by increasing the hydrogen ion concentration. We might expect the currents at the equivalence point to increase with increasing chloride concentration up to a certain concentration and then to decrease as the chloride concentration is further increased. The measurements made when the chloride concentration was greater than approximately 4 VF. were not reproducible enough that any comparison of theory and experiment can be made on this point. On the other points previously mentioned, there was rough qualitative agreement.

Since reproducible quantitative results could not be obtained, this system was not investigated further.

B. THE COULOMETRIC TITRATION OF ANTIMONY WITH CHLORINE.

Introduction

The oxidation of tripositive antimony by bromine is not complete at the equivalence point in hydrochloric acid solutions of concentrations greater than approximately 3.5 VF. (22). Because of the greater oxidizing power of chlorine, the titration of antimony in more concentrated hydrochloric solutions seemed possible if electrolytically generated chlorine was used instead of bromine. Therefore, the coulometric titration of tripositive antimony with chlorine was investigated. The effects of varying the concentrations of hydrogen ion and chloride, and of varying the indicator potential were studied.

Experimental

Chemicals. All chemicals used were reagent grade.

A stock standard solution of tripositive antimony was prepared by the following modification of the procedure of Schuhmann (26). The starting material was antimony trichloride instead of antimony trioxide and the purification procedure was stopped when antimony oxychloride was obtained. This antimony oxychloride was dissolved in the smallest volume of 6 VF. hydrochloric acid and reprecipitated by dilution. It was then filtered off and dissolved in sufficient 2 VF. hydrochloric acid that a solution of tripositive antimony which was approximately 0.1 N. resulted. This solution was standardized against a standard potassium iodate solution according to the procedure of Hammock, Brown, and Swift (27).

The hydrochloric acid used was sufficiently free of extraneous oxidizing and reducing agents that it was used without treatment. Boiled distilled water was used in making up all solutions.

Apparatus. The apparatus used was that described by Meier, Myers, and Swift (8) with the modifications of Farrington and Swift (28). The generation rates were about 10^{-8} and 10^{-7} equiv./sec. The indicator potentials used are indicated in Tables XII and XIII. An applied potential of 300 millivolts was used for earlier titrations since Farrington and Swift (28) found that the indicator current due to the chloride-chlorine half-cell was least sensitive to applied potential at this potential. Later experiments showed that sharper end points are obtained in concentrated hydrochloric acid solutions when a smaller potential is applied.

Procedure. For the titrations in hydrochloric acid alone, the desired quantities of antimony and of hydrochloric acid were pipetted into the titration cell, and sufficient boiled distilled water was added to make the final volume 50 ml. For the titrations in which the hydrogen ion and chloride concentrations were varied, either 12 VF. perchloric acid or 6.0 VF. lithium chloride was added in combination with hydrochloric acid to produce the desired concentrations. The titration cell was then placed on the apparatus and the titration was made to the amperometric end point as described by Farrington and Swift (28). Blanks were run on solutions whose compositions were the same as those titrated except that the antimony solution was replaced with distilled water.

TABLE XII. Results of the Coulometric Titration With Chlorine of
Antimony in Solutions of Varying Hydrogen Ion and
Chloride Ion Concentrations.

Applied Indicator Potential = 300 millivolts

Number of Titrations	Titration Solution	Antimony, Micrograms				Per Cent Error
		Taken	Found	Error	Mean Dev.	
5	1.6 VF. HCl	2380	2384	+4	0.4	+0.2
4	1.6 VF. HCl	2380	2387	+7	1.5	+0.3
2	1.6 VF. HCl	2380	2383	+3	0.5	+0.1
2	1.6 VF. HCl	2382	2385	+3	0.0	+0.1
5	1.4 VF. HCl	1185	1186	+1	1.0	+0.1
3	2.0 VF. HCl	1184	1184	0	0.7	0.0
3	4.0 VF. HCl	1185	*			
3	3.0 VF. H^+ 0.4 VF. Cl^-	1184	1183	-1	0.7	-0.1
2	4.0 VF. H^+ 0.8 VF. Cl^-	1184	1186	+2	1.1	+0.2
2	5.0 VF. H^+ 0.8 VF. Cl^-	1184	1165	-18		-6.6
			1186	+2		+0.2
5	1.4 VF. HCl	119	120	+1	0.6	+0.8
8	1.4 VF. HCl	119.0	120.0	+1.0	0.9	+0.8
5	1.3 VF. HCl	59.2	59.7	+0.5	0.6	+0.8
5	1.3 VF. HCl	14.8	14.7	-0.1	0.4	-0.7

* End Point Uncertain.

TABLE XIII. Results of the Coulometric Titration With Chlorine of Antimony in Solutions of Varying Hydrochloric Acid Concentration.

Applied Indicator Potential = 200 millivolts

Number of Titrations	Titration Solution	Antimony, Micrograms				Per Cent Error
		Taken	Found	Error	Mean Dev.	
4	1.4 VF. HCl	2916	2922	+6	1.2	+0.2
7	1.3 VF. HCl	1452	1456	+4	2.1	+0.3
2	2.5 VF. HCl	1452	1456	+4	0.3	+0.3
2	3.7 VF. HCl	1452	1455	+3	1.9	+0.2
2	5.5 VF. HCl	1452	1466	+14	4	+1.9
6	1.2 VF. HCl	72.4	72.6	+0.2	0.4	+0.3
6	1.2 VF. HCl	14.6	14.1	-0.5	0.4	-3

Discussion

1. Indicator Current Phenomena.

The Effect of Acid and Chloride Concentrations. The indicator currents observed during a titration of tripositive antimony with chlorine in hydrochloric acid solutions depend on both the hydrogen ion and chloride concentrations. The currents observed during a titration of 1400 micrograms of antimony in 6 VF. hydrochloric acid when the indicator potential was 140 millivolts are shown in Figure 1. The increasing currents as the tripositive antimony is first oxidized followed by decreasing currents as the end point is approached indicate that species of both tripositive antimony and pentapositive antimony are present which react at the indicator electrodes to give an indicator current.

When the concentration of chloride was increased while holding the hydrogen ion concentration constant, the magnitude of these currents increased. When generation was stopped midway in a titration in a solution in which the chloride concentration was 6 VF. and the hydrogen ion concentration was 2 VF., stirring continued, and the indicator current measured as a function of time, a stable current was obtained within three minutes after stopping generation. This indicates that under these conditions the electrode-reactive species of antimony are relatively stable.

When the concentration of hydrogen ion was increased while holding the chloride concentration constant, the magnitude of the currents observed during the titration also increased. However, the current observed midway in the titration when the hydrogen ion concentration
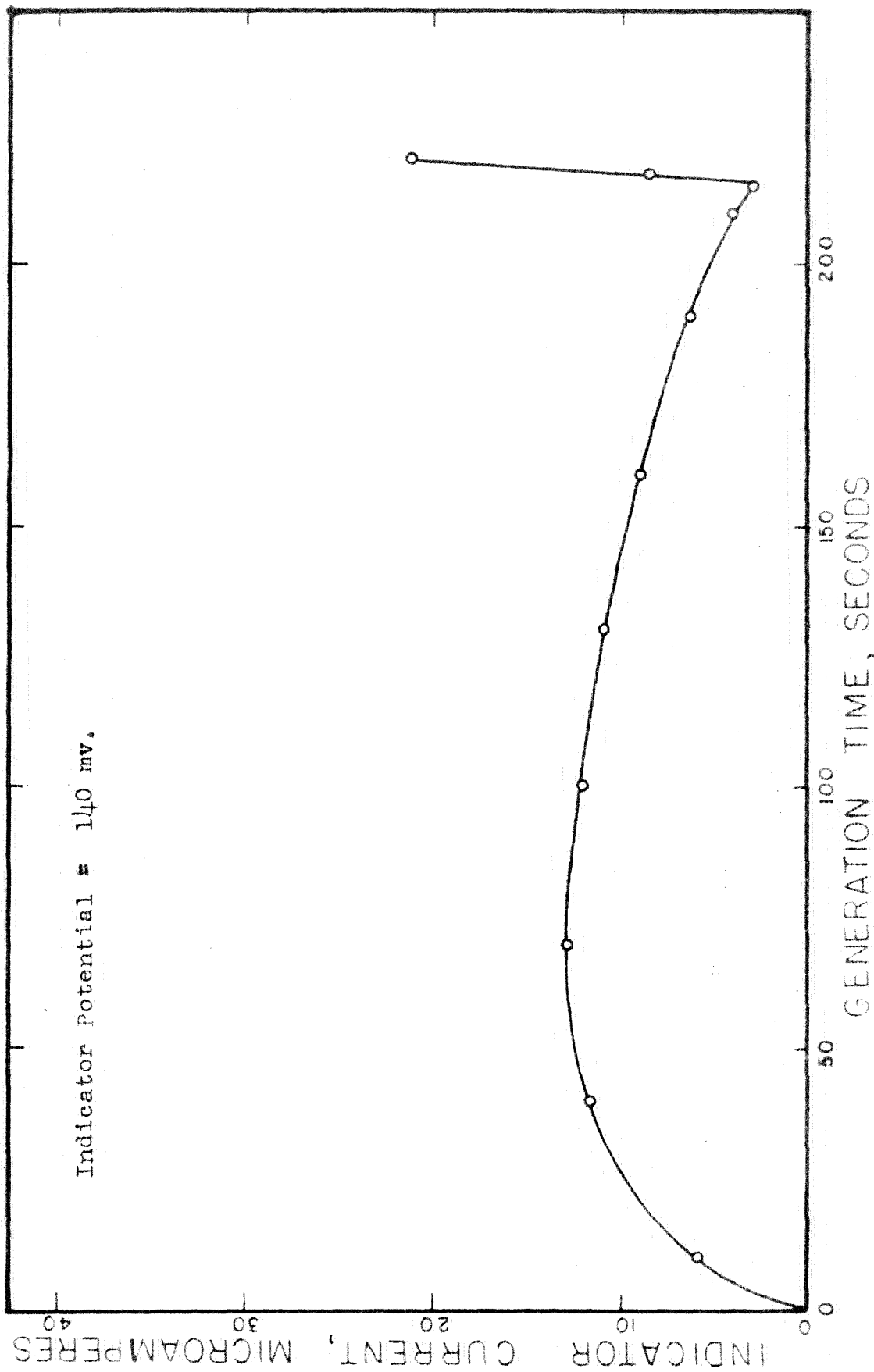
Figure 1. The Indicator Currents Observed in a Coulometric Titration
in 6 VF. Hydrochloric Acid of Sb(III) with Chlorine

was 6 VF. and the chloride concentration was 2 VF. was so unstable that
it was still decreasing significantly seven minutes after generation
was stopped. In 6 VF. hydrochloric acid a stable current was observed
within three minutes after stopping generation at this same point in
the titration.

At a given indicator potential the end point is sharper for
high hydrogen ion concentrations and low chloride concentrations than
it is for high hydrogen ion and high chloride concentrations. When
the indicator potential was 300 millivolts, a sharp end point was
obtained in a solution in which the hydrogen ion concentration was
5 VF. and the chloride concentration was 0.8 VF.; but, when the
hydrogen ion and chloride concentrations were both 4 VF., the changes
in the indicator currents near the end point were so gradual that it
was impossible to determine the position of the end point.

These observations give additional support for the existence
of equilibria of the type proposed earlier. The electrode-reactive
species are chloro complexes of tripositive and pentapositive antimony.
The formation of chloro complexes is favored by increasing both the
hydrogen ion concentration and the chloride concentration. The chloro
complexes of pentapositive antimony are hydrolyzed more rapidly when
the chloride concentration is decreased and the hydrogen ion concentra-
tion is held constant than when the acid concentration is decreased
and the chloride concentration is held constant.

The Effect of the Indicator Potential. At higher hydrochloric
acid concentrations lower applied indicator potentials result in
sharper end points. When the indicator potential was 300 millivolts,
the end point in 4 VF. hydrochloric acid was not sharp and relatively

large indicator currents were observed during the titration. When the indicator potential was 200 millivolts, a sharp end point was observed in 5.5 VF. hydrochloric acid and the indicator currents observed during the titration were much smaller.

The different results observed with different indicator potentials can be explained by considering the effect of applied potential on the indicator current of the antimonous-antimonic half-cell in hydrochloric acid solution. When the ratio of the concentrations of tripositive antimony to pentapositive antimony was 0.04 and the hydrochloric acid concentration was 6 VF., a graph of indicator current versus applied potential was obtained which was shaped like that of the cerous-ceric half-cell shown in Figure 9. The shape of the curve indicates that there is a significant overvoltage. If there were no overvoltage, a horizontal portion of this curve would be observed at applied potentials somewhere between 100 and 300 millivolts. Increasing the applied potential from 200 to 300 millivolts resulted in an indicator current increase of over 20 per cent. The percentage increase would be even larger near the mid-point of the titration.

Near the end point of a titration in 6 VF. hydrochloric acid a graph of indicator current versus applied potential is similar to the graph shown for the ferrous-ferric half-cell in Figure 9. The indicator current with an applied potential of 300 millivolts is about three times as large as that with an applied potential of 200 millivolts.

Some other half-cell besides the antimonous-antimonic half-cell is taking part in the electrode reactions near the equivalence point in the titration at these applied potentials. The standard

potential of the chloride-chlorine half-cell is -1.360 volts (29); the
formal potential of the antimonous-antimonic half-cell in a freshly
prepared solution in 4 VF. hydrochloric acid is -0.84 volts (23). Near
the end point when the ratio of chlorine to chloride is very small and
the ratio of Sb(V) to Sb(III) is very large, conditions are most
favorable for the net electrode reactions

Anode   Cathode

$$Cl^- \rightarrow \frac{1}{2} Cl_2 + e^- \qquad\qquad 2e^- + Sb(V) \rightarrow Sb(III)$$

These are the most likely electrode reactions which could result in
indicator currents near the equivalence point. It is probable that
these reactions are of such significance when the indicator potential
is 300 millivolts that higher currents are observed and the end point
is less distinct than when the indicator potential is 200 millivolts.

2. Analytical Results.

The results of the titrations at varying chloride and hydrogen
ion concentrations are shown in Tables XII and XIII. The results depend
on the hydrogen ion and chloride concentrations and on the applied
potential.

When the indicator potential was 300 millivolts, the titrations
of 1200-2400 microgram quantities resulted in mean errors of less than
+0.3 per cent. The mean errors for titrations of 15-120 microgram
quantities of antimony were less than +0.8 per cent.

The titration was more successful at high hydrogen ion con-
centrations when the chloride concentration was low. Although the mean
titration error was +0.2 per cent in a solution 4 VF. in hydrogen ion
and 0.8 VF. in chloride, the end point was so indistinct in 4 VF.

hydrochloric acid that the uncertainty in the position of the end point was several per cent.

When the indicator potential was 200 millivolts, 1400-2900 microgram quantities of antimony were titrated in 1.4 VF. to 3.7 VF. hydrochloric acid with a mean error of less than +0.3 per cent. The mean error for titrations of 15-75 microgram quantities was less than +0.6 per cent. The error of +1.9 per cent observed when the titration was made in 5.5 VF. hydrochloric acid is possibly due to oxidation of platinum by chlorine.

Conclusions

The titration of tripositive antimony with electrolytically generated chlorine under optimum conditions yields results of accuracy and precision similar to the results obtained when the titration is made with bromine. When chlorine is used, the titration can be made in solutions in which the hydrochloric acid concentration is higher. The use of applied potentials lower than the 300 millivolts previously used for titrations with chlorine is recommended for this titration since sharper end points then result when the titration is made in solutions in which the hydrochloric acid concentration is high.

C. THE REDUCTION OF PENTAPOSITIVE ANTIMONY WITH ELECTROLYTICALLY
GENERATED CUPROUS COPPER IN HYDROCHLORIC ACID SOLUTION.

The reduction of pentapositive antimony with electrolytically
generated cuprous copper in hydrochloric acid solutions was investigated
in order to determine the feasibility of a differential titration of
tri- and pentapositive antimony with the dual intermediates, cuprous
copper and chlorine. The tripositive antimony could be oxidized to
pentapositive antimony with chlorine, and, if the reduction with
cuprous copper was possible, the total antimony present could then be
determined by reduction with cuprous copper. Although cuprous copper
was not a powerful enough reducing agent, the preliminary experiments
yielded some interesting information about the complexes of antimony
in hydrochloric acid solution.

The experiments consisted of oxidizing a known amount of tri-
positive antimony to pentapositive antimony with chlorine in a solution
which was 1.4 VF. in hydrochloric acid and 0.2 VF. in copper sulfate.
After oxidation to pentapositive antimony with chlorine, cuprous
copper was generated in an attempt to reduce the freshly oxidized
antimony. Although a relatively sharp end point was reached, the
number of oxidizing equivalents found was less than the number of
oxidizing equivalents of chlorine previously generated. Since the end
point was sharp, the reaction between cuprous copper and the species
being reduced seemed complete as far as it went. Chlorine was again
generated in the solution until the tripositive antimony was oxidized
to pentapositive antimony again. Then cuprous copper was generated
again. This procedure of alternately generating oxidizing agent and

reducing agent was continued several times. The number of oxidizing and reducing equivalents found in each of these cycles during a typical experiment is shown in the table below:

TABLE XIV. The Oxidizing and Reducing Equivalents Found During Consecutive Oxidations and Reductions of a Solution of Tripositive Antimony.

Cycle	Microequivalents Found	
	Reducing	Oxidizing
1	21.6	11.2
2	11.2	7.3
3	7.3	5.0
4	5.0	3.4
5	3.4	2.3
6	2.4	

After every reduction the same number of reducing equivalents were found on oxidation, but the number of oxidizing equivalents which the cuprous copper was capable of reducing became smaller. Apparently the pentapositive antimony slowly forms a more stable complex which is not reduced by cuprous copper.

In hydrochloric acid solutions of this concentration and with an indicator potential of 300 millivolts, the antimonous-antimonic half-cell gave an indicator current. The electrode-reactive species of pentapositive antimony must react rapidly with cuprous copper in the presence of the platinum electrodes since this reaction can take place through the agency of a platinum electrode even if the reaction

in solution is slow. Thus, the more stable species of pentapositive antimony can not be electrode-reactive.

The nature of the complexes formed is uncertain, but this behavior constitutes additional evidence for complexes of the type already proposed. The electrode-reactive chloro complexes first formed by pentapositive antimony in hydrochloric acid solution react rapidly with cuprous copper, but also hydrolyze more slowly to more stable hydroxy complexes which are not rapidly reduced by cuprous copper.

PART III. COULOMETRIC AND AMPEROMETRIC STUDIES OF THE OXIDATION
STATES OF IODINE.

A. THE REDUCTION OF IODATE WITH ELECTROLYTICALLY
GENERATED CUPROUS COPPER.

An investigation of the reduction of iodate with electro-
lytically generated cuprous copper was undertaken because of the
possibility of effecting a differential titration of iodate and some
other oxidizing agent such as chromate. The feasibility of such a
titration would depend on the possibility of obtaining at least two
end points. If the other oxidizing agent was reduced to a stable
state when iodate was reduced to ICl_2^-, and if the iodate could then
be reduced quantitatively to iodide, two amperometric end points could
be obtained which would correspond to the reductions to ICl_2^- and I^-.
An end point corresponding to reduction of the iodate to iodine would
not be expected in the hydrochloric acid solutions which are required
for the use of cuprous copper as a reducing intermediate (9).

The indicator currents observed in two preliminary titrations
of iodate with cuprous copper when a potential of 50 millivolts was
applied between the indicator electrodes are shown in Figure 2. One
of these titrations was made in a solution which was 0.6 VF. in
hydrochloric acid, 0.6 VF. in perchloric acid, and 0.02 VF. in copper
sulfate. Only small currents were observed during the first 460
seconds of this titration. After 460 seconds of generation, the
current increased to a maximum, decreased to a minimum at 585 seconds,
increased to another maximum, and finally decreased to another minimum
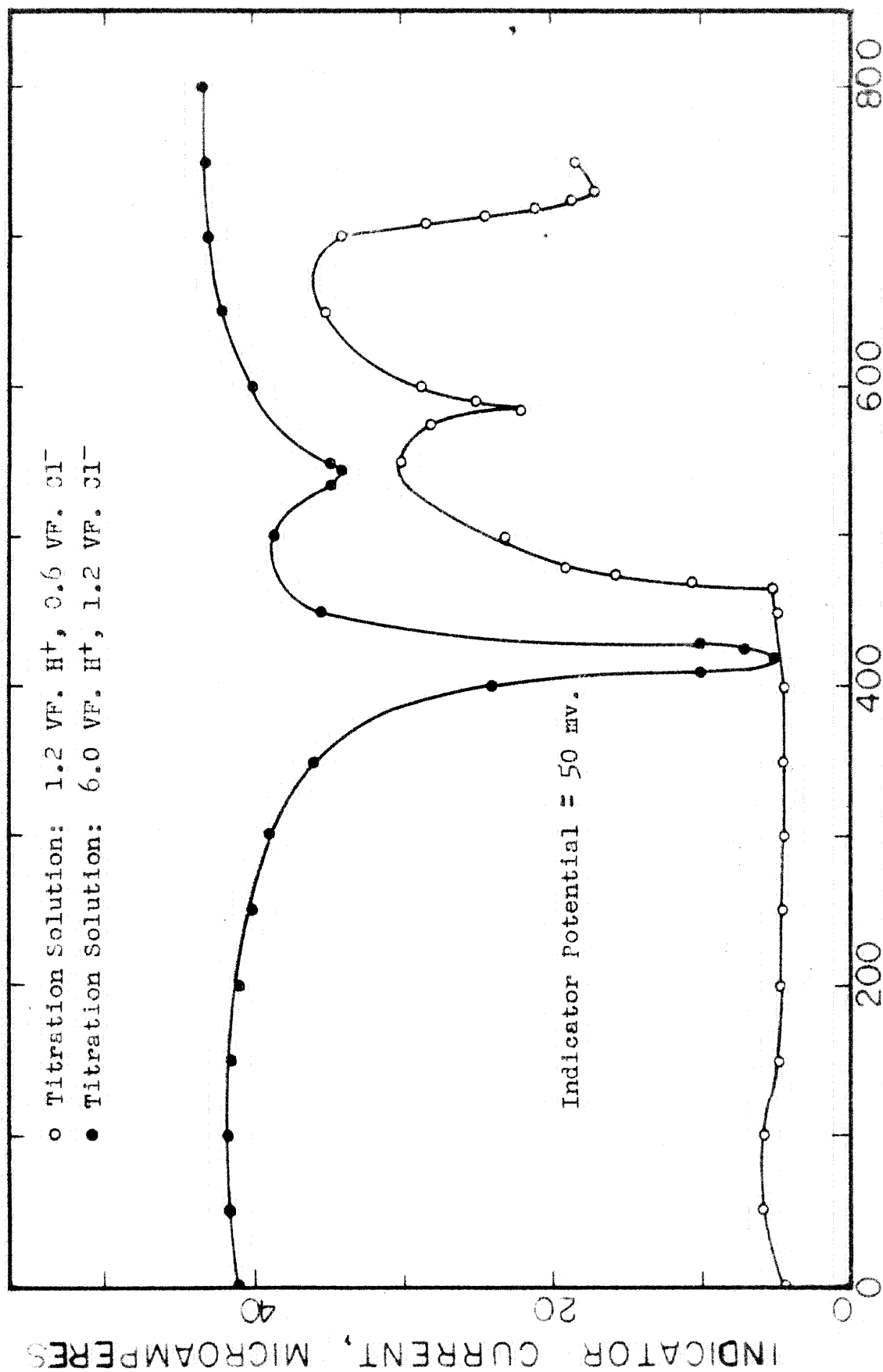at 630 seconds. The ratio of these times is roughly as 4:5:6,

Figure 2. The Indicator Currents Observed During Titrations of Iodate with Cuprous Copper.

corresponding to reduction to ICl_2^-, to I_2, and to I^-. The existence
and positions of the current minima corresponding to reduction to I_2
and I^- are so critically dependent on the applied potential, the
hydrogen ion concentration, and the chloride concentration that the
value of these end points for accurate quantitative work is doubtful.
The effect of changing the conditions of the titration on these current
minima is discussed more fully in the next section. The other titration
which was made in a solution which was 1.2 VF. in hydrochloric acid,
4.8 VF. in perchloric acid, and 0.02 VF. in copper sulfate shows that
the existence of a current minimum corresponding to reduction to iodide
is dependent on the conditions of the titration. The large currents
observed during the first 420 seconds of the titration are due to the
presence of chlorine formed in one or both of the following reactions:

$$6H^+ + 6Cl^- + IO_3^- = ICl_4^- + Cl_2 + 3H_2O$$

$$6H^+ + 6Cl^- + IO_3^- = ICl_2^- + 2Cl_2 + 3H_2O$$
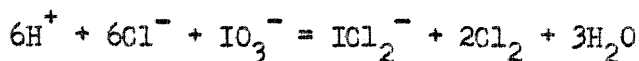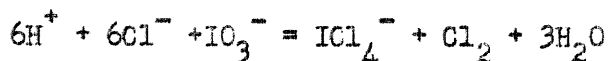
Some of this chlorine escaped from the solution or was reduced by the
electrodes resulting in the appearance of the ICl_2^- end point at
420 seconds instead of at 460 seconds. The rate of formation of
chlorine increased as both the hydrogen ion and chloride concentrations
were increased, but appeared to be much more dependent on acid con-
centration than on chloride concentration.

In view of the above experimental facts, a differential
titration seemed impossible. The only reproducible end point was the
ICl_2^- end point. A few titrations were made in order to determine if
iodate alone could be titrated quantitatively with cuprous copper to

this end point. The currents obtained after this end point became more stable as the hydrochloric acid concentration was increased, but increasing the hydrochloric acid concentration resulted in low values because of the formation and escape of chlorine. This difficulty was partially avoided by making the titrations in the following way. Five milliliters of a solution which was 12 VF. in hydrochloric acid and 0.2 VF. in copper sulfate were diluted with 30 milliliters of distilled water in a titration cell. Then 10 milliliters of standard dilute iodate solution were pipetted into the cell, the cell was placed on the coulometric apparatus, and cuprous copper was generated until about 5 seconds of generation time remained before the end point. Then 10 milliliters of 12 VF. hydrochloric acid were added and the titration was completed. The results of such titrations are shown in Table XV.

TABLE XV. Results of the Titrations of Iodate with Electrolytically Generated Cuprous Copper.

| Titration | Micromoles of Iodate | | Per cent Error |
	Taken	Found	
1	6.201	6.185	-0.3
2		6.193	-0.1
3		6.103	-1.6
4		6.156	-0.7
5		6.190	-0.2

These results indicate that an oxidizing agent, probably chlorine, is lost under the conditions of these titrations. This investigation was not pursued further.

B. THE OXIDATION OF IODIDE WITH ELECTROLYTICALLY GENERATED CHLORINE.

Introduction

Iodide is oxidized by chlorine in hydrochloric acid solution first to iodine and then to iodine monochloride. Since both the iodide-iodine and the iodine-iodine monochloride half-cells are electrode-reactive, the indicator current behavior during the titration would be as follows if no complicating reactions occurred:

1. An increase in current -- the current is first limited by diffusion of iodine to the cathode and increases as the concentration of iodine increases.

2. A maximum, followed by a decrease -- eventually the iodide concentration becomes so small that diffusion of iodide to the indicator anode determines the current and the current decreases as the iodide concentration decreases.

3. When the iodide is quantitatively oxidized to iodine, essentially no current is observed since only one constituent of an electrode-reactive half-cell is present in the solution.

4. An increase in current -- as iodine is oxidized to iodine monochloride the current is limited by diffusion of iodine monochloride (and ICl_2^-) to the cathode.

5. A maximum, followed by a decrease -- when diffusion of iodine to the anode becomes the current-limiting process, the current decreases as the concentration of iodine decreases.

6. When the iodine is quantitatively oxidized to iodine mono-chloride, essentially no current is observed.

7. A current increase -- as excess chlorine is generated, a current due to the chloride-chlorine half-cell is observed.

In order to simplify the discussion, the indicator current minimum at or near that point in a titration corresponding to quantitative oxidation or reduction to iodine will be designated the iodine minimum.

Although an iodine minimum was observed when iodate was reduced with cuprous copper in hydrochloric acid solutions, no iodine minimum was observed by Wooster, Farrington, and Swift (30) when iodide was oxidized with electrolytically generated chlorine in hydrochloric acid solutions. Instead of two current maxima, Wooster, Farrington, and Swift observed only one. An investigation was undertaken to determine the cause of this difference. The effects of varying the chloride concentration, the total iodine concentration, and the indicator potential are reported below.

Experimental Behavior

The indicator currents observed when iodide was oxidized with electrolytically generated chlorine in solutions in which the chloride concentration was varied from 0.35 to 1.2 VF. are shown in Figure 3; the initial iodide concentration was 1.0×10^{-4} VF., the hydrogen ion concentration was 0.1 VF., and the indicator potential was 145 millivolts. As the chloride concentration was increased, the current became greater at the iodine minimum and the minimum became less pronounced.
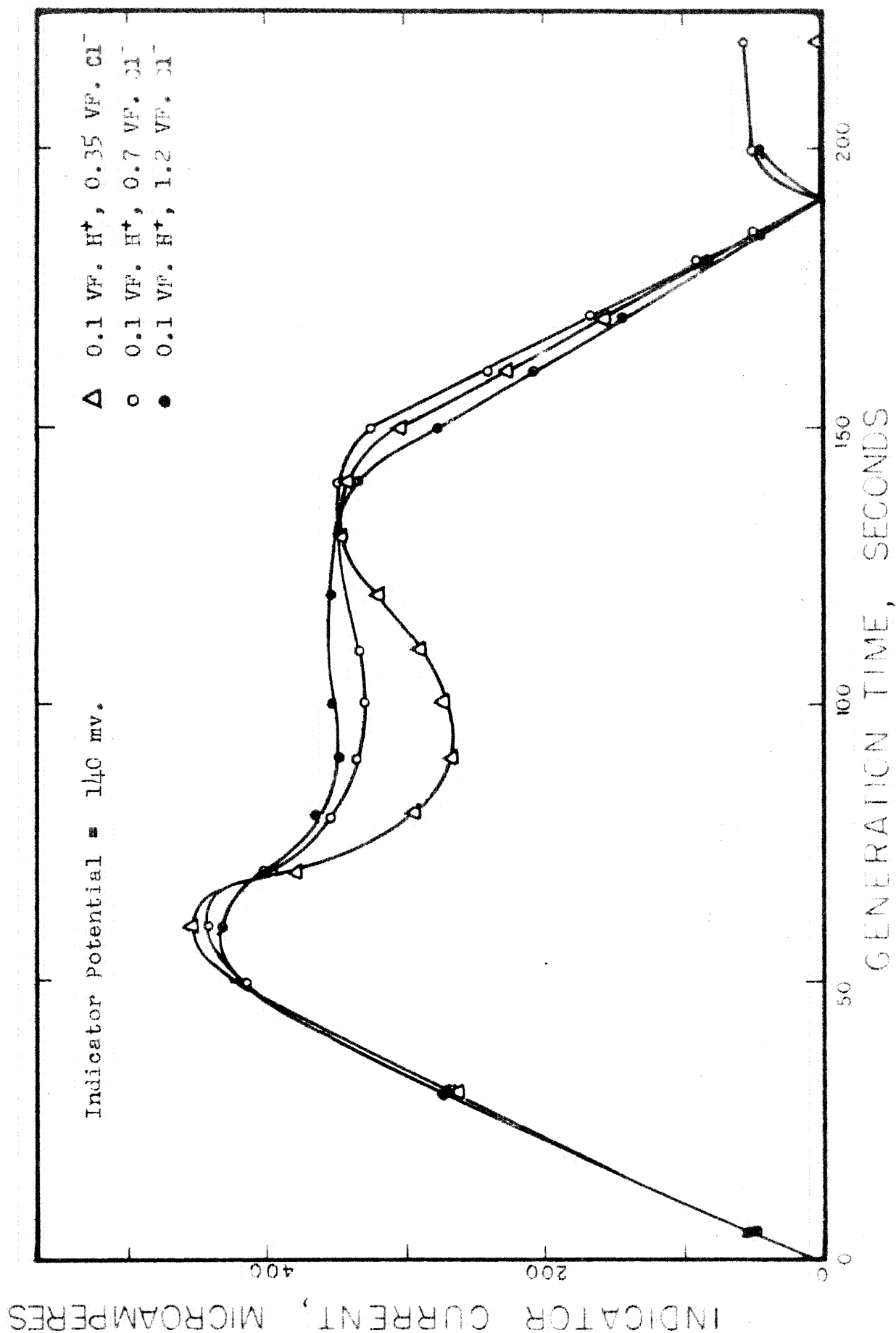
Figure 3. The Effect of Chloride Concentration on the Indicator
Currents Observed in Coulometric Titrations of Iodide with Chlorine.

The indicator current behavior observed when the chloride con-
centration was varied from 1.2 to 4.8 VF., the hydrogen ion concentra-
tion was 1.2 VF., the initial iodide concentration was 1.0×10^{-4} VF.,
and the indicator potential was 145 millivolts, was slightly different.
As the chloride ion concentration was increased, the iodine minimum
continued to become less pronounced and finally disappeared. In contrast
to the observed behavior at lower chloride concentrations, the current
at this point decreased as the chloride concentration was increased.

When the initial iodide concentration was varied with the applied
potential 145 millivolts and the hydrochloric acid concentration 1.2 VF.,
the currents shown in Figure 4 were observed. As the initial iodide
concentration was increased, the current increased at the point in the
titration corresponding to oxidation to iodine and a minimum (the
iodine minimum) appeared at this point and became more pronounced.

That the currents observed are also dependent on the applied
potential is shown by Figure 5. The data plotted there were taken in a
single titration in which the iodide was partially oxidized, the
indicator current measured as a function of applied potential, more
chlorine generated, the indicator currents at different potentials
again measured, and this process continued until the iodide was
oxidized to ICl_2^-. Data taken in this way are not quantitatively
reproducible, but the following effects are qualitatively reproducible;
1. At potentials of less than 200 millivolts, there is an iodine
minimum. 2. As the indicator potential is increased to 200 millivolts,
the minimum current increases and the minimum becomes less pronounced.
3. At 300 millivolts only one current maximum is observed whose position
moves with increasing potential toward the position originally occupied
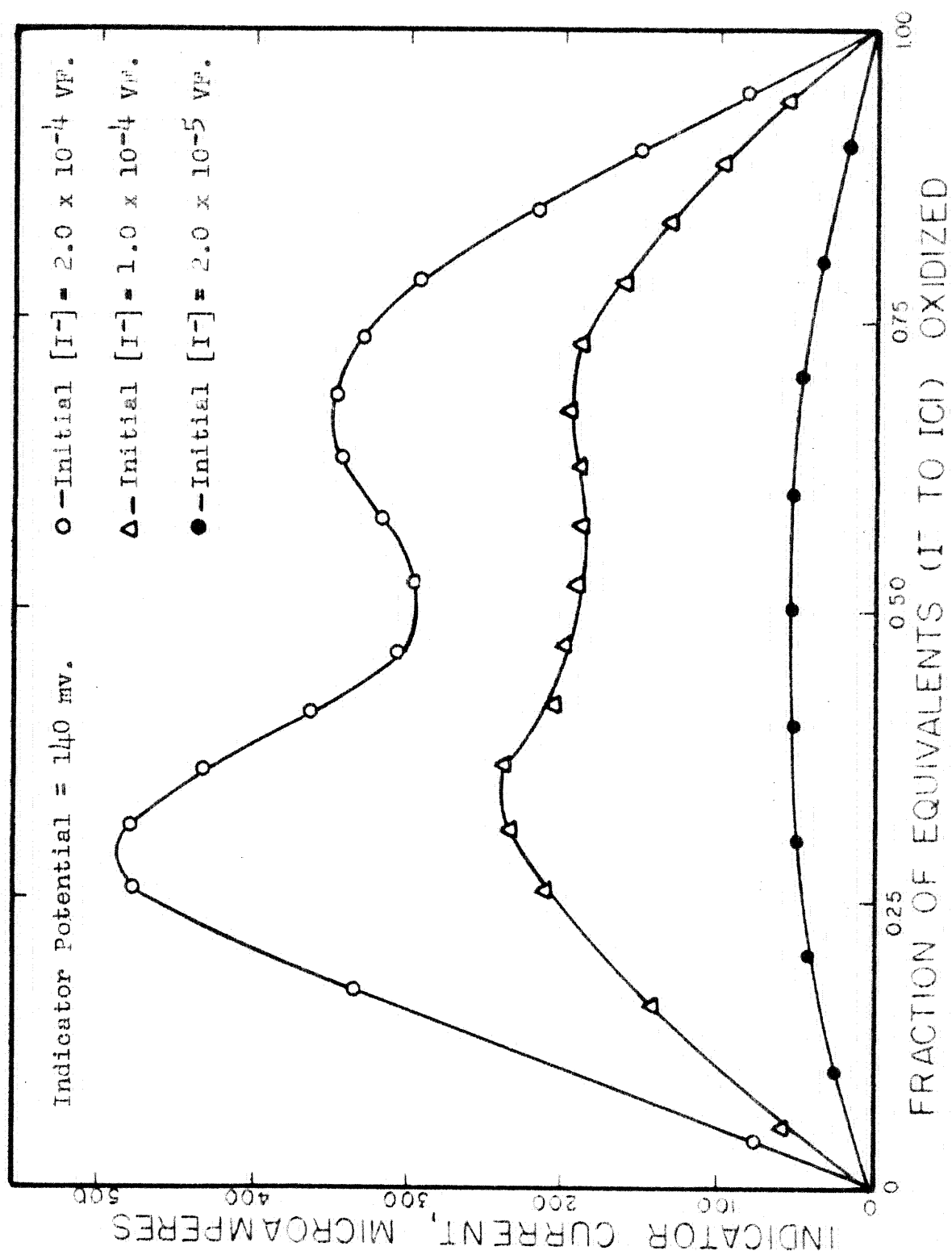by the iodine minimum.

Figure 4. The Effect of Initial Iodide Concentration on the Indicator Currents Observed in Coulometric Titrations in 1.2 VF. Hydrochloric Acid of Iodide with Chlorine.
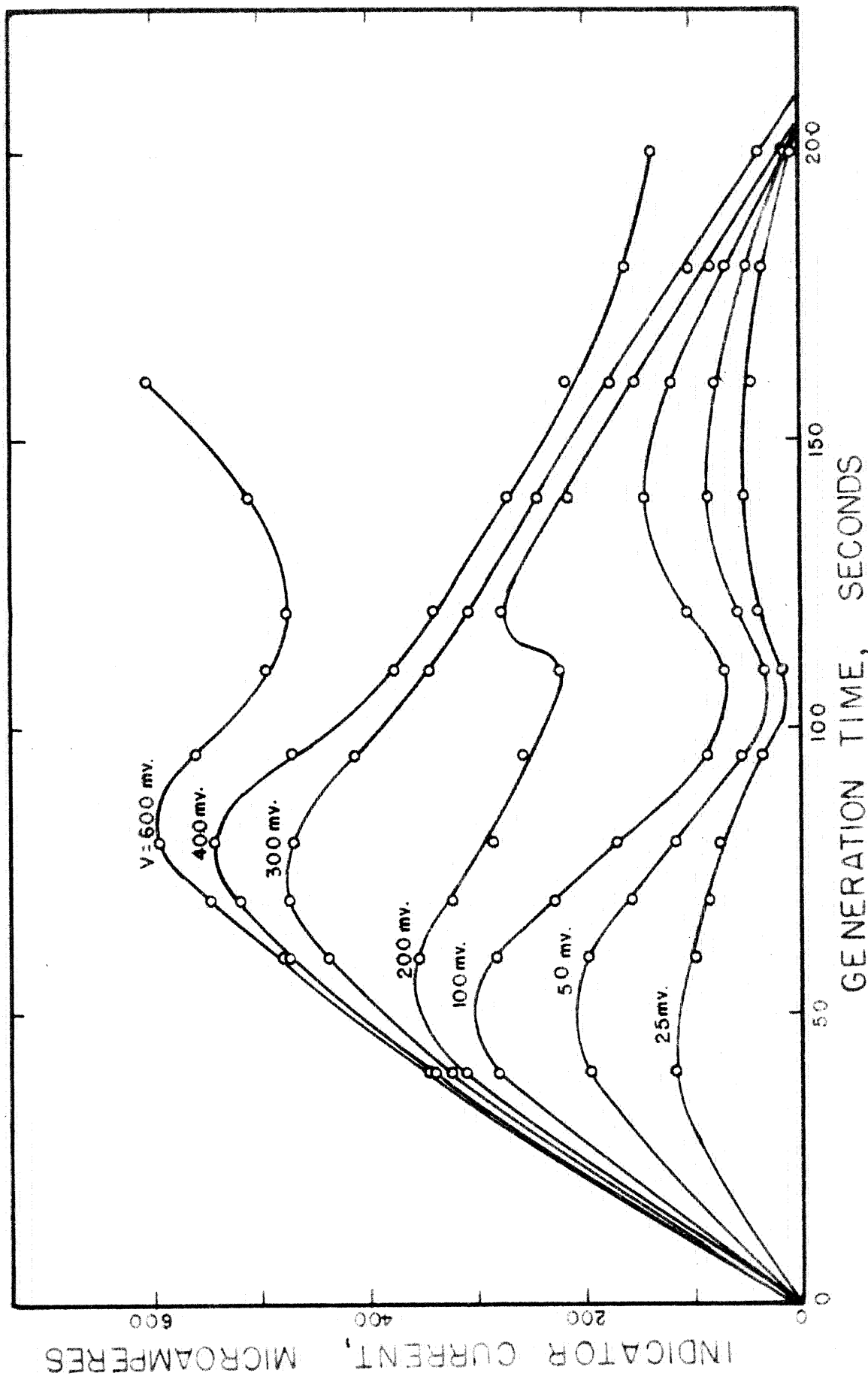
Figure 5. The Effect of Applied Potential on the Indicator Currents Observed During a Coulometric Titration in 0.3 VF. Hydrochloric Acid of Iodide with Chlorine.

Discussion

The indicator currents observed during the oxidation of iodide in hydrochloric acid solutions depend on the chloride concentration and on the initial iodide concentration in the way described in the previous section. The reaction of iodine with hydrochloric acid must be considered in order to explain the observed currents at the point in the titration corresponding to oxidation to iodine.

In a hydrochloric acid solution iodine disproportionates according to the reaction

$$I_2 + 2Cl^- = ICl_2^- + I^-.$$
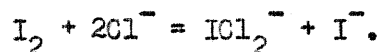
Other equilibria are

$$I_2 + I^- = I_3^- \qquad \text{and} \qquad ICl + Cl^- = ICl_2^-.$$
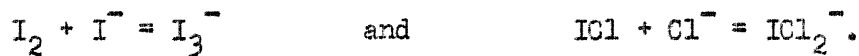
The equilibrium constants are (31, 32)

$$\frac{[I_3^-]}{[I^-][I_2]} = K_1 = 7.1 \times 10^2$$

$$\frac{[ICl][Cl^-]}{[ICl_2^-]} = K_2 = 6 \times 10^{-3}$$

$$\frac{[ICl_2^-][I^-]}{[I_2][Cl^-]^2} = K_3 = 1.5 \times 10^{-7}.$$

The following treatment considers these equilibria only when exactly enough chlorine has been generated to oxidize all of the iodide to iodine. The situation is the same as if an equivalent amount of elemental iodine had been added to a hydrochloric acid solution.

Thus,

$$[ICl] + [ICl_2^-] = [I_3^-] + [I^-]$$

and the fraction D of the total iodine present which is dispro-
portionated is

$$D = \frac{[ICl] + [ICl_2^-]}{T}$$

where

$$T = [I^-] + [ICl] + [ICl_2^-] + 2[I_2] + 3[I_3^-].$$

Since the total original iodide T varied experimentally from
2.0×10^{-5} to 2.0×10^{-4} VF.,

$$\frac{[I_3^-]}{[I_2]} \leq 710(1 \times 10^{-4}) = 0.071.$$

This represents the maximum possible value for this ratio. As a
simplifying approximation, the $[I_3^-]$ will be neglected. Also, since
the lowest chloride concentration investigated was 0.35 VF.,

$$\frac{[ICl_2^-]}{[ICl]} = \frac{[Cl^-]}{6 \times 10^{-3}} \geq \frac{0.35}{6 \times 10^{-3}} = 6 \times 10^1.$$

Thus, the [ICl] may be neglected. The fraction disproportionating is
then

$$D = \frac{[ICl_2^-]}{T} \qquad \text{and} \qquad T = [I^-] + [ICl_2^-] + 2[I_2].$$

On solving for D in terms of T and $[Cl^-]$, we obtain

$$D = \frac{-\dfrac{K_3[Cl^-]^2}{2} + \sqrt{\dfrac{K_3^2[Cl^-]^4}{4} + \dfrac{T}{2} K_3[Cl^-]^2}}{T}$$

Under the experimental conditions only the last term under the radical is significant. Thus, to a good approximation

$$D = \sqrt{\frac{K_3}{2T}} \ [Cl^-].$$

According to this simplified treatment the fraction disproportionating increases with increasing chloride concentration and decreases with increasing initial iodide taken.

When iodine disproportionates to give I^- and ICl_2^-, both components of two electrode-reactive half-cells are present in the solution and, consequently, an indicator current which does little chemical work can exist. Therefore, at applied potentials of less than 150 millivolts an indicator current can exist whose magnitude is roughly proportional to the degree of disproportionation. As the chloride concentration is increased, the fraction of the total iodine present which disproportionates increases. Hence, the currents at the iodine minimum increase and the minimum tends to disappear as the chloride concentration increases. However, as the total initial iodide concentration is increased and the chloride concentration is held constant, the fraction of the total iodine present disproportionating decreases even though the $[I^-]$ and the $[ICl_2^-]$ increase. Thus, the current at the iodine minimum increases, but the minimum becomes more pronounced.

Although the experimental observations can be explained qualitatively in this way, the observed currents are too large to be due the equilibrium chemical disproportionation of iodine. If no chemical work was done by electrolysis, the maximum current would be given by the sums of the maximum diffusion currents of ICl_2^- to the
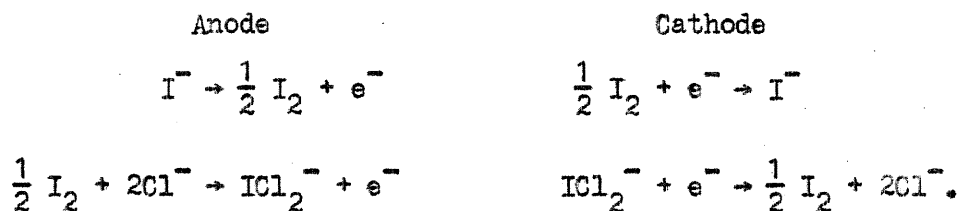
cathode and of I^- to the anode. Under conditions most favorable to
disproportionation, i.e., with

$$T = 1.0 \times 10^{-4} \qquad \text{and} \qquad [Cl^-] = 4.8,$$

$$D = 0.29.$$

This value is too small to account for the observed currents completely,
especially in those cases in which the iodine minimum disappears; there-
fore the electrode reactions must be examined in more detail and the
effect of the applied potential considered.

Two sets of half-cell reactions involving iodine can take place
at the indicator electrodes

Anode	Cathode
$I^- \rightarrow \frac{1}{2} I_2 + e^-$	$\frac{1}{2} I_2 + e^- \rightarrow I^-$
$\frac{1}{2} I_2 + 2Cl^- \rightarrow ICl_2^- + e^-$	$ICl_2^- + e^- \rightarrow \frac{1}{2} I_2 + 2Cl^-$.

As long as the reaction at one electrode is the reverse of the reaction
at the other electrode, the composition of the solution is unchanged
by the indicator current; therefore no net chemical work is done, and
only a small applied potential is needed to produce an indicator
current. However, if the electrode reactions are

Anode	Cathode
$\frac{1}{2} I_2 + 2Cl^- \rightarrow ICl_2^- + e^-$	$\frac{1}{2} I_2 + e^- \rightarrow I^-$
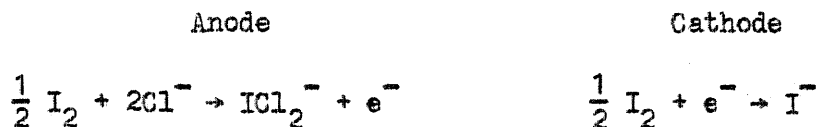
chemical work is done by this electrolytic disproportionation even
though the ICl_2^- and I^- react on diffusing into the body of the solution
and the composition of the solution is not changed. Additional energy

and therefore higher potentials are required for such electrode reactions which change the composition of the solution in the immediate vicinity of the electrodes. This energy re-appears as heat when the I^- and ICl_2^- react in the body of the solution.

This electrolytic disproportionation current is limited by the diffusion of iodine to both electrodes. Thus, as the applied potential is increased, a current maximum should appear near the point in the titration where the iodine minimum appeared at lower applied potentials. The position of this maximum would depend on the diffusion coefficients of the involved species as well as their concentrations.

The current behavior shown in Figures 3, 4, and 5 is best explained by a combination of the equilibrium disproportionation and the electrolytic disproportionation of iodine in hydrochloric acid solutions. These data support the view of Wooster, Farrington, and Swift (30) that diffusion of iodine to the indicator electrodes controlled the current throughout the titration under their experimental conditions.

It should be noted in Figure 5 that when the applied potentials were less than 200 millivolts, the indicator currents can be extrapolated to the same end point. When the applied potentials were greater than 200 millivolts, another reaction began to take place at the electrode (the anode) which controls the current in the final fourth of the titration. This reaction is probably

$$Cl^- \rightarrow \frac{1}{2} Cl_2 + e^-.$$
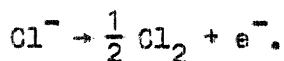
When the applied potential was 600 millivolts, this reaction became so predominant that the indicator current increased instead of

decreasing as the equivalence point was approached. The fact that when the applied potential was 400 millivolts, an indicator current nearly proportional to generation time was observed which extrapolated to an end point resulting in an error of about 2 per cent emphasizes that care must be exercised in choosing the applied potential when the amperometric end point is used.

C. THE OXIDATION OF IODIDE WITH ELECTROLYTICALLY
GENERATED CERIC CERIUM

A preliminary investigation of the indicator currents obtained with a constant applied potential during the oxidation of iodide to iodine with permanganate in the absence of chloride was made by Ramsey (30). It seemed desirable to study these indicator currents as a function of applied potential. In order to generate the oxidant coulometrically ceric cerium was used (33). Fifty-two milliliters of a solution which was 2×10^{-4} VF. in potassium iodide, 0.2 VF. in perchloric acid, and 0.8 saturated with cerous sulfate were titrated. Figure 6 shows the indicator currents observed when iodide was titrated coulometrically with ceric cerium in this solution and the applied potential was varied. In later experiments cerous sulfate was replaced by the more soluble cerous nitrate. The data plotted in Figure 6 were taken during a single titration. Ceric cerium was generated for a given length of time, generation was stopped, and the indicator current was measured as a function of the applied potential at this point in the titration. This process was repeated at other points in the titration. The expected indicator maximum was observed near the mid-point in the titration of the iodide to iodine. The curvature of the left-hand portions of the curves may be due to the formation of tri-iodide or it may be due to irreversible behavior at the indicator electrodes.

Figure 6 illustrates a point also mentioned in connection with Figure 5. For applied potentials up to 200 millivolts the observed indicator currents may be extrapolated linearly to the same end point.
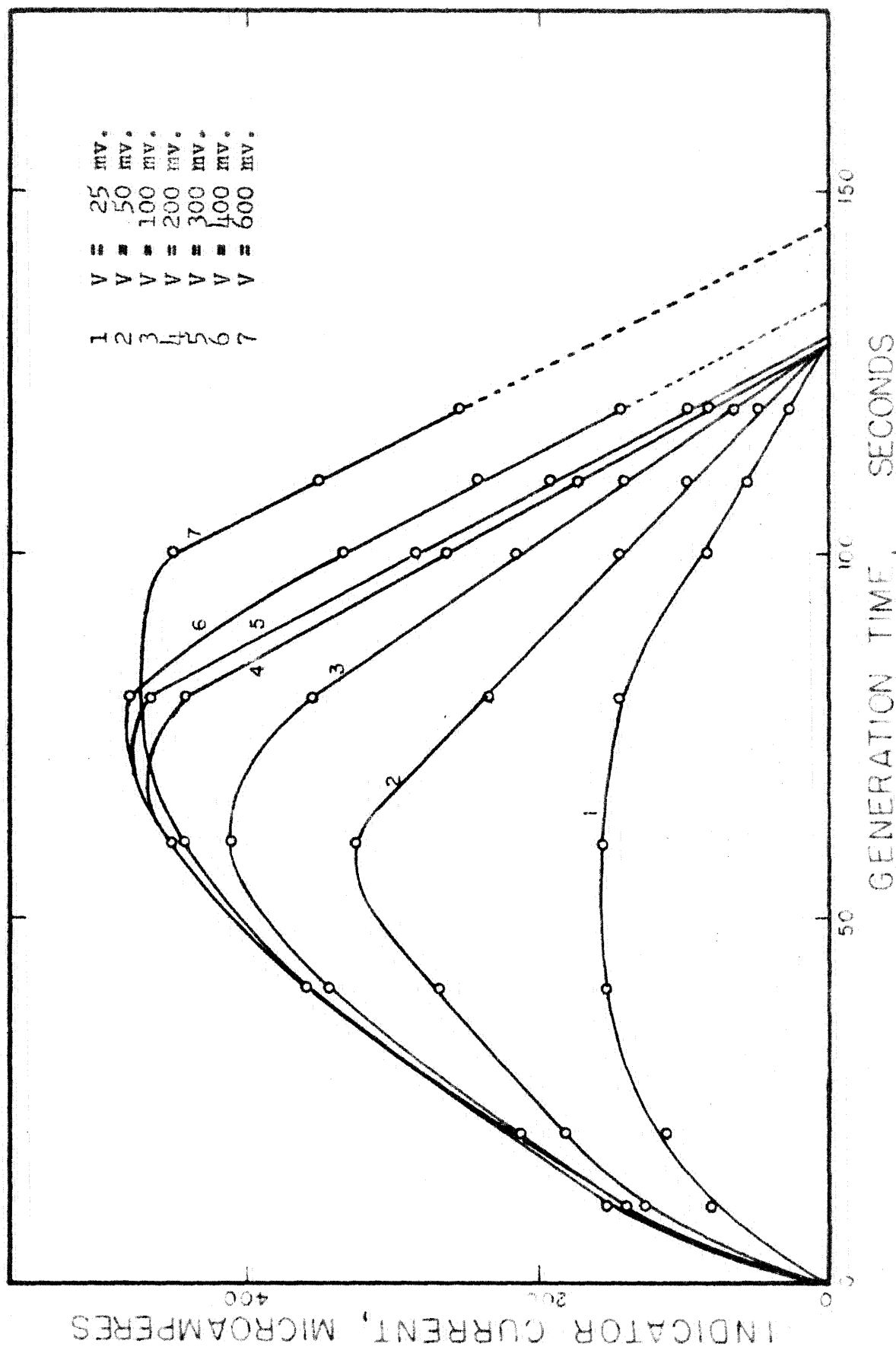
Figure 6. The Effect of Applied Potentials on the Indicator Currents Observed in a Coulometric Titration of Iodide with Ceric Cerium.

For potentials of 300 millivolts and above, although a linear extrapolation appears possible, it leads to results several per cent higher than the result obtained when the indicator potential was less than 200 millivolts.

The most striking feature of the curves in Figure 6 is the approach to a limiting current throughout the titration at an applied potential between 200 and 300 millivolts. This fact suggests that a quantitative study based on diffusion as the only current-determining step might be made of the indicator current as a function of the applied potential and of the fraction oxidized during such a titration Such a study was made and is described in the next section.

IV.   AMPEROMETRIC MEASUREMENTS AND THE SO-CALLED
DEAD-STOP END POINT.

INTRODUCTION

This investigation was undertaken in an effort to obtain a
more quantitative understanding of the principles underlying the
amperometric system used in this laboratory with coulometric titrations
(30, 34, 35, 36). This system is fundamentally the same as that
used in obtaining the so-called "dead-stop" end point of Foulk and
Bawden (37). There has been a tendency to consider the "dead-stop"
end point as a phenomenon depending upon a vaguely defined "polarization"
(8, 37, 38, 39, 40), rather than as a special case of the general use
of amperometric measurements for the purpose of obtaining end points.
The recent discussions of Delahay (41) and especially of Reilley,
Cooke, and Furman (42) are examples of a trend away from such explanations
toward considerations which examine in increasing detail the mechanism
of the electrolytic processes involved. The approach in this paper is
similar to that of Reilley et al.; however, the electrode processes,
the effect of a second electrode, and the assumptions involved, have
been considered in more detail.

The current in this amperometric system has been observed
to depend mainly on the potential applied between the two electrodes
and on the concentrations of the species in the solution which are
capable of reacting at these electrodes (34). A series of equations
relating the current to the applied potential and concentrations has
been derived. Simple and somewhat idealized situations have been

assumed; however, these situations are experimentally realizable, and
are often closely approximated in titrations. The derivations of
these equations and experimental evidence of their validity are
presented below.

DISCUSSION OF AMPEROMETRIC SYSTEMS

For purposes of the following discussion the overall process
at an electrode will be divided into the following general steps:

1. Movement of the reacting species to the electrode.

2. Reaction at the electrode.

3. Movement of reacted species away from the electrode.

The rate of any single step, or the rates of a combination of steps
at either or both electrodes may control the current. The movement
of reacting and reacted species may be under the influence of either
an electric field (conduction) or an activity gradient (diffusion)
or both.

Definition of Terms.

The term, amperometric, will be used to describe determinations
of concentration which depend on a measurement of an electrolysis
current. This is a broader definition than that of Kolthoff and
Lingane (43) in that the measurements are not specifically limited to
a constant potential, and, in addition, the current can be controlled
by either or both electrodes. It is convenient to work at a constant
potential since otherwise the interpretation of current measurements
is more complicated. Analytically, the most convenient range of
potentials is that in which the current is limited by diffusion.

An electrode-reactive species is any species which is capable
of being oxidized or reduced at an electrode at such a rate that a
current can be observed.

An electrode-reactive half-cell is any half-cell having at least
one electrode-reactive species in both of its oxidation states.

A reversible half-cell is an electrode-reactive half-cell con-
sisting of species which react so rapidly at an electrode that the
current is not measurably controlled by the rate of the electrode
reaction, but is controlled by the rates of diffusion to or away from
this electrode or by the rate or rates of some step in the overall
reaction at the other electrode.

According to these definitions, species and half-cells may be
electrode-reactive or reversible under some conditions and not under
others.

The term, polarization, as applied to electrodes, has been used
frequently to denote a departure from equilibrium in at least one of
the processes taking place at or near the electrode with the result
that the electrode potential is different from the equilibrium potential.
Since lack of clarity can result when polarization is used in place of
more precise and informative terms, we have attempted to discuss
electrode processes without recourse to its use.

An amperometric system consists of two electrodes, an arrange-
ment for controlling and measuring the potential between these
electrodes, and a meter for measuring the current between the electrodes.
The potential between the two electrodes will be called the applied
potential, and the current will be called the indicator current.

The amperometric methods which have been most frequently used can be classified into two categories which are based upon the types of electrodes used. The amperometric end point developed by Kolthoff and co-workers (44, 45, 46) makes use of a dropping mercury electrode or a rotating platinum electrode with a calomel or some other reference electrode whose potential is constant and whose part in controlling the current is negligible. The amperometric system used in this laboratory (34, 35) consists of two electrodes of the same metal, usually platinum. The applied potential is of the order of a few hundred millivolts. The solution in which the measurements are made is stirred vigorously. There are two fundamental differences between these two methods. First, the method developed by Kolthoff has only one variable potential electrode whereas in the second system the potentials of both electrodes vary during the course of the titration. Second, both electrodes of the system with which we are especially concerned are of the same metal and usually the same half-cell reaction takes place at both electrodes, but in opposite directions, and there-fore, the composition of the solution is unchanged. Hereafter, in order to distinguish between these two systems, the first one will be designated the <u>univariable electrode system</u> and the second one the <u>bivariable electrode system</u>.

The dead-stop end point is a special case of a system of the second type and makes use of two inert metal electrodes, usually platinum, and a small applied potential of the order of 10-20 millivolts. The indicator current is measured with a galvanometer and, as con-ventionally used, the end point is that point at which a current is no longer observed. This method is actually a result of the limitations

of the galvanometer in measuring small currents, and therefore, the method is in effect a qualitative modification of the bivariable electrode system.

## Current Behavior with the Bivariable Electrode System.

When the potential applied between two platinum electrodes in a solution containing only the electro-oxidizable species R^m of the half-cell,

$$R^m = O^{m+n} + ne^-,$$
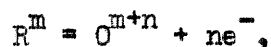
is slowly increased, essentially no current will be observed until the applied potential reaches a value sufficient to cause the reaction,

$$R^m \rightarrow O^{m+n} + ne^-$$
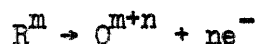
to take place at the anode and another reaction involving a different half-cell to take place at the cathode. If however, both R^m and O^{m+n} are present and the half-cell is electrode reactive, the reaction

$$O^{m+n} + ne^- \rightarrow R^m$$
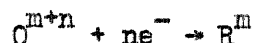
can take place at the cathode while the reverse reaction takes place at the anode. The net reaction does not change the composition of the solution; therefore no chemical work is done. Although energy is required to bring the reactive species to the electrodes, to overcome the resistance in the external circuit, and, if the rate of the reaction at the electrode surface is slow, to overcome the resultant overvoltage, a current should be observed when only a small potential is applied.

The behavior of indicator currents during a titration in which the bivariable electrode system is used will depend on the electrode

reactivity of both the titrant half-cell and the half-cell of the substance being titrated. If the oxidized and reduced states of both the titrant and the substance being titrated form electrode-reactive half-cells, indicator currents will be observed on both sides of the equivalence point. Examples are the titrations of iodide and Tl(I) with electrolytically generated chlorine (30, 47). If only one of the half-cells involved is reactive, a significant current will be observed on only one side of the equivalence point. Examples of this situation are the titrations of thiodiglycol and As (III) with electrolytically generated bromine (34, 35). When species reactive at only one electrode are present in the solution, no current will be observed.

DERIVATION OF EQUATIONS

Although this paper grew out of efforts to explain quantitatively the indicator current behavior when amperometric measurements were used to follow and determine the end points of coulometric titrations, and the derived equations have been influenced accordingly, the derived relationships can easily be applied to volumetric titrations. An equation has been derived which expresses the indicator current as a function of the applied potential and of the concentrations of the oxidized and reduced constituents of a reversible half-cell. In case the volume remains constant throughout the titration, this equation may be simplified to a form more suitable for experimental verification by using as a variable the fraction oxidized of the sum of the concentrations of the oxidized and reduced constituents in place of the concentrations themselves. This equation can be used to calculate

the change in current at a given potential throughout the course of the titration of either constituent of an electrode-reversible half-cell.

If the titrant is one constituent of an electrode-reversible half-cell, the equation can be used to calculate the current obtained after the end point. Usually the equation can be simplified for this case since only a slight excess of titrant is added, and therefore the fraction oxidized approaches either zero or one.

Another equation has been derived which is applicable to a bivariable potential electrode system which is composed of two electrodes of an active metal which is dissolved from the anode and plated on the cathode.

Still another equation has been derived for an electrode system consisting of two inert metal electrodes and relates the distribution of the applied potential between the indicator electrodes to the fraction oxidized and to the applied potential.

In all of the derivations concentrations will be used in place of activities.

Assumptions.

The assumptions on which the subsequent derivations are based have been made primarily in order to minimize the number of variables and are as follows:

1. Only a single reaction is taking place at the electrode surfaces and this reaction is reversible. Because the investigation of the rates of electrode reactions is often complicated and experimentally difficult, the considerations are limited to electrode-reversible

half-cells. If the concentrations of the reversible species at the electrode surfaces are known, the potential of each of the indicator electrodes then can be calculated by the Nernst equation.

2. Only a single species of each of the two oxidation states forming the reversible half-cell exists in the solution. Complications introduced by reactions in the diffusion layer are thus avoided.

3. The current is at all times completely controlled by the rate of diffusion of the reversible species to and from the electrodes. The species in the solution are transported predominantly by the stirring to within a very short distance of the electrode surface where they diffuse across the relatively undisturbed layer adjacent to the electrodes. The presence of an excess of inert, "supporting", electrolyte insures that diffusion, not conduction, will control the current.

4. The current is proportional to the difference between the concentrations of reversible species at the electrode surface Y_e and in the body of the solution Y_s, and the current i is given by the equations

$$i = \frac{nF\, D_x\, A}{\ell} (Y_s - Y_e)$$ for diffusion to the electrode,

and

$$i = \frac{nF\, D_x\, A}{\ell} (Y_e - Y_s)$$ for diffusion away from the electrode,

where

    n is the number of electrons involved in the reaction

    F is the Faraday

    D_x is the diffusion coefficient for the species Y

A is the area of the electrode

ℓ is the effective width of the diffusion layer.

Because of the stirring and the shapes of the electrodes, the exact nature of the diffusion layer is uncertain. This assumption is often made in connection with calculations involving the rotating platinum electrode.

5. **A steady state is attained in the system.**

The Dependence of Current on Applied Potential and On Concentration.

Inert Metal Electrodes. The case in which the oxidized and reduced state of the substance being titrated form a reversible half-cell will be considered first. The potential of the indicator anode, E_a, is given by

$$E_a = E^O - \frac{RT}{nF} \ln \frac{O_a}{R_a}$$

while the potential of the indicator cathode, E_c, is given by

$$E_c = E^O - \frac{RT}{nF} \ln \frac{O_c}{R_c} \, .$$

The potential between the two electrodes, V, is

$$V = E_c - E_a = \frac{RT}{nF} \ln \frac{O_a \, R_c}{R_a \, O_c} \tag{1}$$

where

O_s is the concentration of the oxidized species in the body of the solution,

O_c is the concentration of the oxidized species at the cathode surface,

O_a is the concentration of the oxidized species at the anode surface,

R_s is the concentration of the reduced species in the body of the solution,

R_c is the concentration of the reduced species at the cathode surface,

R_a is the concentration of the reduced species at the anode surface.

The subscripts a, c, and s will be used to denote the anode, cathode and solution, respectively, in further notation.

Since the current is entirely controlled by diffusion of reactive species across the diffusion layer, and since, under steady state conditions, the net number of equivalents of reacting species diffusing to an electrode is equal to the net number of equivalents diffusing away, the current, i, and the concentrations of reversible species are related by the following equations:

$$i = k_1(O_s - O_c) = k_2(R_c - R_s) = k_3(R_s - R_a) = k_4(O_a - O_s)$$

(2)

where

$$k_1 = \frac{nF\ D_O\ A_c}{\ell_1} \ , \qquad k_2 = \frac{nF\ D_R\ A_c}{\ell_2} \ , \qquad k_3 = \frac{nF\ D_R\ A_a}{\ell_3} \ ,$$

$$k_4 = \frac{nF\ D_O\ A_a}{\ell_4}$$

in which

D_O is the diffusion coefficient for the species O,

D_R is the diffusion coefficient for the species R,

A_c is the area of the cathode,

A_a is the area of the anode.

The ℓ values, the effective widths of the diffusion layers, are not necessarily the same in any two cases. On rearrangement of these equations and substitution into Equation 1:

$$V = \frac{RT}{nF} \ln \frac{\left(\dfrac{k_4 O_s + i}{k_4}\right)\left(\dfrac{k_2 R_s + i}{k_2}\right)}{\left(\dfrac{k_3 R_s - i}{k_3}\right)\left(\dfrac{k_1 O_s - i}{k_1}\right)} .$$

Let $\alpha = e^{\frac{nVF}{RT}}$. Then on solving for the current,

$$i = \frac{\left(\alpha + \dfrac{k_3}{k_2}\right) k_1 O_s + \left(\alpha + \dfrac{k_1}{k_4}\right) k_3 R_s}{2\left(\alpha - \dfrac{k_1 k_3}{k_2 k_4}\right)}$$

$$-\frac{\sqrt{\left[\left(\alpha + \dfrac{k_3}{k_2}\right) k_1 O_s + \left(\alpha + \dfrac{k_1}{k_4}\right) k_3 R_s\right]^2 - \left(4(\alpha - 1)\right)\left(\alpha - \dfrac{k_1 k_3}{k_2 k_4}\right) k_1 k_3 O_s R_s}}{2\left(\alpha - \dfrac{k_1 k_3}{k_2 k_4}\right)}$$

$$(3)$$

In order to simplify this equation for experimental verification, two additional assumptions will be made. First, the volume will be considered to remain constant, as will be the case during a coulometric titration. Then the sum of the concentrations of the oxidized and reduced species is a constant, that is, $O_s + R_s = C$, where C represents the total concentration of the substance titrated. Second, the two indicator electrodes will be considered to be of equal size and situated in equivalent positions; then $k_2 = k_3$ and $k_1 = k_4$. Letting $X = \dfrac{O_s}{C}$ and substituting these relationships into Equation 3, we obtain

$$i = \frac{C}{2} \left[(k_1 - k_2) X + k_2\right] \left[\frac{\alpha + 1}{\alpha - 1}\right]$$

$$-\frac{C}{2} \sqrt{[(k_1 - k_2)X + k_2]^2 \left[\frac{\alpha + 1}{\alpha - 1}\right]^2 - 4 k_1 k_2 X(1 - X)} \qquad (4)$$

This may be written alternatively in a form which emphasizes the approach of the current to limiting values at high applied potentials:

$$i = \frac{1}{2} \left[(i_{L1} + i_{L2}) \right] \left[\frac{\alpha + 1}{\alpha - 1} \right]$$

$$- \sqrt{(i_{L1} + i_{L2})^2 \left(\frac{\alpha + 1}{\alpha - 1} \right)^2 - 4 i_{L1} i_{L2}} \qquad (5)$$

in which

$i_{L1} = k_1 O_s$ the limiting current when $k_1 O_s < k_2 R_s$ and the cathode is the limiting electrode at high applied potentials;

and $i_{L2} = k_2 R_s$ the limiting current when $k_2 R_s < k_1 O_s$ and the anode is the limiting electrode at high applied potentials.

The root with the minus sign in front of the radical is taken since i must be positive but can not be greater than the smaller of the two quantities, $k_1 O_s$ and $k_2 R_s$.

The case in which the titrant is a constituent of a reversible half-cell, and the substance titrated is not, can be treated by a modification of the equation just derived. No significant current will be observed until an appreciable concentration of the titrant is present. If, for example, a coulometric titration is being made and the intermediate is an oxidizing agent, the reduced species of the intermediate half-cell is present in much larger concentrations than the oxidized species, i.e., $O_s \ll C$, in which case Equation 4 reduces to

$$i = k_1 O_s \left(\frac{\alpha - 1}{\alpha + 1} \right) \qquad (6)$$

For a reducing intermediate, when $R_s \ll C$, Equation 4 reduces to

$$i = k_2 R_s \left(\frac{\alpha - 1}{\alpha + 1} \right) \qquad (7)$$

In both of these cases, when no other half-cell reactions occur, at any given applied potential the dependence of indicator current on concentration approaches linearity, and, as the applied potential becomes very large, the current approaches limiting values, namely $k_1 O_s$ and $k_2 R_s$.

Active Metal Electrodes. When a plating process is taking place at the indicator cathode and a solution process is taking place at the anode, only diffusion to the cathode and away from the anode must be considered. If the indicator electrodes are in equilibrium with the metal ion solutions at their surfaces, the potential of the cathode is given by

$$E_c = E^o - \frac{RT}{nF} \ln [M^{n+}]_c.$$

While the potential of the anode is given by

$$E_a = E^o - \frac{RT}{nF} \ln [M^{n+}]_a.$$

The applied potential V is then

$$V = E_c - E_a = \frac{RT}{nF} \ln \frac{[M^{n+}]_a}{[M^{n+}]_c} .$$

Since the current is related to the concentrations by the following equations:

$$i = k_c ([M^{n+}]_s - [M^{n+}]_c) = k_a ([M^{n+}]_a - [M^{n+}]_s)$$

in which

$$k_c = \frac{nFDA_c}{\ell_c} \, , \qquad k_a = \frac{nFDA_a}{\ell_a}$$

It will be assumed that $k_c = k_a$. Then on solving for the current we obtain

$$i = i_L \left(\frac{\alpha - 1}{\alpha + 1} \right) \tag{8}$$

where α has the same meaning as previously and $i_L = k_a [M^{n+}]_s$.

A silver electrode system has been used in investigating the assumed dependence of diffusion on concentration. If the indicator current is measured as a function of the potential between the indicator cathode and a reference electrode, a single electrode can be considered and the uncertainties and complications introduced by the solution process at the indicator anode can be avoided. Since the composition of the solution is not changed by the passage of the indicator current, a silver electrode in equilibrium with the solution should make a satisfactory reference electrode.

The potential of a silver wire reference electrode in equilibrium with the solution is given by

$$E_s = E^o - \frac{RT}{F} \ln [Ag^+]_s.$$

The potential between the indicator cathode and the reference electrode is

$$E_c - E_s = \frac{RT}{F} \ln \frac{[Ag^+]_s}{[Ag^+]_c} = \frac{RT}{F} \ln \frac{[Ag^+]_s}{[Ag^+]_s - i/k} \, .$$

Let $\gamma = e^{\frac{(E_c - E_s)F}{RT}}$. Then $\gamma = \frac{[Ag^+]_s}{[Ag^+]_s - i/k} \, .$

Since $k[Ag^+]_s = i_L$, the limiting diffusion current,

$$i = i_L \left(\frac{\gamma - 1}{\gamma} \right) \quad . \tag{9}$$

The Distribution of Applied Potential Between the Indicator Electrodes.

The distribution of the applied potential between the two electrodes of a bivariable electrode system can be measured by comparing their potentials to the potential of a third platinum electrode which is in equilibrium with the solution.

An equation relating the distribution of the applied potential between the two indicator electrodes to the applied potential and the fraction of the total concentration of the half-cell constituents oxidized is derived below. The derivation is based on the previously listed assumptions. The potential of the platinum electrode which is in equilibrium with the solution is given by

$$E_s = E^o - \frac{RT}{nF} \ln \frac{O_s}{R_s} \ .$$

The potential between the solution and indicator anode is

$$E_s - E_a = \frac{RT}{nF} \ln \frac{k_3 R_s (k_4 O_s + i)}{k_4 O_s (k_3 R_s - i)} \quad .$$

The fraction P of the applied potential between the solution and the indicator anode is

$$P = \frac{E_s - E_a}{V} = \frac{RT}{nVF} \ln \frac{k_3 R_s (k_4 O_s + i)}{(k_3 R_s - i) k_4 O_s} \tag{10}$$

The expression for the current as a function of the concentrations in the body of the solution and of the applied potential is given by Equation 4 which may be substituted in Equation 10.

EXPERIMENTAL

The Choice of Half-Cells for Testing Equations.

The number of half-cells on which amperometric measurements may be made in order to test the derived equations is limited because of the assumptions which were made in order to keep the treatment simple and still illustrate the important features.

The most important assumption made above is assumption 4 which relates the current to the difference in concentrations. In spite of experimental verification of this assumption for the rotating platinum electrode, the experimental situation under discussion is sufficiently different that it is necessary to determine the validity of this assumption before a reasonable discussion can be made of the agreement between theory and experiment.

Measurements which test assumption 4 must be made on a solution containing a half-cell which is reversible at platinum electrodes. The problem of finding such half-cells is difficult. One criterion of a reversible half-cell is that the shape of the indicator current vs. applied potential curve for the half-cell should not be dependent on previous treatment of the electrode. Since this criterion is not sufficient, the other evidence must also be considered.

Figure 8 shows the effect of applied potential on the indicator current observed in solutions containing the halogen-halide half-cells when the halide concentration is much larger than the halogen concentration. The curve for iodine more nearly resembles a polarographic wave than do the other curves. There is a definite range of applied potentials in which the current is almost independent of potential.
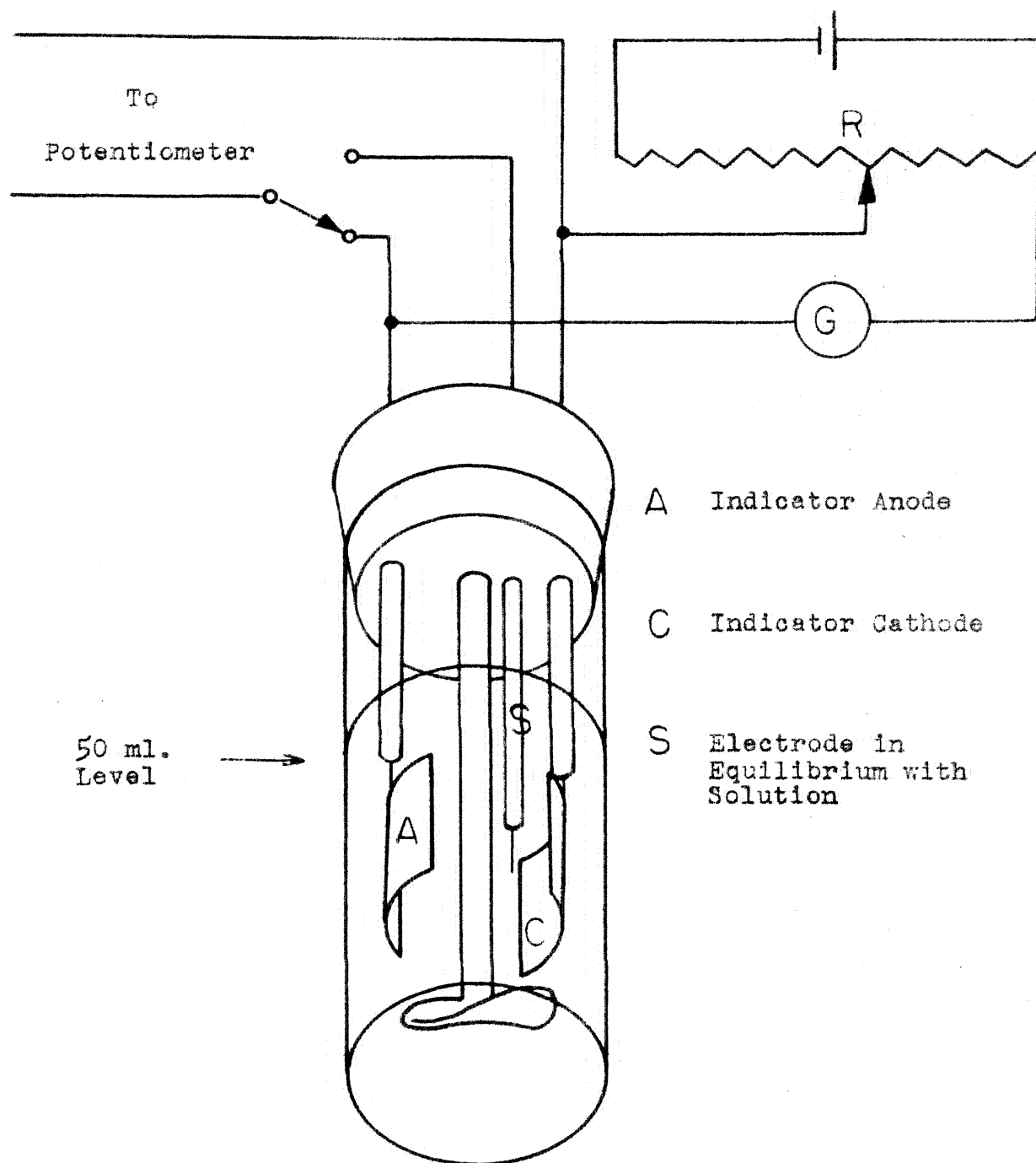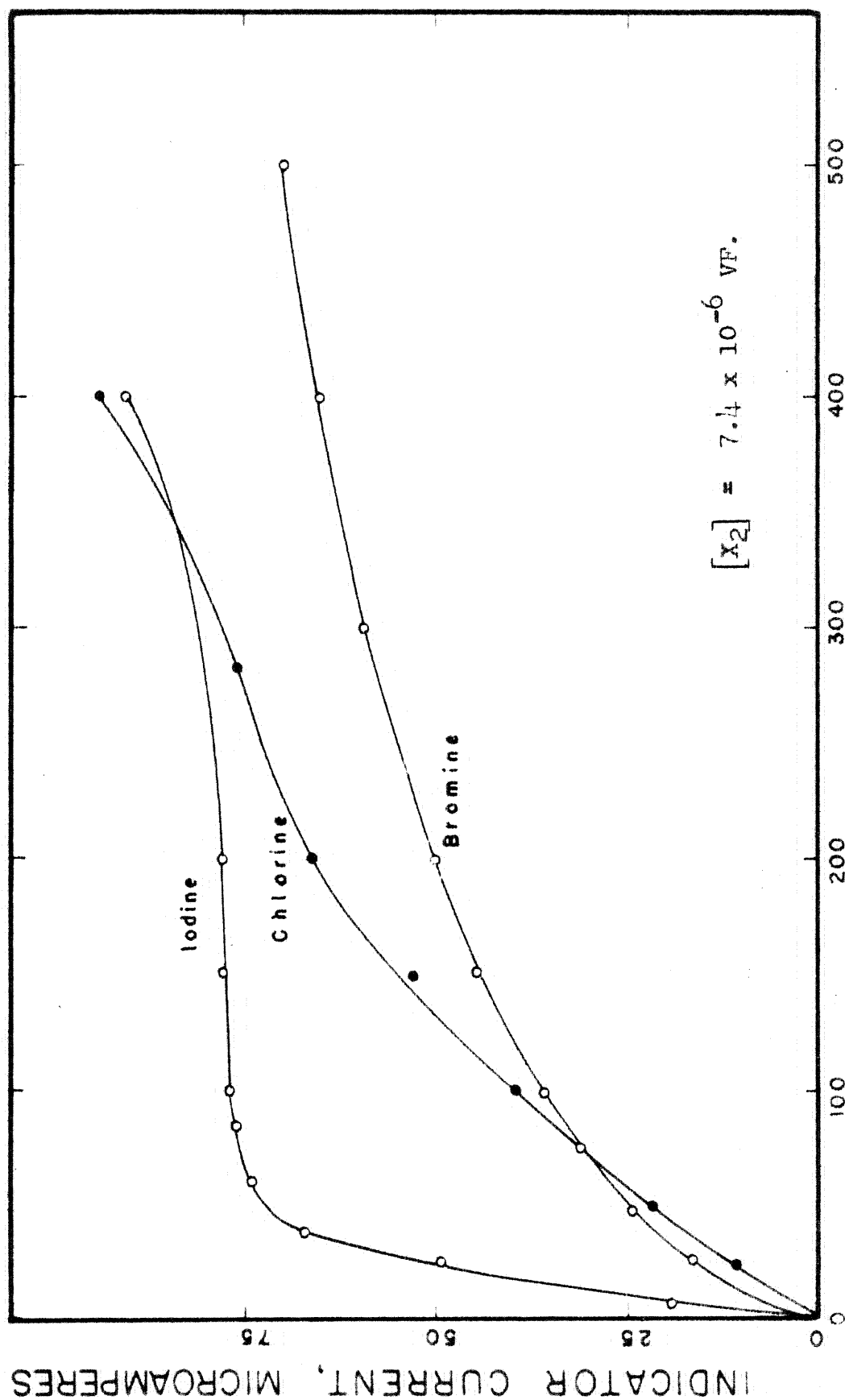
Figure 7. Apparatus Used for Amperometric
Measurements.

APPLIED POTENTIAL, MILLIVOLTS

$[x_2] = 7.4 \times 10^{-6}$ VF.

Figure 8. The Effect of Applied Potential on the Indicator Currents Observed in Solutions Containing Halogen-Halide Half-Cells When the Halide Concentration is Much Larger than the Halogen Concentration.

Arranged in order of increasing reproducibility of such curves the
halogen-halide half-cells are chloride-chlorine, bromide-bromine, and
iodide-iodine. This is also the order of decreasing overvoltage (48).
Since the iodide-iodine half-cell closely approaches reversibility,
use was made of this half-cell for testing assumption 4.

The iodide-iodine half-cell can not be used to test Equation 4
because of the complications introduced by the formation of tri-iodide.
However, in testing assumption 4 with this half-cell, a large concentra-
tion of iodide and a small concentration of iodine are used. Under
these conditions no complications are caused by tri-iodide formation,
and Equation 6 should express the behavior of the indicator current
as a function of the applied potential. Such measurements have been
made and are discussed below. A detailed discussion justifying the
use of the iodide-iodine half-cell for testing Equation 6 is given in
an appendix.

Figure 9 shows the effect of applied potential on the indicator
currents observed in solutions containing various electrode-reactive
half-cells. The indicator currents in ferrocyanide-ferricyanide
solutions are least dependent on the applied potential when it is
greater than 100 millivolts. The curve for this half-cell was also the
most reproducible of the curves shown. Consequently, the ferrocyanide-
ferricyanide half-cell seemed best suited for testing Equation 4. It
meets most of the requirements listed as assumptions in the derivation.
Ferricyanic acid is a strong acid and the fourth ionization constant
of ferrocyanic acid is 5.6×10^{-5} (49). Therefore, essentially only
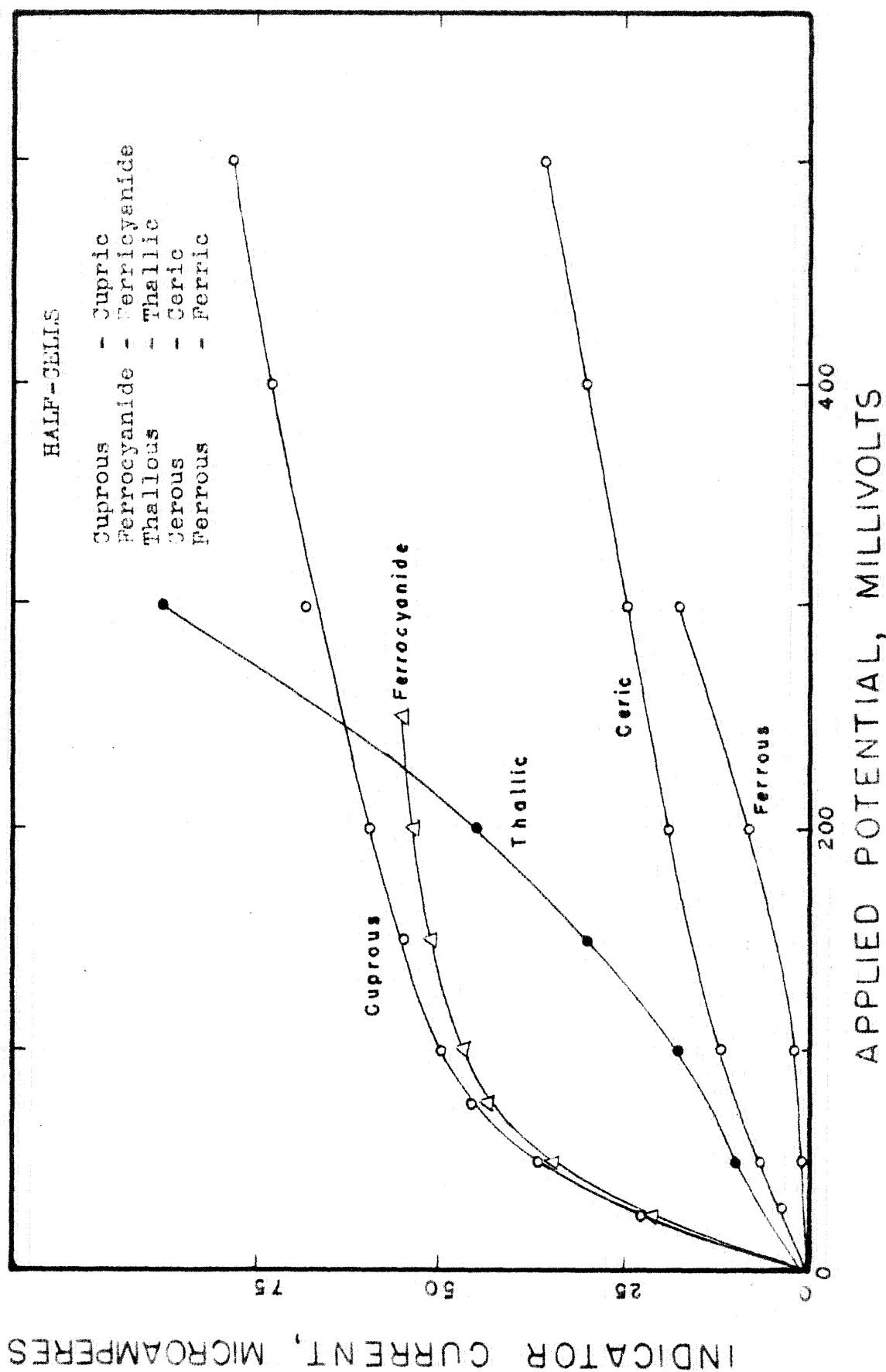one oxidized species, $Fe(CN)_6^{\equiv}$, and one reduced species, $Fe(CN)_6^{\equiv}$, are

Figure 9. The Effect of Applied Potential on the Indicator Currents
Observed in Solutions Containing Various Electrode-Reactive Half-Cells.
The Current-Limiting Constituent is Named by Each Curve.

present in a solution at pH 7. The half-cell meets the requirement of reversibility least satisfactorily. The rates of both the reduction of ferricyanide and the oxidation of ferricyanide appear to be dependent on the treatment of the electrode and the length of time it is used. Although not ideal, the ferrocyanide-ferricyanide half-cell has been used for testing Equation 4.

The calculated diffusion coefficients of ferrocyanide and ferricyanide at infinite dilution are 0.74×10^{-5} cm.^{2}/sec. for ferrocyanide and 0.89×10^{-5} cm.^{2}/sec. for ferricyanide (50). If it is assumed that the ratio of these two diffusion coefficients remains approximately the same under the experimental conditions, Equation 4 then becomes

$$\frac{2I}{k_2 C} = (0.20\ X + 1)\left(\frac{\alpha + 1}{\alpha - 1}\right) - \sqrt{(0.20\ X + 1)^2 \left(\frac{\alpha + 1}{\alpha - 1}\right)^2 - 4.80(X - X^2)}$$

$$(11)$$

The terms on both sides of this equation are dimensionless.

On substituting this value for the ratios of the diffusion coefficients into Equation 10, it reduces to

$$P = \frac{RT}{nVF}\ \ln\ \frac{\left(1.20\ X + \frac{1}{k_2 C}\right)\ (1 - X)}{1.20\ X\ \left(1 - X - \frac{1}{k_2 C}\right)} \qquad (12)$$

Instead of the calculated ratio of the diffusion coefficients at infinite dilution, the experimental ratio could have been used. The experimentally observed ratio of the diffusion constants for a stationary platinum microelectrode is 1.12 (51, 52). The main effect of changing the value of this ratio is to shift the position of the

maxima of the theoretical curves. Using 1.12 instead of 1.20 shifts the maxima from $F = 0.45$ to $F = 0.48$. Since the experimental precision was of the same order of magnitude, it is doubtful that use of this experimental ratio would result in significantly better agreement.

Reagents.

All chemicals used were reagent grade. Potassium ferrocyanide trihydrate and potassium ferricyanide were each recrystallized three times from water. The potassium ferrocyanide trihydrate was dried over a saturated solution of sodium bromide dihydrate (53). The potassium ferricyanide was dried in an oven at 100° C. Stock solutions of these salts which were 2.50×10^{-3} VF. were prepared by weight; solutions which were 2.50×10^{-4} VF. were prepared by dilution. These solutions were protected from light. All water used was "conductivity " water. The potassium ferrocyanide solutions were stabilized by the addition of 0.2 g. of sodium carbonate per liter (53).

Apparatus.

The cell and circuit used are shown in Figure 7. The conditions and apparatus were essentially the same as those used for coulometric titrations by Swift and co-workers (9, 30, 35) except that the generator electrodes were removed and a third electrode of platinum wire was added. The cell consisted of a 40 x 80 mm. weighing bottle which was placed on a rubber stopper containing the two platinum indicator electrodes, the third electrode of platinum wire, and the stirrer. The stirring rate was 1660 RPM. The potential applied between the two indicator electrodes was measured with a Queen student potentiometer.

The dimensions of each of the indicator electrodes were 20 x 25 mm. The current measurements were made with a L. and N. box-type reflecting galvanometer. The sensitivity was varied by using appropriate shunts. All measurements were made at a room temperature of 26° C.

When making the measurements on the iodide-iodine solutions, two platinum generator electrodes were used to generate small known amounts of iodine coulometrically.

The silver indicator electrodes used in making the measurements on silver solutions were of the same area and shape as the platinum indicator electrodes. The platinum wire electrode was replaced with a silver wire electrode. The rest of the apparatus was the same.

Procedure.

The procedure for preparing the ferrocyanide-ferricyanide solutions was as follows. Measured volumes of both 2.5×10^{-4} VF. potassium ferrocyanide and 2.5×10^{-4} VF. potassium ferricyanide were added to the cell from a buret. The sum of these volumes was kept constant at 40.0 ml. for all measurements while the ratio was varied from 1/39 to 39/1. One gram of sodium hydrogen carbonate and "conductivity" water were added and the solution was saturated with carbon dioxide in order to buffer the solution at a pH of 7. For all solutions the total volume was 50 ml. and the sum of the ferro-cyanide and ferricyanide concentrations was 2.00×10^{-4} VF. These small concentrations were chosen for convenience of current measurements.

Measurements were made on iodide-iodine solutions which were prepared by pipetting into a cell 5 ml. of 1.0 VF. potassium iodide and 45 ml. of water. One gram of sodium hydrogen carbonate was added and

the solution was saturated with carbon dioxide in order to buffer it at a pH of 7. The cell was placed on the apparatus and the desired amount of iodine was generated in the solution.

A solution which was 1.6×10^{-4} VF. in silver nitrate and 0.02 VF. in nitric acid was placed in the cell for measurements with the amperometric electrode system consisting of two silver electrodes. In order to obtain reproducible results it was found necessary that the solution contain about 0.01 per cent gelatin (52).

After preparing a solution, the cell was placed on the apparatus and the stirring was started. The potentiometer was set for one of the desired potential readings, the resistance R was varied until the potentiometer balanced for this setting, and the current was read from the galvanometer. Then the potentials between each of the indicator electrodes and the wire electrode in equilibrium with the solution were measured. The process was repeated for other potential settings. The whole procedure was then repeated over the desired potential range until reproducible values were obtained. The applied potential ranged from 0 to 250 millivolts. A steady state was generally attained within 15 seconds after changing the potential and the current readings were reproducible to within 0.3 microamp. so that usually it was necessary to repeat the procedure only once.

DISCUSSION OF MEASUREMENTS

Dependence of Diffusion on Concentrations.

Measurements with the Iodide-Iodine Half-Cell. As stated above, in a solution in which the concentration of iodide is very large compared

to the concentration of iodine, the dependence of indicator current on the applied potential should be given by Equation 6 if the assumed dependence is correct. The theoretical plot and the experimental points obtained when the current was measured as a function of the applied potential in a solution 0.1 VF., in potassium iodide and 7.7×10^{-6} VF. in iodine are shown in Figure 10. The agreement is within the experimental error.

The other curves shown in Figure 10 are also plots of Equation 6 in which n, the number of electrons involved in the electrode reaction, is different from two.

It should be noted that reversibility of the iodide-iodine half-cell at smooth platinum electrodes is dependent on the previous treatment of the electrodes. Before the data shown in Figure 10 were taken, the electrodes were washed carefully and ignited. When the electrodes were not so treated, significant deviations from theory were observed. The deviations were always in a direction indicating a low rate of reaction at the electrode surfaces.

Measurements with the Silver-Silver Ion Half-Cell. The experimental points obtained with silver indicator electrodes are shown in Figure 11 along with the plot of Equation 7. The agreement with theory is satisfactory although not as good as that with the iodide-iodine half-cell. This is not surprising in view of the large deviations from reversible behavior observed by Laitinen and Kolthoff (52) with a rotating microelectrode. The smaller deviations observed could be due to the fact that the current density was only about one-fifth as great.
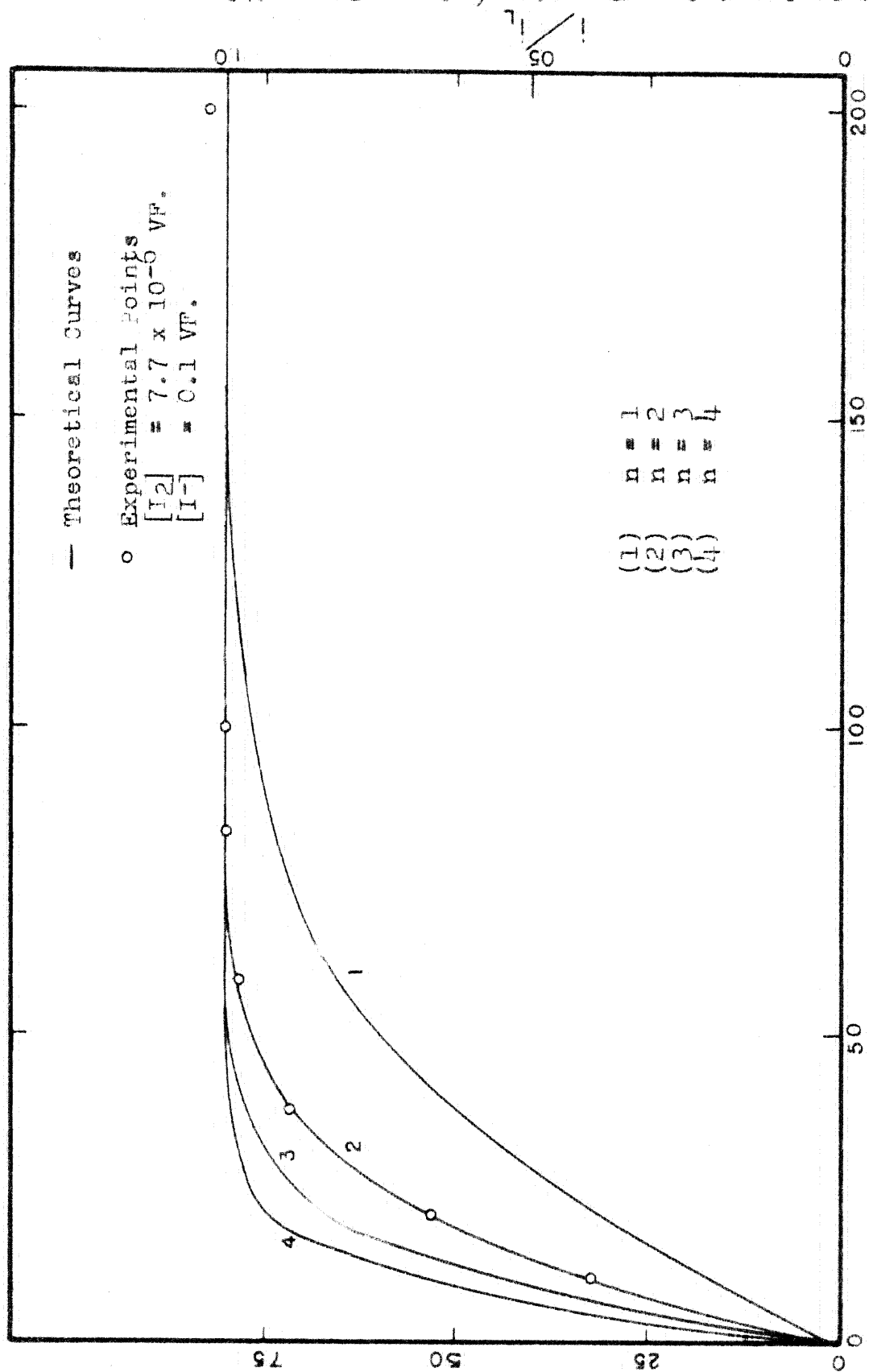
Figure 10. The Effect of Applied Potential on Indicator Current.

INDICATOR CURRENT, MICROAMPERES

APPLIED POTENTIAL, MILLIVOLTS

Calculated from Equation 6 for a Reversible
n-Electron Half-Cell.

i_L

— Theoretical Curves

o Experimental Points
[I_2] = 7.7 x 10^{-5} VF.
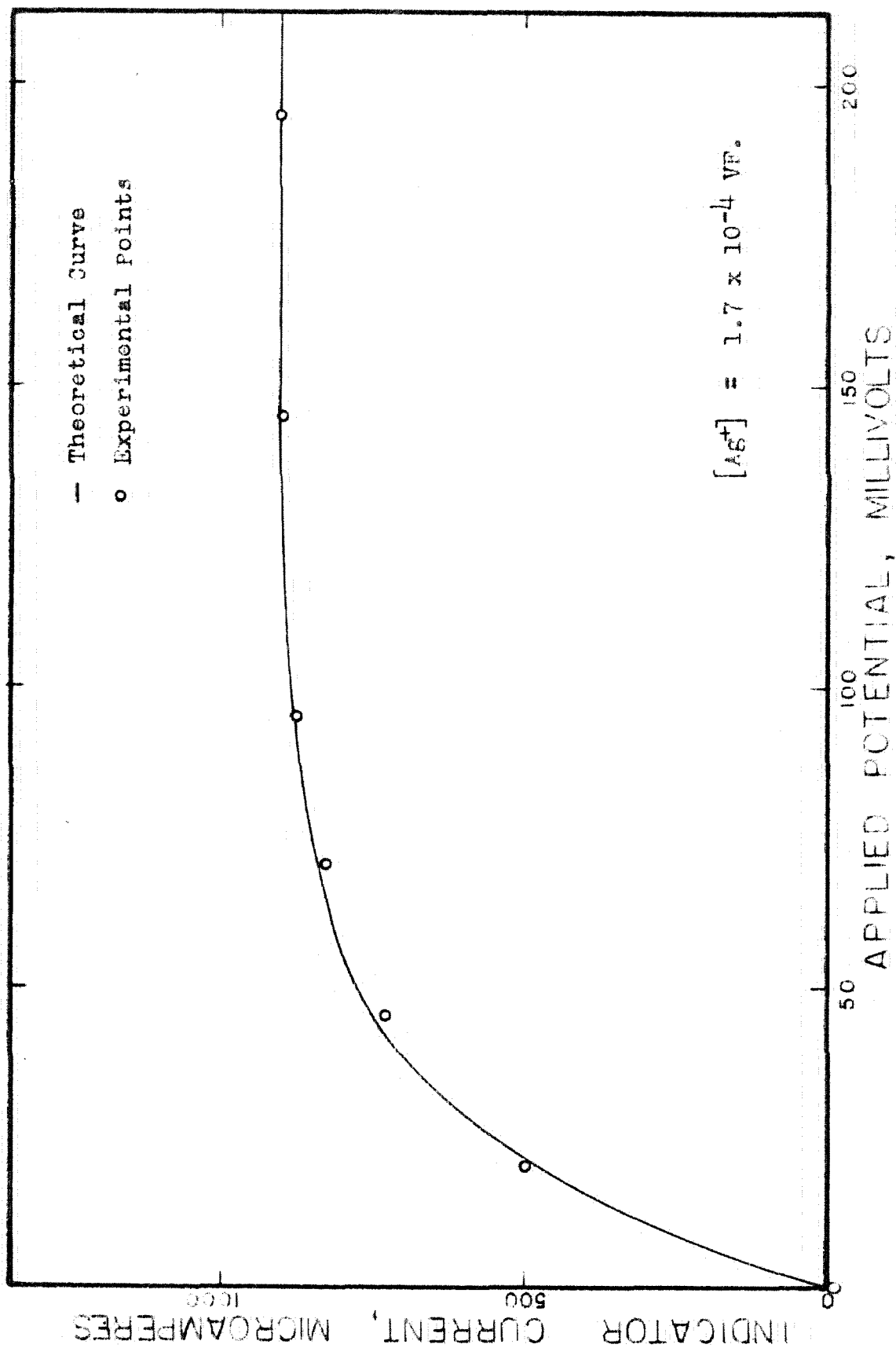[I^-] = 0.1 VF.

(1) n = 1
(2) n = 2
(3) n = 3
(4) n = 4

Figure 11. The Effect of Applied Potential on the Indicator Current Between Silver Indicator Electrodes Immersed in a Silver Nitrate Solution.

Dependence of the Indicator Current on Applied Potential and Fraction
Oxidized.

The plots of indicator current versus fraction oxidized calculated
from Equation 4 and those obtained experimentally are shown in Figures
12 and 13, respectively. The series of curves represent the indicator
currents which would be observed with different applied potentials
during a titration in which ferrocyanide was oxidized to ferricyanide.
In Figure 12, $\frac{i}{k_2 C}$ is plotted against fraction oxidized for the various
applied potentials on such a scale that the slopes obtained when $V = 250$ mv.
are the same as in the curves in Figure 13. This is equivalent to
determining k_2 experimentally and must be done because the effective
width of the diffusion layer is unknown.

There is qualitative agreement; however, the observed deviations
are greater than the experimental errors. The data plotted in Figure
13 were taken just after the two platinum electrodes had been allowed to
stand in hot chromic acid for about half an hour, had been washed care-
fully, and had been ignited to a dull red color in an oxidizing flame.
When further data were taken for a similar curve without repeating this
method of preparing the electrodes, the currents observed were smaller
and the plotted curves were more rounded. The rate of the reaction at
the electrode surface is apparently dependent on the treatment of the
surface. This behavior is compatible with that observed by Laitinen
and Kolthoff (52) when ferrocyanide was oxidized at a rotating platinum
electrode.

The Distribution of Potential.

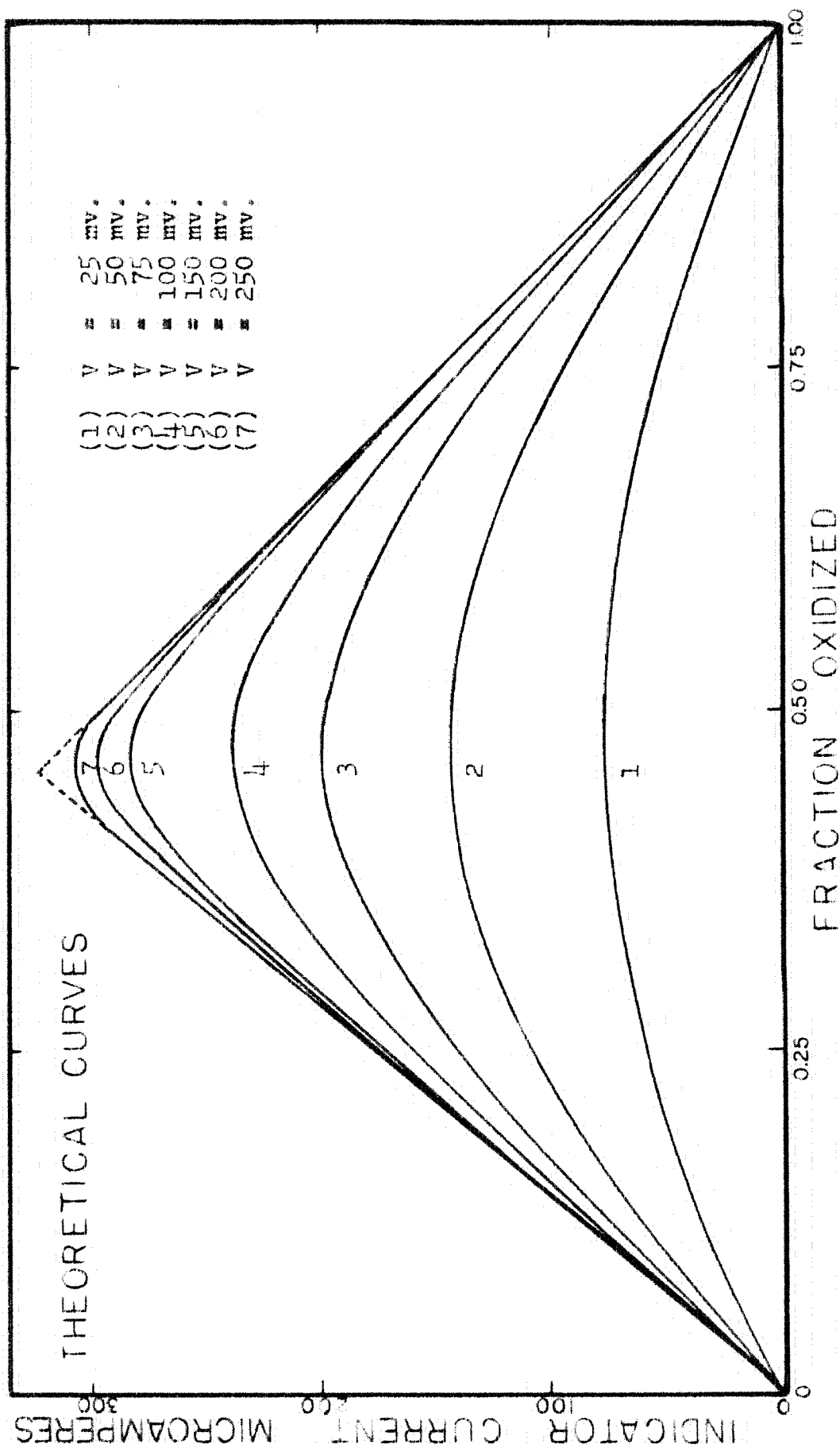Figure 14 shows the plot of the fraction of the applied voltage

Figure 12. The Calculated Effect of Applied Potential and Fraction Oxidized on the Indicator Currents in a Solution Containing a Reversible One-Electron Half-Cell.
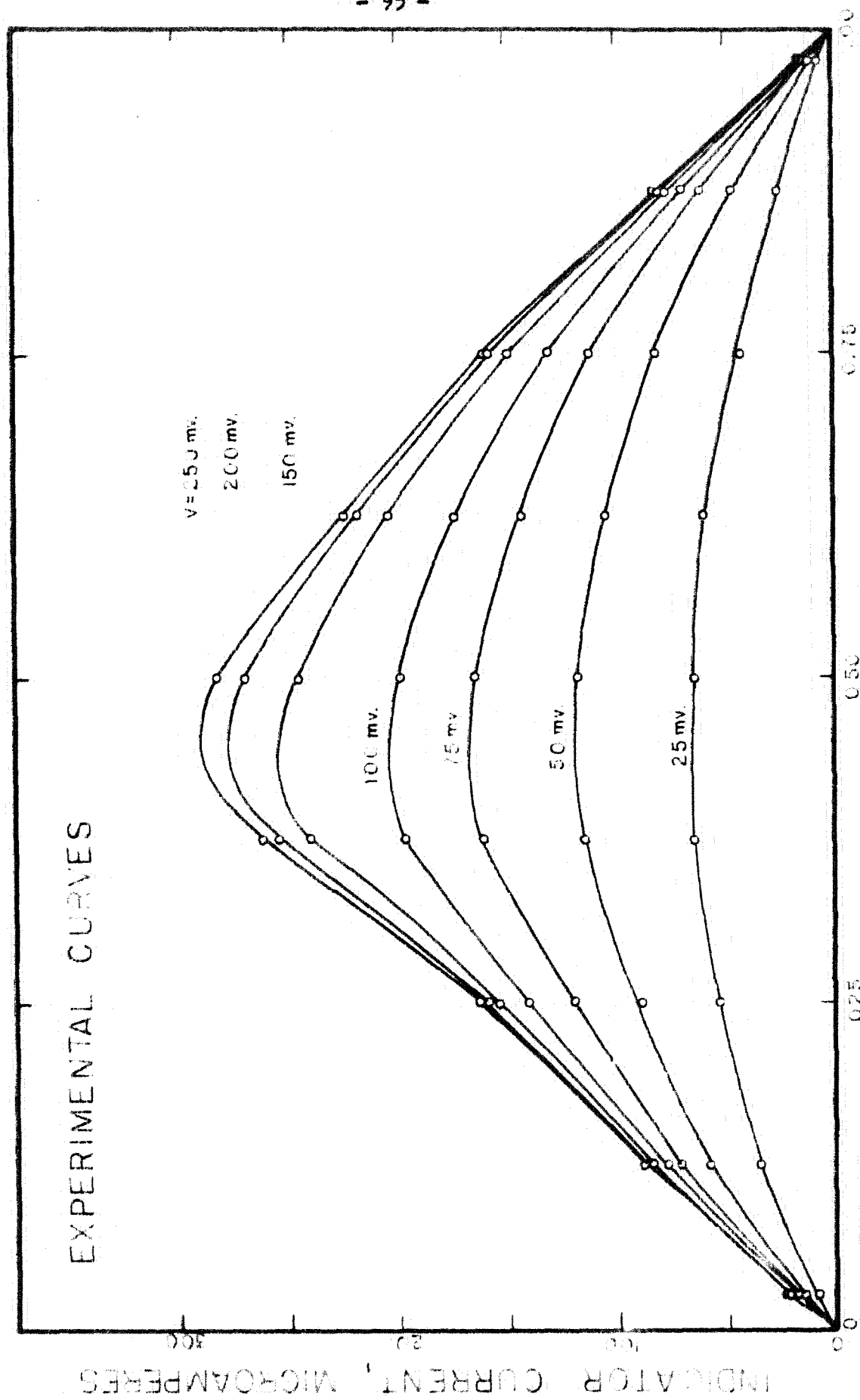
Figure 13. The Effect of Applied Potential and Fraction Oxidized on Indicator Currents in a Solution Containing Ferrocyanide and Ferricyanide. The Sum of the Concentrations of Ferrocyanide and Ferricyanide is Constant.

between the solution and the anode against the fraction oxidized as
calculated from Equation 10; Figure 15 shows the plot of experimental
values. Again the qualitative agreement is good. Quantitatively, the
deviations are such that they can be explained by low reaction rates
at the electrodes both for the oxidization of ferrocyanide and the
reduction of ferricyanide.

The presence of a rapid change in the fraction of the applied
potential carried by the anode at a position corresponding to approx-
imately 50 per cent oxidation is of interest. The deviation of the
point of inflection from that corresponding to 50 per cent oxidation
is caused mainly by the difference in diffusion coefficients of the
species involved. It is doubtful that this point of inflection can
be exploited for analytical purposes unless the precision of the
measurements can be improved by better control of experimental
conditions.

It should also be noted that even when the fraction oxidized is
very small, a significant fraction of the applied potential exists
between the indicator anode and the solution. When the fraction
oxidized is small compared to 1 , Equation 7 reduces to

$$ P = \frac{RT}{nVF} \quad \ln \left(1 + \frac{\alpha-1}{\alpha+1} \right) $$

As the applied potential becomes very large and no other half-cell
reactions occur, P approaches $\frac{RT}{nVF}$ ln 2. The potential of the
indicator anode is almost the same as that of a similar electrode in
equilibrium with the solution, but even though the indicator cathode
is the limiting electrode, not all of the applied potential is between
it and the solution; the concentrations at the surface of the indicator
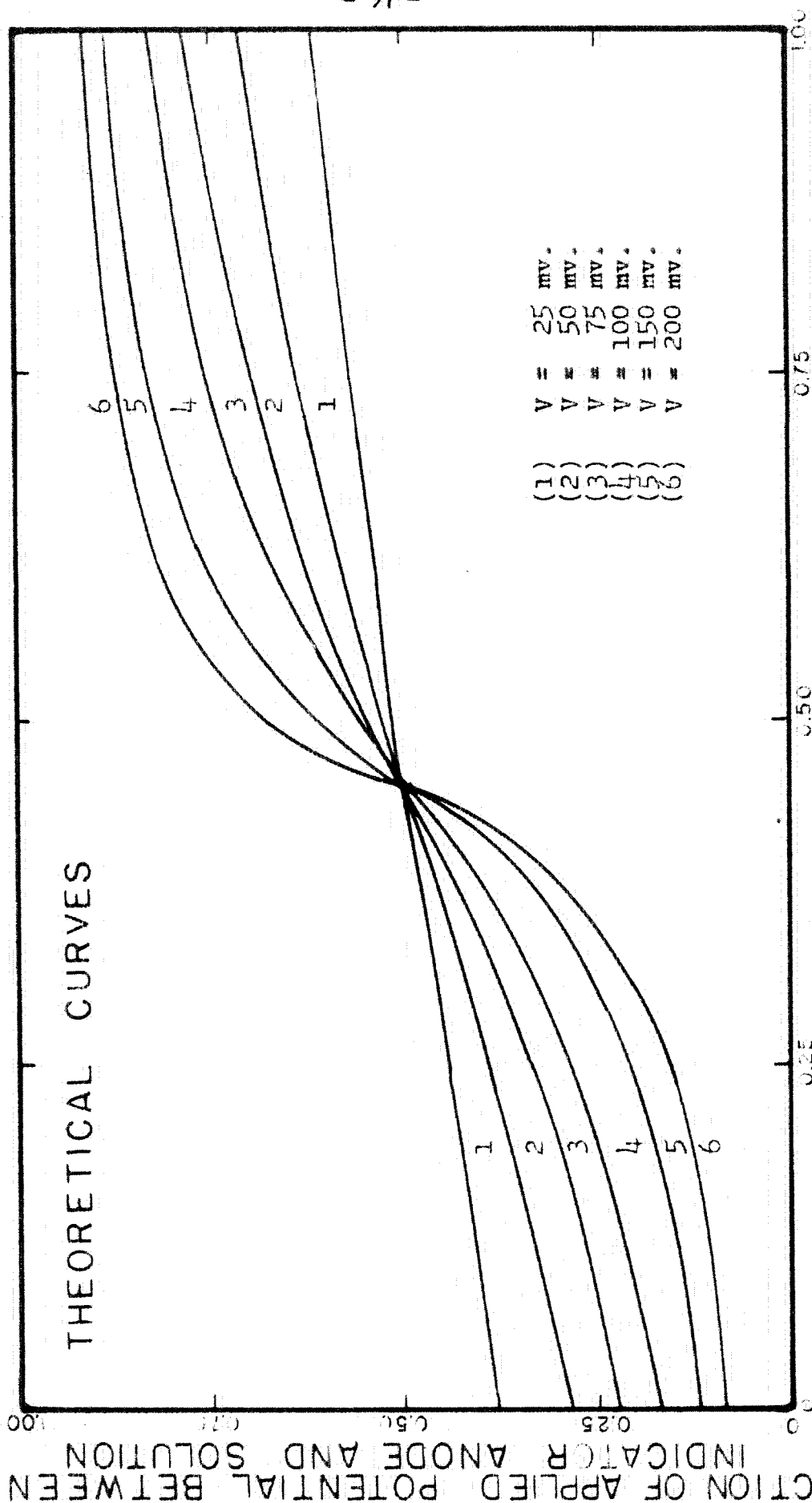
Figure 14. The Calculated Distribution of Applied Indicator Potential as a Function of Fraction Oxidized and Applied Indicator Potential for a Reversible One-Electron Half-Cell.
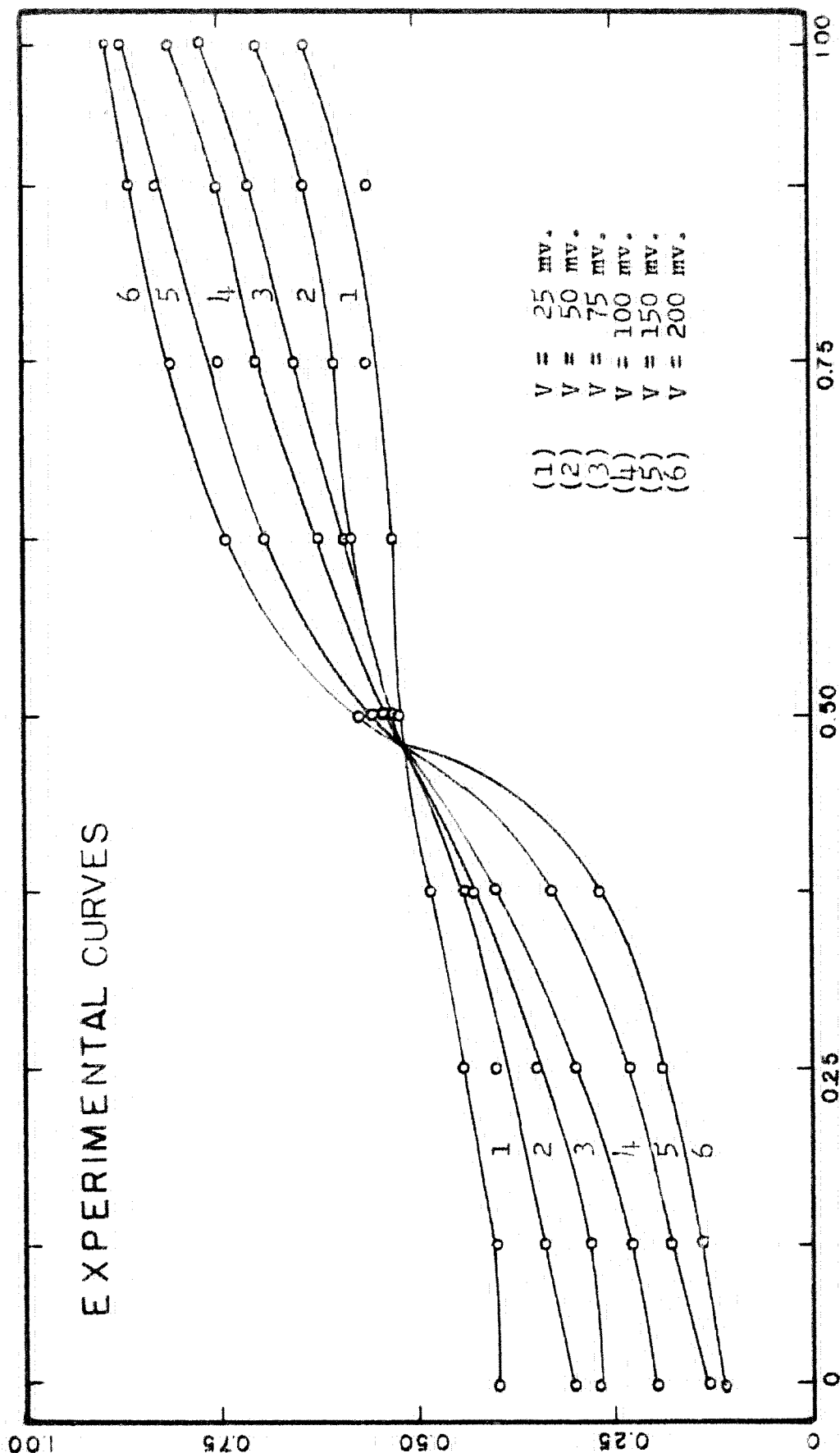
Figure 15. The Distribution of Applied Indicator Potential as a Function of Fraction Oxidized and Applied Indicator Potential for the Ferrocyanide-Ferricyanide Half-Cell. The Sum of the Concentrations of Ferrocyanide and Ferricyanide is Constant.

anode must be different from those in the body of the solution in order that reacting and reacted species may diffuse to and from the electrode as required by the current. When the fraction oxidized is very nearly unity, similar conclusions apply to the indicator cathode.

CONCLUSIONS AND APPLICATIONS

The Bivariable Electrode System.

The so-called "dead-stop" is a result of the limitations of instruments in measuring small currents. In a titration involving at least one electrode-reactive half-cell, zero current will be observed at the equivalence point only if the equilibrium constant for the reaction between the titrant and the substance titrated is infinite. Since this is not the case for any actual reaction, small, but not necessarily detectable, currents will exist at the equivalence point. If the half-cells for both the titrant and the substance titrated are electrode-reactive, the indicator current will be a linear function of titrant added on both sides of the equivalence point, but near the equivalence point the curve will be rounded. The sharpness of the intersection of the two lines increases as the equilibrium constant for the reaction between the titrant and the substance being titrated approaches infinity. As Farrington, Meier, and Swift (36) have shown, the point of minimum current is not necessarily the equivalence point.

Some investigators (8, 40) have reported values for the smallest concentration of iodine necessary to "depolarize" the indicator cathode. This quantity is dependent on the size and shape of the electrode, the

potential, the stirring, and the sensitivity of the current-measuring
instrument. Unless these factors are closely controlled, it is not
surprising that different values will be found. When the applied potential
is less than 60 millivolts, the indicator current is especially sen-
sitive to changes in potential as can be seen from Figure 10. Such
data are of doubtful value unless all of the conditions are reported.

The maximum sensitivity of the system is not utilized when the
applied potential is of the order of 10-20 millivolts. The potential
which should be applied during titrations involving at least one
reversible half-cell depends primarily on the number of electrons,
n, involved in the electrode reactions. Equations 6 and 7, which are
applicable near the end point, can both be written as $i = i_L \left(\dfrac{\alpha - 1}{\alpha + 1} \right)$.
It is desirable that a potential be applied which is in the range
of potentials in which the current is limited by diffusion. When
the lower limit is calculated from this equation by arbitrarily
taking $i = 0.98\ i_L$ as the lowest desirable current, the following
lower applied potential limits are obtained (see Figure 10 also):

n	Lower Limit of V
1	95
2	47
3	32
4	24

No matter what value for the ratio, i/i_L, is chosen, the potential
obtained from this equation is proportional to $1/n$. The upper
applied potential limit is set by the onset of other electrode
reactions, and will depend on the constituents of the solution being
titrated. There is little advantage in using an applied potential

greater than 250 mv. since with this applied potential a limiting diffusion current is obtained throughout almost the entire titration (see Figure 12). Of course, at best these conclusions apply only qualitatively to titrations involving irreversible electrode-reactive half-cells. In any case it is best to measure the current as a function of applied potential on both sides of the end point and for other similar titrations to use an applied potential which is in a region in which the current is not changing rapidly with changes in applied potential.

The current also depends on the size and material of the electrode. The electrodes should be made of a material at which one of the half-cells involved in the titration most nearly approaches reversibility. By varying the sizes of the electrodes, the magnitude of the current can be adjusted for convenient measurement.

Comparison of End Points.

Amperometric versus Potentiometric. Because both the amperometric and potentiometric end points depend on electrode reactions, they are applicable to many of the same titrations. The use of electrodes at which one of the involved half-cells approaches reversibility is desirable for both end points. In general, measurements can be made more rapidly with an amperometric system, whose use requires the attainment of a steady state, than with a potentiometric system whose use requires the attainment of equilibrium between the electrode and the solution. The current is directly dependent on concentrations while the potential is dependent on the logarithms of concentrations; hence, the relative magnitude of changes

of current at the end point is much greater than the relative
magnitude of changes of potential. The linear relation between
current and concentration lends itself more easily to extrapolation
to an end point than the logarithmic relation between potential
and concentration. For this reason, an amperometric system is
probably more useful when the reaction is so incomplete at the
equivalence point that the potential change is not sharp.

In Figures 16 and 17 the amperometric and potentiometric end
points are compared in two titrations of bromine with cuprous
copper at different applied potentials. The potentiometric end
point was obtained by measuring the potential between a platinum
electrode in equilibrium with the solution and a calomel reference
electrode. The potentials of the two indicator electrodes with
respect to the reference electrode are also shown.

In both titrations the potential between each of the indicator
electrodes and the platinum electrode in equilibrium with the solution
undergoes its greatest change near the equivalence point. The applied
potential is redistributed as the current control is shifted from
one electrode to the other. The largest fraction is between the con-
trolling electrode and the solution (the equilibrium platinum
electrode).

When the applied potential was 55 millivolts, the potentials
of the indicator electrodes with respect to the reference electrode
changed more sharply at the end point than when the applied potential
was 45 millivolts. This behavior is due to the fact that the
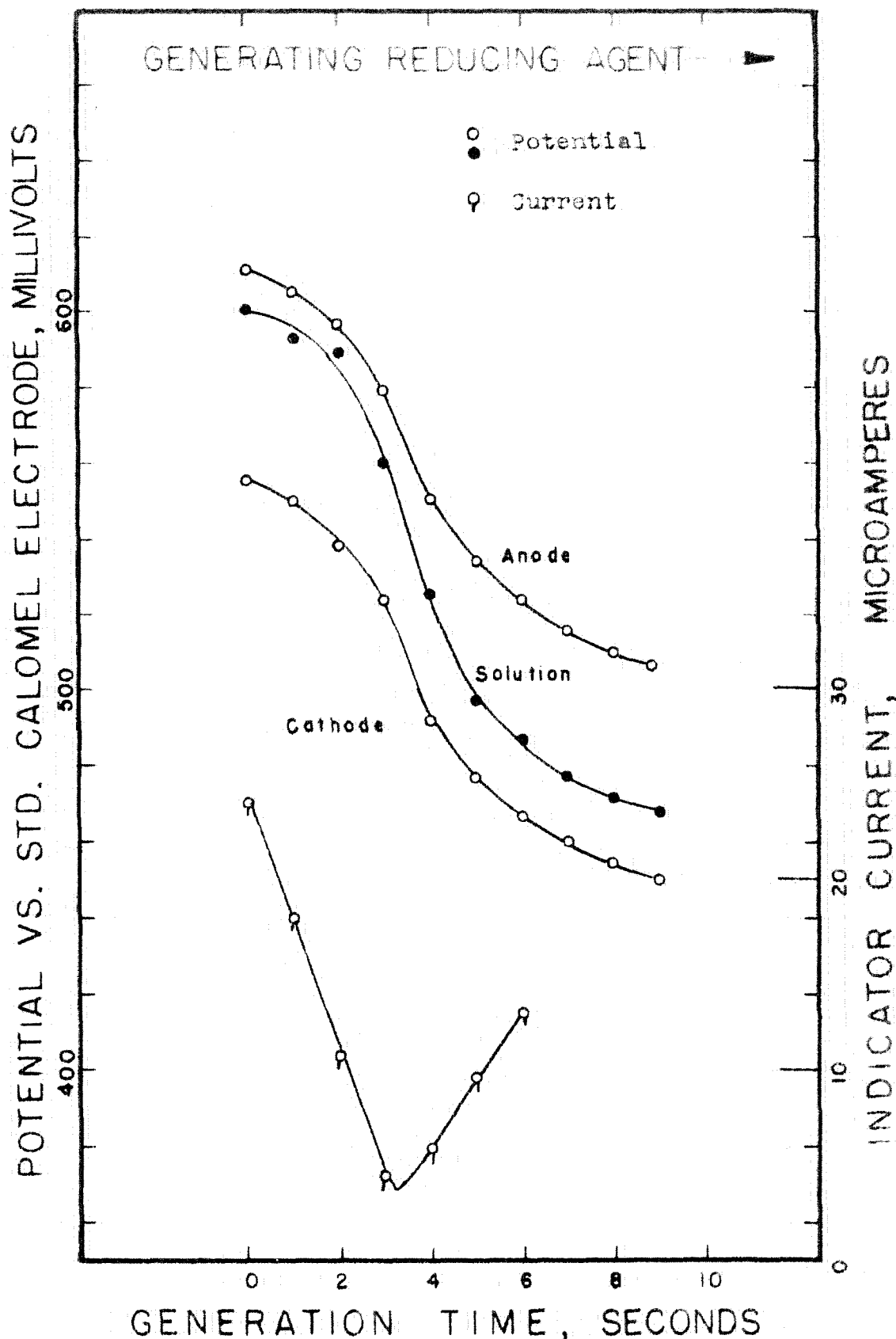equilibrium constant (36) for the reaction

Figure 16. A Comparison of the Potentiometric and Amperometric End Points for a Coulometric Titration of Bromine with Cuprous Copper with an Applied Potential of 55 Millivolts.
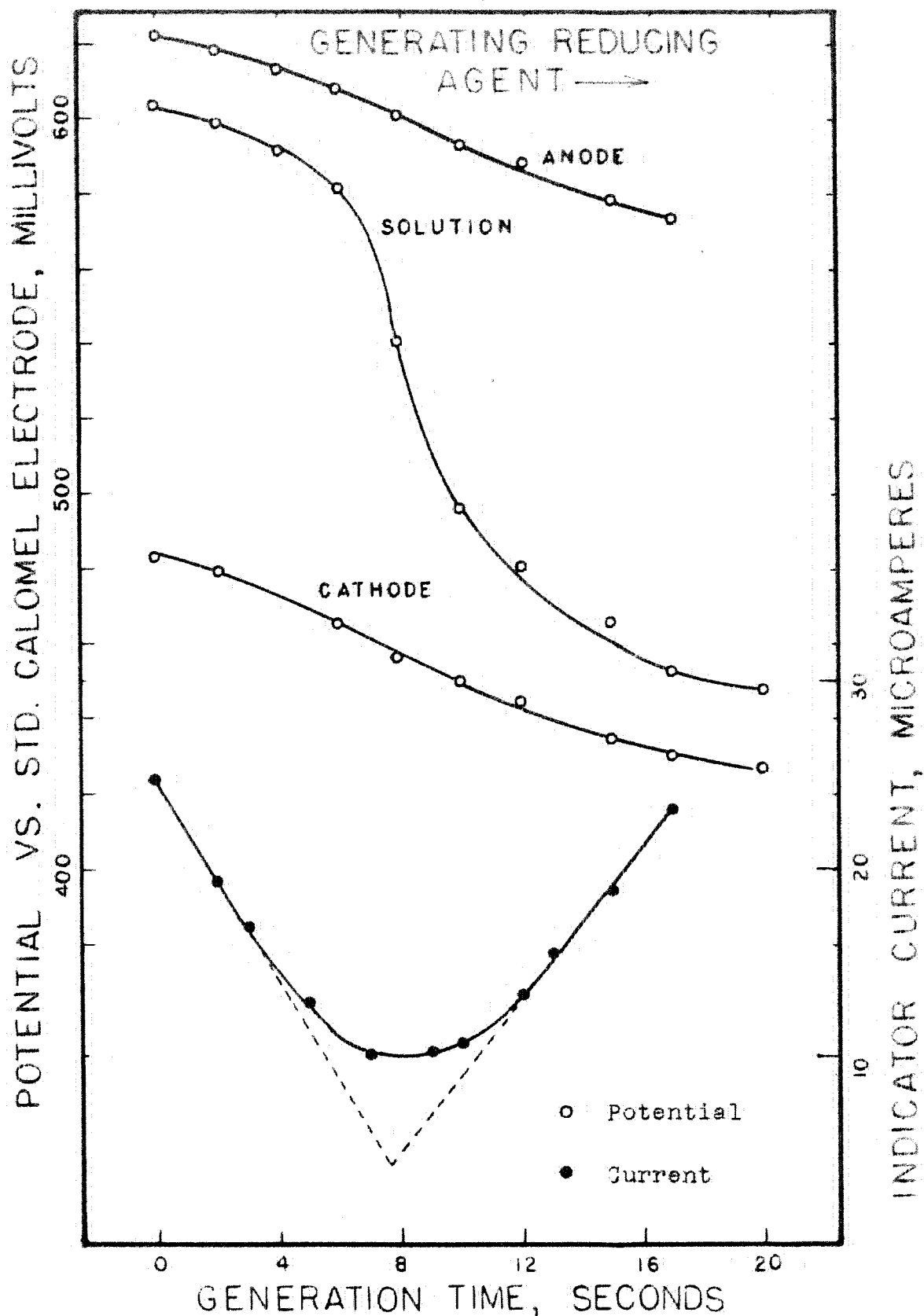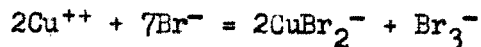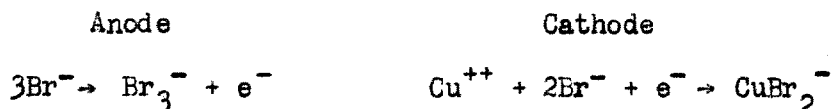
Figure 17. A Comparison of the Potentiometric and Amperometric End Points for a Coulometric Titration of Bromine with Cuprous Copper with an Applied Potential of 145 Millivolts.

$$2Cu^{++} + 7Br^- = 2CuBr_2^- + Br_3^-$$

is so large that in these solutions there are amperometrically significant concentrations (approximately 10^{-6} VF.) of $CuBr_2^-$ and Br_3^- at the equivalence point. Since the concentrations of Br^- and Cu^{++} are large compared to the concentrations of $CuBr_2^-$ and Br_3^-, the potential between the indicator cathode and anode may be written (assuming the electrodes are in equilibrium with the solutions at their surfaces)

$$E_c - E_a = \frac{RT}{2F} \ln [CuBr_2^-]_c^2 [Br_3^-]_a - \frac{RT}{2F} \ln [CuBr_2^-]_s^2 [Br_3^-]_s .$$

Since the last term is a constant, the $[Br_3^-]_a$ and $[CuBr_2^-]_c$ must both increase when the applied potential is increased. The concentrations of these two species depend on the electrode reactions

<table>
<tr><td>Anode</td><td>Cathode</td></tr>
<tr><td>$3Br^- \rightarrow Br_3^- + e^-$</td><td>$Cu^{++} + 2Br^- + e^- \rightarrow CuBr_2^-$</td></tr>
</table>

The concentrations at electrode surfaces and in the body of the solution are related by the following equations.

$$i = k_3([Br_3^-]_s - [Br_3^-]_c) + k_2 ([CuBr_2^-]_c - [CuBr_2^-]_s)$$

$$= k_3([Br_3^-]_a - [Br_3^-]_s) + k_2([CuBr_2^-]_s - [CuBr_2^-]_a).$$

Near the end point $[CuBr_2^-]_s$ and $[Br_3^-]_s$ are changing rapidly. At low applied potentials when the $[Br_3^-]_a$ is of the same order of magnitude as $[Br_3^-]_s$ and the $[CuBr_2^-]_c$ is of the same order of

magnitude as $[CuBr_2^-]_s$, the $[Br_3^-]_a$ and $[CuBr_2^-]_c$ are sensitive to the $[Br_3^-]_s$ and $[CuBr_2^-]_s$ and the potentials of the indicator electrodes with respect to a reference electrode change rapidly near the end point. When the applied potential is larger and the $[CuBr_2^-]_c$ and $[Br_3^-]_a$ are large compared to $[CuBr_2^-]_s$ and $[Br_3^-]_s$, the potentials of the two indicator electrodes with respect to a reference electrode become much less sensitive to changes in $[CuBr_2^-]_s$ and $[Br_2^-]_s$. Thus, these potentials remain almost constant while titrating through the equivalence point.

Univariable Electrode Amperometric versus Bivariable Electrode Amperometric. The univariable electrode amperometric system is probably of more general applicability than the bivariable system. The requirement for a current in the univariable system is that a species reactive at the variable potential electrode be present in the solution, while for the bivariable system, species reactive at both electrodes must be present. Since a different half-cell reaction is taking place at each electrode in the univariable system, the passage of current changes the composition of the solution. This can introduce errors which will be most significant when very small quantities are being titrated. These errors will depend on the magnitude of the current and the length of time of its passage. The fact that the indicator current in most cases does not change the composition of the solution recommends the bivariable electrode system for use in detecting end points in the titration of small quantities. Besides the detection of end points, both amperometric systems are useful in obtaining physico-chemical data requiring the measurement of concentrations.

APPENDIX I.   DETAILED DISCUSSION OF AMPEROMETRIC MEASUREMENTS ON

THE IODIDE-IODINE-TRI-IODIDE SYSTEM.

Whenever more than one species of the oxidized or reduced

state exist in the solution, the treatment becomes more complicated

because of the possibility of reactions in the diffusion layer in-

volving electrode-reactive species. The indicator current then depends

on the rates of the reactions in the diffusion layer, the width of

the diffusion layer, the concentrations of all involved species in

the body of the solution, their diffusion coefficients and the applied

potential. The situation is especially complicated when the con-

centrations of more than one of the species involved in the complex

are changed during the titration.

As an example of this latter situation, both the oxidized and

reduced states of the iodine-iodide half-cell are composed of two

species because of the equilibrium, $I_3^- = I_2 + I^-$. During a titration

of iodide to iodine the concentrations of all three species are

changing. The dependence of diffusion on the concentrations in the

body of the solution and at the electrode surface is itself dependent

on the degree of attainment of the tri-iodide equilibrium in the

diffusion layer. As one extreme, if this equilibrium is attained so

slowly that the iodide, iodine, and tri-iodide pass through the

diffusion layer without any adjustment of concentrations according

to the tri-iodide equilibrium, then the iodide, iodine, and the tri-

iodide will diffuse to and away from the electrodes independently.

As the other extreme, equilibrium is attained at every point in

the diffusion layer. The actual situation can be anywhere between

these two extremes.

Both of the extreme situations will be treated using the iodide-iodine half-cell as an example. It will be shown that Equation 6 is valid for both extreme situations when the concentration of iodide is much larger than the concentration of iodine. Thus, the treatment below constitutes a justification for the use of the iodide-iodine half-cell in testing assumption 4. It also serves as an example of the general treatment of such situations in which a reaction may take place in the diffusion layer.

Some relations which apply to both extreme situations are given below. For simplicity, only one-dimensional diffusion will be considered. According to Fick's law, the number of a given species diffusing across a small unit area parallel to the electrode surface in the diffusion layer is proportional to the concentration gradient of that species at that point in the diffusion layer. Thus,

$$\frac{dI_3^-}{dt} = D_3 \frac{d[I_3^-]}{dx}, \quad \frac{dI_2}{dt} = D_2 \frac{d[I_2]}{dx}, \quad \text{and} \quad \frac{dI^-}{dt} = D_1 \frac{d[I^-]}{dx}$$

(13)

in which $\frac{d[I_3^-]}{dx}$, $\frac{d[I_2]}{dx}$, and $\frac{d[I^-]}{dx}$ are the concentration gradients of these species; D_3, D_2, and D_1 are their diffusion coefficients; and $\frac{dI_3^-}{dt}$, $\frac{dI_2}{dt}$, and $\frac{dI^-}{dt}$ are the number of moles per second of these species which pass through the given small unit area. Because I_3^-, I_2, and I^- are the only species reacting at the electrodes, and of these only I_3^- and I^- are charged,

$$-\frac{i}{FA} = \frac{dI_3^-}{dt} + \frac{dI^-}{dt}$$

(14)

where i is the current, F is the Faraday, and A is the area of the electrode. Because of conservation of mass and the existence of a steady state, within the diffusion layer

$$3I_3^- + 2I_2 + I^- = C$$

where C is the total number of atoms of iodine in the diffusion layer. Differentiating this expression with respect to time, we obtain

$$3\ \frac{dI_3^-}{dt} + 2\ \frac{dI_2}{dt} + \frac{dI^-}{dt} = 0 \tag{15}$$

When Equation 15 is substituted into Equation 14, we obtain

$$\frac{i}{FA} = 2\ \frac{dI_3^-}{dt} + 2\ \frac{dI_2}{dt} \tag{16}$$

When Equations 13 are substituted into Equations 14 and 16, we obtain

$$-\frac{i}{FA} = \frac{1}{D_3}\ \frac{d[I_3^-]}{dx} + \frac{1}{D_1}\ \frac{d[I^-]}{dx} \tag{17}$$

and

$$\frac{i}{FA} = \frac{2}{D_3}\ \frac{d[I_3^-]}{dx} + \frac{2}{D_2}\ \frac{d[I_2]}{dx} \tag{18}$$

Case 1 -- No Reaction in the Diffusion Layer. First, let us consider the situation in which no adjustment of concentration according to the tri-iodide equilibrium takes place in the diffusion layer. The time in which significant quantities of I_3^-, I_2, and I^- react is long compared to the time required for passage through the diffusion layer. These three species are at equilibrium in the body of the solution; since we will assume that all three species are reversible at a platinum electrode, they must also be in equilibrium at the

electrode surface. Therefore, the boundary conditions are

$$\frac{[I_3^-]}{[I_2][I^-]} = K$$

at $x = 0$, i.e., at the electrode surface, and at $x =$, i.e., at the effective boundary between the diffusion layer and the body of the solution. Within the diffusion layer there is no interaction.

Because there is no interaction in the diffusion layer, and because there is a steady state, $\frac{dI_3^-}{dt}$, $\frac{dI_2}{dt}$, and $\frac{dI^-}{dt}$ are all constants and have the same value for all values of x. Hence, on integration of Equations 3, we obtain

$$[I_3^-]_x = [I_3^-]_{x=0} + \frac{1}{D_3}\frac{dI_3^-}{dt} x$$

$$[I_2]_x = [I_2]_{x=0} + \frac{1}{D_2}\frac{dI_2}{dt} x$$

$$[I^-]_x = [I^-]_{x=0} + \frac{1}{D_1}\frac{dI^-}{dt} x$$

Let the subscript s denote a concentration in the body of the solution and the subscript e a concentration at the electrode surface. Then

$$\frac{D_3}{\ell_3}([I_3^-]_s - [I_3^-]_e) = \frac{dI_3^-}{dt}$$

$$\frac{D_2}{\ell_2}([I_2]_s - [I_2]_e) = \frac{dI_2}{dt} \qquad (19)$$

$$\frac{D_1}{\ell_1}([I^-]_s - [I^-]_e) = \frac{dI^-}{dt}$$

in which the ℓ's are the effective widths of the diffusion layer for the different species. Substituting Equations 19 into Equation 16, we obtain

$$\frac{i}{FA} = 2 \ \frac{D_3}{3} \ ([I_3^-]_s - [I_3^-]_e) + \frac{D_2}{2} \ ([I_2]_s - [I_2]_e)$$

Since the $[I^-]$ is large and essentially constant throughout the diffusion layer,

$$[I_2]_s = \frac{[I_3^-]_s}{K[I^-]_s} \qquad \text{and} \qquad [I_2]_e = \frac{[I_3^-]_e}{K[I^-]_s}$$

Thus,

$$\frac{i}{FA} = 2 \left(\frac{D_3}{3} + \frac{D_2}{2 \ K[I^-]} \right) \ ([I_3^-]_s - [I_3^-]_e) \tag{20}$$

and the current is proportional to the difference between the concentration of tri-iodide in the body of the solution and at the electrode surface.

Equation 20 is applicable to either electrode if the sign of the current at the anode is opposite that of the cathode. As we have defined the current, it is positive at the cathode and negative at the anode. Thus, for the cathode,

$$\frac{i}{FA} = 2 \left(\frac{D_3}{3} + \frac{D_2}{2 \ K[I^-]} \right) ([I_3^-]_s - [I_3^-]_c) \tag{21}$$

while for the anode

$$-\frac{i}{FA} = 2 \left(\frac{D_3}{3} + \frac{D_2}{2 K[I^-]} \right) ([I_3^-]_s - [I_3^-]_a) \tag{22}$$

The potential of the cathode is

$$E_c = E^o - \frac{RT}{2F} \ln \frac{[I_3^-]_c}{[I^-]_c^3} = E^o - \frac{RT}{2F} \ln \frac{[I_3^-]_s - i/k_c}{[I^-]_c^3}$$

in which

$$k_c = 2FA_c \left(\frac{D_3}{\ell_3} + \frac{D_2}{\ell_2 \, K[I^-]} \right)$$

It will be assumed again that the areas of the two electrodes are equal and that they are situated in equivalent positions so that the effective widths of the diffusion layers are equal. Thus

$$k_c = k_a = k$$

The potential of the anode is then

$$E_a = E^o - \frac{RT}{2F} \ln \frac{[I_3^-]_a}{[I^-]_a^3} = E^o - \frac{RT}{2F} \ln \frac{[I_3^-]_s + i/k}{[I^-]_a^3}$$

Since $[I^-]_c$ and $[I^-]_a$ are very nearly equal, the applied potential is

$$V = E_c - E_a = \frac{RT}{2F} \ln \frac{[I_3^-]_s + i/k}{[I_3^-]_s - i/k}$$

Thus,

$$i = i_L \left(\frac{a - 1}{a + 1} \right) \tag{23}$$

since $a = e^{\frac{2VF}{RT}}$ and $i_L = k[I_3^-]_s$. Equation 23 is identical with Equation 6.

Case 2 — Equilibrium in the Diffusion Layer. The situation in which equilibrium is attained throughout the diffusion layer is more complicated. Then

$$[I_3^-] = K[I_2][I^-] \qquad \text{for all values of x.}$$

Differentiating this expression with respect to x, we obtain

$$\frac{d[I_3^-]}{dx} = K[I_2] \frac{d[I^-]}{dx} + K[I^-] \frac{d[I_2]}{dx}$$

Substituting the expression for $\frac{d[I^-]}{dx}$ from Equation 17 and rearranging, we obtain

$$\frac{d[I_3^-]}{dx} = \frac{K[I_2] \frac{1}{D_1 FA} + K[I^-] \frac{d[I_2]}{dx}}{1 + K[I_2] \frac{D_3}{D_1}}$$

On rearrangement of Equation 18, we obtain

$$2D_3 \frac{d[I_3^-]}{dx} = -2D_2 \frac{d[I_2]}{dx} - \frac{1}{FA}$$

Eliminating $\frac{d[I_3^-]}{dx}$ and rearranging, we obtain

$$\frac{d[I_2]}{dx} = \frac{-\frac{1}{FA}\left(1 + 3K[I_2] \frac{D_3}{D_1}\right)}{2D_3 K[I^-] + 2D_2 \left(1 + K[I_2] \frac{D_3}{D_1}\right)} \tag{24}$$

Only the case in which $[I^-] \gg [I_2]$ will be considered. Although $\frac{d[I^-]}{dx}$ is of the same order of magnitude as $\frac{d[I_3^-]}{dx}$ and $\frac{d[I_2]}{dx}$ and can not be considered zero, the concentration of iodide is essentially constant throughout the diffusion layer. Hence, we can consider $[I^-]$ a constant in the above expression. On integration of Equation 24, we obtain

$$\frac{1}{FA} x = \left(\frac{6KD_3[I^-] + 4D_2}{9K \frac{D_3}{D_1}}\right) \ln\left(1 + 3K \frac{D_3}{D_1}[I_2]\right) + \frac{2D_2}{3}[I_2] + M \tag{25}$$

where M is a constant of integration. When $x = \ell$, $[I_2] = [I_2]_s$.

Thus

$$\frac{1}{FA}(\ell - x) = \left(\frac{6KD_3[I^-] + 4D_2}{9K \frac{D_3}{D_1}} \right) \ln \frac{\left(1 + 3K \frac{D_3}{D_1} [I_2]_s \right)}{(1 + 3K \frac{D_3}{D_1} [I_2])}$$

$$+ \frac{2}{3} D_2([I_2]_s - [I_2]) \tag{26}$$

This is as far as this treatment can be carried without applying particular experimental conditions. Since measurements were made on a solution in which the $[I_2]_s \sim 10^{-7}$, since D_3 and D_1 are of the same order of magnitude, and since $K = 710$, $3K \frac{D_3}{D_1} [I_2]_s \sim 10^{-4}$. Hence we may use the expansion,

$$\ln (1 + x) = x - \frac{1}{2} x^2 + \ldots\ldots ,$$

and retain only the first term. On applying this expansion to Equation 26, we obtain

$$\frac{1}{FA} \ell = (2KD_3[I^-] + 2D_2) ([I_2]_s - [I_2]_e)$$

and since

$$[I_3^-]_s = K[I^-]_s [I_2]_s \qquad \text{and} \qquad [I_3^-]_e = K[I^-]_s [I_2]_e$$

$$\frac{1}{FA}\ell = 2 \left(D_3 + \frac{D_2}{K[I^-]} \right) ([I_3^-]_s - [I_3^-]_e) \tag{27}$$

This expression is identical with Equation 20. Hence, for this case also,

$$i = i_L \left(\frac{\alpha - 1}{\alpha + 1} \right) \tag{28}$$

Thus, it has been shown that Equation 6 is applicable to both extreme cases under the experimental conditions.

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PROPOSITIONS

1. In calculating the equilibrium constant for the reaction

$$2Cu^{++} \quad + \quad 7Br^- \quad = \quad CuBr_2^- \quad + \quad Br_3^-$$

from amperometric data, Farrington, Meier, and Swift (1) assumed that a limiting diffusion current is obtained at both indicator electrodes. This assumption does not seem justified.

> (1) Farrington, P.S., Meier, D.J., and Swift, E.H., Anal. Chem., 25, 591 (1953).

2. A coulometric titration of microgram quantities of silver with iodide generated from iodine is proposed.

3. The existence of Al(I) and Al(II) in liquid ammonia solutions is doubtful. The supporting evidence (2,3) is unconvincing and, if anything, argues against the existence of these oxidation states.

> (2) Bennett, W.E., Davidson, A. W., and Kleinberg, J., J. Am. Chem. Soc., 74, 732 (1952).
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4. Information on the rates of electrode reactions can be obtained by using radioactive tracers to measure the rate of exchange between two oxidation states of a half-cell in the presence of metal surfaces.

5. The elemental analysis and magnetic data presented by Kappanna and Talaty(4) as evidence for the existence of AgO_2 are insufficient. A simple measurement of the number of oxidizing equivalents per mole of silver could disprove the existence of this oxide.

> (4) Kappanna, A.N., and Talaty, E.R., J. Ind. Chem. Soc., 28, 413 (1951).

6. It is proposed that cerous cerium can be determined coulometrically in concentrated carbonate solutions with ferricyanide.

7. Haight (5) has discarded several possible electrode reactions by which tripositive arsenic may be oxidized polarographically in sodium hydroxide solutions on the basis that the reaction products are not reduced polarographically. It is proposed that this is not sufficient justification for discarding these reactions.

(5) Haight, G.P., J. Am. Chem. Soc., 75, 3848 (1953).

8. The use of different metals for the two indicator electrodes of an amperometric system should be investigated with the object of extending the applicability of such systems.

9. (a) A simple explanation for the catalysis at metal surfaces of oxidation-reduction reactions in solution is that electrode reactions are involved in the overall reaction. Examples are the oxidation of bromide with ceric cerium, the oxidation of iodide with ferricyanide, and the reduction of water with Mo(III).

(b) Kinetic data taken with an amperometric system for the reaction between species of two electrode-reactive half-cells, e.g., the ferrous-ferric and bromide-bromine half-cells, are of doubtful value since the reaction can take place through the agency of the indicator electrodes.

10. In order to increase campus efficiency, coffee schedules should be posted conspicuously at the doors of all campus offices and shops.

11. Basing his argument on one of the fundamental vibrations of fluorobenzene, Garg (6) has stated that he believes that the fluorobenzene molecule has no symmetry. The experimental evidence does not support this view.

(6) Garg, S.N., *J. Chem. Phys.*, 21, 1907 (1953).