# AND AMPEROMETRIC ANALYSIS

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Thesis by

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#### ABSTRACT

I

The coulometric determination of chromates and vanadates by means of electrolytically generated cuprous ion has been investigated. For samples of chromate larger than 170 micrograms, the error in the determination was less than 0.1 percent. The presence of oxygen has been shown to give a positive error of about 0.5 percent when determining vanadates. When oxygen was excluded, the error in determining 750 micrograms was less than 0.15 percent.

- II The use of electrolytically generated argentic silver for the determination of manganous ion, cerous ion and arsenious acid has been investigated and has been shown to be impractical because of the slow rate of oxidation by the argentic silver.
- III The determination of Bromine Numbers with electrolytically generated bromine has been investigated. For olefins which rapidly add bromine, the use of a 50 percent acetic acid solution of sodium bromide as the titration medium has been shown to give good results. A means has been proposed for the electrolytic determination of Bromine Numbers for slowly reacting olefins.
- IV An amperometric method for determining the formal potential of the reaction 2 Cu<sup>++</sup>+7Br<sup>-</sup> = 2CuBr<sub>2</sub><sup>-</sup>+Br<sub>3</sub><sup>-</sup> has been investigated. The formal potential was found to be -.384 v. for solutions 0.017 formal in cupric ion, 0.44 formal in bromide ion, an 0.7 formal in sulfuric acid.

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#### PART I

THE COULOMETRIC DETERMINATION OF CHROMATES AND VANADATES BY MEANS OF ELECTROLYTICALLY GENERATED CUPROUS ION, AND AN AMPEROMETRIC END-POINT

#### Introduction:

The use of electrolytically generated bromine as an oxidizing agent for the determination of many substances has been described by Sease, Niemann, and Swift(1). Myers and Swift<sup>(2)</sup>. Wooster<sup>(3)</sup> and Brown<sup>(4)</sup>. In order to extend the methods of coulometric analysis using amperometric end-points to oxidizing substances. Mr. R. Myers. in this laboratory, investigated various ions which could be electrolytically reduced with 100 percent current efficiency and which would establish a reversible couple so that amperometric end-points could be used. Of the many substances tried, the most promising was the cuprouscupric couple in approximately 2 formal hydrochloric acid. Preliminary investigations using this couple to determine chromates and vanadates showed that the method was feasible. However, several difficulties soon became apparent. The accuracy attained was not as good as that in the systems using bromine, and the solution of copper sulfate in 12 formal hydrochloric acid was not stable. Therefore, this investigation was undertaken to attempt to resolve these difficulties and to determine the accuracy that could be expected in this type of determination.

#### Experimental Part:

#### Chemicals:

The standard potassium dichromate solutions were prepared gravimetrically from Bureau of Standards material. As mentioned previously, Mr. Myers had found that the solutions of copper sulfate in 12 formal hydrochloric were not stable; on standing the solution developed reducing properties. It was felt that this instability might possibly be due to impurities in the copper sulfate. and that if suitably purified the solution would be stable. The copper sulfate was purified by two recrystallizations from water, the first and last crystals in each recrystallization being discarded. During the first recrystallization. 3 ml of 3 percent hydrogen peroxide was added and the solution boiled. The resulting crystals were dried and the calculated amount was dissolved in reagent grade 12n hydrochloric acid to give a 0.2 formal copper sulfate solution. The solution was found to give a titer corresponding to approximately 2x10<sup>-6</sup> equivalents of reducing material per 10 ml, which was shown to arise from the hydrochloric acid. This was eliminated by addition of the requisite amount of a saturated solution of chlorine in 6 formal hydrochloric acid. When prepared in this manner, the solution of copper sulfate in concentrated hydrochloric acid was found to be stable for weeks.

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The sodium vanadate solution used was prepared by Mr. R. Myers according to the method of Ramsey<sup>(5)</sup>, by boiling ammonium metavanadate with an excess of c.p. sodium carbonate. It was standardized iodometrically, using weight burets, by the method of Ramsey<sup>(5)</sup>, against a sodium thiosulfate solution. The sodium thiosulfate solution was standardized against Bureau of Standard's potassium dichromate. This standardization of the sodium vanadate solutions gave results with an average deviation of less than 0.02 percent.

Occasionally, the laboratory distilled water contained small quantities of an oxidizing agent, thought to be chlorine, which could be removed by boiling the water while passing a current of air through it. At all times boiled distilled water was used in this work. Apparatus:

The apparatus used was similar to that described by Myers and Swift<sup>(2)</sup>, except that an electronic circuit had been added to improve the constant current characteristics. The details of this circuit will be described in another paper by Mr. Myers<sup>(6)</sup>. A simplified diagram appears in Figure 1. The stirrer was a four pole, shaded pole, induction motor which had been tested in this laboratory by Mr. Brough and Mr. Phillips for constant speed. It was found to have a speed of 1650

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r.p.m. which did not vary measurably (-10 r.p.m.) between no load and stirrer load and which was constant for a half-hour period within the limits of experimental error.

The titration cell is illustrated in Figure 2. The generating anode was isolated from the cell by enclosing the anode in a sintered glass filter stick of fine porosity. In order to prevent diffusion of the solution being titrated into the filter stick, the solution ( $6nH_2SO_4$ ) in the filter stick was maintained at a higher level than that of the solution in the titration cell.

The indicator electrodes had areas of 2.25 and 6 square centimeters. The instrument was provided with a reversing switch so that the polarity of the indicating electrodes could be changed at will. A potential of 200 millivolts was impressed across the indicator electrodes. Experiments by Mr. Myers had indicated that minor fluctuations in the applied indicator potential had the least effect on the indicator current when a potential of 200 m.v. was used. The current which flowed between them was determined by the concentration of the reversible couples present. This current will hereafter be referred to as the indicator current.

All titrations were made in 40x80 mm. weighing

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bottles, and at a solution volume of 45 ml.

After use, the electrodes were shorted together and stored in a solution of 10 ml. of the 0.2 formal CuSO4 in 12 formal HCl and 35 ml. water. It was found that storing the electrodes in 6n  $H_2SO_4$  an anomalously greater sensitivity developed for the first two or three titrations and, consequently, these titrations were of no value. After two or three titrations the sensitivity became and remained constant. The use of the copper sulfate-hydrochloric acid solution eliminated this trouble.

The generating circuit was calibrated by measuring the potential drop across a standardized 199.8 ohm coil from a Leeds and Northrup No. 4716 resistance with a student potentiometer. Since the absolute accuracy of the current setting was dependent on the accuracy of the standard cell used, this cell was occasionally checked against a Weston Standard Cell which had been calibrated by the United States Bureau of Standards. During the course of titrations the standard cell used did not change by more than 0.2 m.v. The 90 volt power supply was obtained from the laboratory switchboard instead of by use of two 45 volt "B" batteries. This was done to give better constant current characteristics to the circuit. With the batteries, a linear decay of the current

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was noticed of about 0.1 percent per 4 minutes, necessitating frequent changes in the current setting dial. By the use of the laboratory power supply, the current decay was reduced to about 0.1 percent per 20 minutes.

The instrument was built so as to provide three rates of generation, approximately 1 milliamp. 4 milliamps and 10 milliamps. corresponding to about  $10^{-8}$ equivalents/second.  $4x10^{-8}$  equivalents/second. and  $10^{-7}$ equivalents/second. It was found that even for the smallest quantities titrated better results could be obtained by using the high rate rather than either of the other generation rates. The reason for this was the lack of reproducibility of the blanks from which the end-point corrections were made. The blanks were reproducible to about 10 percent of the indicator current reading (i.e. ±1 microamp at 20 microamps). Ordinarily, readings of indicator current were not taken at less than 10 microamps. since at values less than this much larger percentage deviations occur. The sensitivity of the indicating system was about 1 microamp/10<sup>-8</sup> equivalent for the cuprous-cupric couple. For a titration that required 20 seconds on the high rate, and for which the indicating current was read at 10 microamps, the end-point correction would be 1 second with an uncertainty of 10 percent or 0.1 second. For the titration this would

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amount to an uncertainty of 0.5 percent. The same titration on the low rate would require about 200 seconds, and, again, if the indicating current was read at 10 microamps, the end-point correction would be 10 seconds with an uncertainty of 1 second. This again would correspond to .5 percent for the titration, so that on this basis there would be no reason to use the low rate, even for the smallest samples. Actually, it was found that the high rate, requiring only one-tenth the titration time of the low rate, gave better results. This is illustrated by the following set of data:

#### High Rate:

28.68

Taken (micrograms)	(micrograms)	(micrograms)
28.68 28.68 28.68 28.68 28.68 28.68	28.63 28.55 28.79 28.79 28.94	05 13 +.11 +.11 +.26
Low Rate:		
<u>Taken</u> (micrograms)	(micrograms)	(micrograms)
28.68 28.68 28.68 28.68	28.13 28.07 28.28 28.37	55 61 40 31

28.03

-.65

For this reason, the high rate was used in every titration.

Preliminary experiments indicated that the concentration of hydrochloric acid in the cell would have to be closely controlled. At low concentrations, copper plated out on the generator cathode. At high concentrations, the oxidation of chloride ion by the chromate or vanadate took place at an appreciable rate. The resulting loss of chlorine from the cell caused low results. Table I shows the results obtained at different cupric ion and hydrogen ion concentrations in a determination of chromate.

#### <u>Table I</u> Effect of Hydrochloric Acid Concentration

#### Cupric Ion Concentration

	120	.02 <u>formal</u>	.04 formal	.16 formal
	0.0f	Plating		
cion	.3f	Plating, unstable indicator current	x	Plating
entrat	.6f	Plating	Plating	No plating, good results
Acid Conce	l.3f	No plating, stable indicator current, good results	No plating, good results	
Hydrochloric	2.6f	No plating, low results, indicator current increased during titration	No plating, low results, indicator current increased during titration	
	4.3f		No plating, indicator current increased	×
	9.6f		No plating, Very low sensitivity	

As can be seen from Table I, at (Cu++) = .02 formal, the hydrochloric acid concentration must be maintained greater than 0.6 formal and less than 2.4 formal. The oxidation of chloride ion to chlorine was indicated by the rise in indicator current during a titration, before the end-point was reached. It can be shown to be chlorine and not cuprous ion that is causing the indicator current increase by switching the polarity of the indicating system. Since the indicating current is limited by the diffusion of either chlorine to the cathode or cuprous ion to the anode, and the diffusion current is proportional to the area of the electrode, then an increase in the indicating current should be noticed when the larger electrode is made the cathode if the indicating current is caused by the chlorine-chloride couple. This was the effect observed. If the indicator current was due to the cuprous-cupric couple; the indicating current would have decreased upon making the cathode the larger electrode. Figure 3 shows typical titration curves for chromate determinations at two hydrochloric acid concentrations, one at 1.3 formal and one at 5.3 formal.

Similar results were obtained when determining vanadate, except that at a cupric ion concentration of 0.02 formal and a hydrochloric acid concentration of

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1.3 formal, copper plated out on the generator cathode.

For the chromate determinations, the cupric ion concentration was set at 0.02 formal and the hydrochloric acid concentration at 1.3 formal. For the vanadate determinations, the cupric ion concentration was set at 0.02 formal and the hydrochloric at 2.6 formal.

#### Experimental Procedure:

The titration procedure was essentially the same as that described by Myers and Swift<sup>(2)</sup>. Blanks were made by diluting 5 ml. of the 0.2 formal copper sulfate in 12 formal hydrochloric acid solution to 45 ml. and generating for 5 periods of one second each. The reproducibility and linearity of the blanks is indicated by Figure 4 in which data from three measurements have been plotted. Except for the initial indicator current reading, the values so obtained were linear. Experiments were carried out to determine if the presence of either chromic ion or the vanadyl ion. VO", had any effect on the sensitivity of the indicator electrodes. Chromic ion was observed to have no appreciable effect, while the presence of the vanadyl ion tended to lower the sensitivity. Thus the end-point correction for the chromate titrations could be made by interpolation from the values obtained from the graph of indicator currents vs. time for the blanks. Another procedure

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had to be adopted to obtain the end-point corrections for the vanadate titrations. By extrapolation of the graph of the indicator current vs. time of the blanks back to 0.0 generation time, the initial indicator current could be determined. (This could not be directly determined with sufficient accuracy since the indicator current reached an equilibrium value very slowly at currents less than 5 microamps). After the vanadate had been reduced and the indicator current had started to rise, the sensitivity of the indicator system was determined by taking four indicator current readings at intervals of one second generation time. By plotting these values and extrapolating the graph back to the current at zero generation time (obtained from the blanks) the equivalent generation time for the vanadate could be determined. This procedure is illustrated in Figure 5.

The results obtained with chromate are tabulated in Table II. With quantities greater than 150 micrograms, the percentage error is of the order of 0.1 percent and is independent of the amount of chromate being determined. As would be expected from the uncertainty in the end-point corrections, the percentage deviations when determining very small quantities become much larger, over 1 percent when determining 17 micrograms.

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Some difficulty was initially encountered when determining vanadate. The results were about 0.5 percent high. The possibility that oxygen was causing these high results was investigated and this investigation indicated that this was the case. Ramsey<sup>(5)</sup> reports that high results are obtained when oxygen is not excluded in an iodometric determination of vanadate; errors as high as 20 percent result from the vanadate catalysis of the oxidation of iodide by oxygen. The effect observed in the electrolytic reduction of vanadate by cuprous ion is evidently similar; vanadate catalyses the oxidation of the cuprous ion by oxygen.

The experimental procedure used in determining vanadate was to take the desired amount of vanadate solution and water and heat this to boiling under an atmosphere of carbon dioxide. After cooling, the desired amount of copper sulfate and hydrochloric acid was added and the determination made on the instrument, still maintaining an atmosphere of carbon dioxide over the solution. The results tabulated in Table III show that this technique gave results accurate to within 0.15 percent for 700 micrograms of vanadium. There was a possibility that the lower results observed after eliminating oxygen from the solutions by boiling were due to the presence of a reducing agent in the solutions which reacted with

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the vanadate when heated, or to the presence of an oxidizing agent such as chlorine which was driven off by heating. In another set of experiments, the vanadate solution was boiled, then resaturated with air after cooling. These determinations gave practically the same results as those with the original unboiled solutions.

	<u>Taken</u> (micrograms	s) (	Found micrograms)	(micrograms)
I	17.81 17.81 17.81 17.81	average	18.04 17.80 18.04 18.10 17.99	+0.23 -0.01 +0.23 +0.29 +0.18
II	35.79 35.79 35.79 35.79	average	35.74 35.98 35.97 35.88 35.89	-0.05 +0.19 +0.18 +0.09 +0.10
III	178.4 178.4 178.4 178.4	average	178.4 178.5 178.3 178.2 178.4	0.0 +0.1 -0.1 -0.2 0.0
IV	358.3 358.3 358.3 358.3	average	358.1 358.4 358.7 358.8 358.5	-0.2 +0.1 +0.4 +0.5 +0.2
v	716.7 716.7 716.7 716.7	average	717.4 717.4 716.2 716.7 716.9	+0.7 +0.7 -0.5 0.0 +0.2
VI	1784.0 1784.0	average	1786.0 1786.0 1786.0	+2.0 +2.0 +2.0

TABLE II Determination of Chromate

	(micrograms)	(mi	<u>Found</u> crograms)	(micrograms)
I	37.62 37.62 37.62 37.62	average	37.61 37.75 37.44 37.61 37.60	-0.01 +0.13 -0.18 -0.01 -0.02
II	75.56 75.56 75.56 75.56	average	76.17 75.85 76.48 76.11 76.15	+0.61 +0.29 +0.92 +0.55 +0.59
III	755.7 755.7 755.7	average	754.6 756.1 756.9 755.9	-1.1 +0.4 +1.2 +0.2
IV	755.9 755.9 755.9 755.9 755.9	average	755.3 755.8 756.1 755.5 755.7 755.7	-0.6 -0.1 +0.2 -0.4 -0.2 -0.2
V	774.7 774.7 774.7 774.7 774.7 774.7 774.7 774.7 774.7	average	776.9 774.2 773.2 776.9 776.9 776.3 775.8 775.3 775.3 775.7	+2.2 -0.5 -1.5 +2.2 +2.2 +1.5 +1.1 +0.6 +1.0

<u>Table III</u> <u>Results of Vanadate Determinations</u>



Figure 1. Simplified Disgram of Apparatus



Figure 2. Titration Cell



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Figure 5.

Procedure for Determining Equivalent Generation Time for Vanadates

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#### PART II

THE USE OF ELECTROLYTICALLY GENERATED ARGENTIC SILVER AS AN OXIDIZING AGENT

FOR THE DETERMINATION OF MANGANOUS ION, CEROUS ION, AND

ARSENIOUS ACID,

USING AN AMPEROMETRIC END-POINT

In order to extend the use of coulometric methods to substances which have a higher oxidation potential than bromine, Professor Swift suggested that the argentous-argentic couple be investigated. Noyes, DeVault, Coryell and Deahl<sup>(1)</sup> describe an electrolytic apparatus in which silver nitrate dissolved in nitric acid is anodically oxidized to a complex argentic nitrate, called argentic oxynitrate.

They achieved an over-all current efficiency of 60 percent when oxidizing a solution of 63 grams of silver nitrate in 1.5 formal nitric acid at 3.0 amperes at 0°. They reported that the argentic oxynitrate rapidly oxidizes  $Mn^{++}$ ,  $HA_s O_2$ ,  $Fe^{++}$ ,  $Hg_2^{++}$ ,  $Cr^{+++}$ ,  $Vo^{+++}$ , $H_2O_2$ ,  $Pb^{++}$ , so that if argentic nitrate could be produced on the titrometer with 100 percent current efficiency and if it established a reversible couple so that amperometric methods could be used, a powerful analytical method could be developed.

Preliminary experiments indicated that in both nitric and perchloric acids, a reversible couple was established by the argentic-argentous silver, so that amperometric end-points could be used.

The first detailed investigations carried out were those relating to indicator system, to determine which concentration of nitric or perchloric acid gave

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the best sensitivity, reproducibility and stability to the indicator system.

In each experiment the silver ion concentration was maintained at 0.40 formal, silver nitrate was used for those experiments involving nitric acid and silver perchlorate for those involving perchloric acid.

All chemicals used were of C. P. or reagent grade.

Experiments by Noyes, Hoard and Pitzer<sup>(2)</sup> indicated that the rate of reduction of argentic silver by water varies inversely as the concentration of nitric acid, so that it was to be expected that the indicator current would become more stable as the concentration of nitric acid was increased. Actually, the inverse was found. As the nitric acid concentration was increased, the stability decreased.

The results are tabulated in Table I. The relative stability is indicated by the magnitude of the decrease of the indicator current per unit time,  $-d(\underline{i.c.})$ . The rate of decomposition of the argentic silver was not constant for solutions of the same composition, varying as much as 50 percent from one sample to another. The values tabulated in Table I are averages from many experiments.

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Stability of Indicator	Current in Nitric Acid	Solutions
(HN0 <sub>3</sub> )	- <u>d (i. c.</u> )	
(formal)	dt (microamps/second)	
1.3	9	
2.6	10	
3.9	15	
5.2	21	
7.0	22	
8.8	27	
10.6	34	

Table T

The experiments were carried out at 22°+ 1° C.

Similar results were obtained using perchloric acid. The results are tabulated in Table II.

Table II Stability of Indicator Current in Perchloric Acid Solutions

$(\text{HCLO}_4)$	$-\frac{d(i.c.)}{dt}$	
(formal)	(microamps/minute)	
1.0	12	
2.0	20	
4.0	19	
6.0	32	

Experiments indicate that the mechanism of the decomposition of argentic silver in these solutions is not that reported by Noyes, Hoard and Pitzer(2), who found that the decomposition of argentic silver by

water followed the rate expression

with the second order term predominating at low concentrations of argentic ion. If it is assumed that the indicator current is proportional to the concentration of argentic silver, and that the second order term predominates at the low concentrations used, then an approximation of the second order rate constant can be made from the decomposition rates given in Tables I and II. Thus at a concentration  $HNO_3$  equal to 3.9 formal,  $k_2$  is approximately  $5 \times 10^5$ /minute. Noyes, Hoard and Pitzer<sup>(2)</sup> report that at 25° and at a nitric acid concentration of 3.36 formal,  $k_2 = 149 \times 10^{-3}$ /minute.

Argentic ion was generated until the indicator current was about 50 microamps. The generating current was stopped and readings of the indicator current were taken every 5 seconds as the argentic silver decomposed. The logarithm of the indicator current readings vs. time is plotted in Figure 1. As can be seen, the curve is linear. If the indicator current is proportional to the argentic silver concentration, then this curve would indicate that the decomposition reaction is first order with respect to the argentic concentration. The mechanism of the decomposition reaction is not clearly understood, but probably involves the platinum

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electrodes in the cell. As mentioned previously the rate of decomposition of the argentic silver varies a great deal in samples of the same composition. This can probably be attributed to the condition of the surface of the platinum.

The sensitivity of the indicating system varied inversely as the concentration of the acid used. Values for the sensitivity of the indicating system for different acid concentrations are tabulated in Table III.

> <u>Table III</u> Sensitivity of the Indicator System

A. Nitric Acid

Concentration (formal)	<u>Sensitivity</u> (microamps/10-7	equiv.)
1.3 2.6 3.9 5.2 7.0 8.8	6.5 6.0 5.2 4.0 3.2 2.5	
10.6	2.5	

B. Perchloric Acid

<u>Concentration</u> (formal)	Sensitivity (microamps/10-7	equiv.)
1.0 2.0 4.0 6.0	4.0 3.0 2.5 1.6	

The larger indicator electrode was made the cathode since it was found that the indicator sensitivity was greater with that arrangement. This would indicate that the argentic silver exists in solution as a cation.

At best, the reproducibility of the blanks was poor. The nitric acid solutions of 2.6 formal gave the best reproducibility, but, whereas the blanks of the cupriccuprous system were reproducible to 10 percent of the indicator current reading, causing an uncertainty of one or two-tenths of a second in the blank correction, the blanks of the argentic-argentous system showed deviations such that an uncertainty of two or three seconds would result in the end-point correction. Thus, for a titration requiring one hundred seconds the accuracy to be expected would not be greater than 2 percent. The sensitivity of the blanks at a given acid concentration was approximately constant, but between four and seven seconds of generation on the high rate would be required before an indicating current was obtained. The cause of this delay is unknown. It was not due to impurities in the reagents which were oxidized upon generation of argentic silver, since the concentration of the reagents was varied widely and little variation in the delay time was noticed. In one experiment,  $50 \times 10^{-7}$  equivalents of argentic silver were produced (50 seconds at high rate) and the solution was allowed to stand overnight so as to decompose the argentic silver. This solution was then electrolyzed on the instrument and it

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showed a four second delay period. It is the variation in this delay period that produces the large deviations in the blanks. After the initial delay period, the indicating current was a linear function of time.

From the standpoint of sensitivity, stability and reproducibility of the indicator current, nitric acid at 2.6 formal was chosen as the acid medium for the determinations.

#### Experimental:

A standard manganous perchloric solution was prepared by reducing a standard potassium permanganate solution with hydrogen peroxide and perchloric acid. The solution was boiled to eliminate the excess hydrogen peroxide.

The desired amount of this standard manganous solution was added to a titration cell containing 20 ml. of 6 formal HNO<sub>3</sub> and 5 ml. of 4.0 formal AgNO<sub>3</sub> and water was added to bring the total volume to 45 ml. This was electrolyzed at the high rate. The equivalent generation time for oxidation of the manganous ion to permanganate should have been about 200 seconds. After approximately twenty-five seconds of generation, the solution turned brown and the indicator current went off scale, indicating that the rate of oxidation of manganous ion by argentic silver was too slow to make the method practical. When generation was stopped, the brown color of the argentic silver rapidly disappeared and the purple permanganate color appeared.

The next experiments were with cerous perchlorate. Similar results to those described for manganous perchlorate were obtained. The rate of oxidation was too slow to make this determination practical.

Arsenious acid was tried next. Again it was found that the rate of oxidation was too slow to make the determination practical.

In order to determine if the rate of oxidation might be greater in less concentrated nitric acid or in perchloric acid solutions, experiments were tried with solutions 1.3 formal in nitric acid and with solutions 1.0 formal in perchloric acid. The same negative results were obtained.

It is surprising that the rate of oxidation by argentic silver in these experiments was too slow to make the determinations practical, since argentous silver is often added as a catalyst when using persulfates as oxidizing agents; the catalytic effect arising from the oxidation of the argentous silver to argentic silver by persulfate and the subsequent oxidation of the reducing agent by the argentic silver. Also, as noted before, Noyes, DeVault, Coryell and Deahl<sup>(1)</sup> reported that argentic

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silver is an unusually kinetically reactive agent, almost immediately oxidizing manganous ion to permanganate, cerous to ceric ion, chromic ion to chromate, etc. Because of the observed slow rate of oxidation and because of the difficulty in obtaining reproducible blanks, the investigation of the use of argentic silver in coulometric analyses was discontinued.



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#### PART III

## THE DETERMINATION OF BROMINE NUMBERS OF OLEFINS WITH ELECTROLYTICALLY GENERATED BROMINE, USING AN AMPEROMETRIC END-POINT

.

#### Introduction:

Sease, Niemann and Swift<sup>(1)</sup> have described a coulometric method by which thiodiglycol, dissolved in 50 percent acetic acid, is oxidized by electrolytically generated bromine. The end-point is determined amperometrically. If the reaction rate involved in the addition of bromine to an olefin is sufficiently rapid, then it should be possible to extend this procedure to the determination of Bromine Numbers (a Bromine Number being defined as the number of grams of bromine adding to 100 grams of the olefin). This procedure would then offer a convenient and rapid means of determining Bromine Numbers for samples of less than one milligram.

#### Chemicals:

The olefin chosen for the experiments was cyclohexene, since it was readily available and was known to rapidly add bromine. Eastman White Label cyclohexene, which was further purified by distilling over sodium, was used.

#### Experimental:

The Bromine Number of the cyclohexene was first determined by volumetrically titrating a weighed sample of cyclohexene which was dissolved in glacial acetic acid containing sodium bromide, with a standard solution of potassium bromate until excess bromine could be detected in the solution. After one minute of shaking, excess potassium iodide was added and the solution titrated with a standard sodium thiosulfate solution to a starch end-point. This procedure for determining Bromine Numbers is described by Johnson and Clark(2).

The electrolytic determinations were carried out on the instrument described in PART I of this thesis. For these determinations, a weighed sample of cyclohexene was dissolved in glacial acetic acid and this solution was diluted to volume. The solutions contained approximately  $5x10^{-4}$  grams of cyclohexene/ml. acetic acid. One milliliter of this solution was pipeted into a titration cell containing 45ml. of 50 percent acetic acid which was approximately 0.3 formal in sodium bromide. Bromine was then produced at the high rate  $(10^{-7}$  equivalents/sec.). The large indicator electrode was the cathode.

The indicator current did not go above 1 microamp until the end-point was reached; after the end-point the indicator current rose rapidly. The indicator current was stable after the end-point was reached. These facts indicated that the rate of addition of bromine to cyclohexene in 50 percent acetic acid was very rapid and was complete at the end-point. The results tabulated in Table I indicate that the electrolytic procedure will give results within about 2 - 3 percent of those which were obtained by use of the bromide-bromate procedure.

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The electrolytic values are lower in every case.

Since the sensitivity of the indicator system was about 6 microamps/10<sup>-7</sup> equivalents  $Br_2$  when a 50 percent acetic acid solution of NaBr was used, and was about 11 microamps/10<sup>-7</sup> equivalents  $Br_2$  when an aqueous solution of NaBr was used, it seemed that greater accuracy could be attained in the end-point corrections if the electrolysis could be carried out in an aqueous medium. However, experiments indicated that the rate of addition of bromine to cyclohexene was too slow in an aqueous medium, large indicator currents were obtained before the end-points were reached, and the indicator current after the end-point was not stable.

The electrolytic determination of bromine numbers will work very well for those compounds which add bromine very rapidly, but there are many in which the rate of addition of bromine is not rapid. Those compounds must be allowed to react with an excess of bromine for period of time, after which the excess is determined. This procedure cannot be used directly on the instrument since the excess bromine cannot be determined if the indicator current is off scale. The excess bromine cannot be cathodically reduced since in the low concentrations of bromine present the diffusion of bromine to the cathode is too slow and hydrogen will be the reduction product.

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This difficulty could be resolved if another ion present in the solution could be cathodically reduced and which would then reduce the excess bromine in the solution. In this manner, the indicator current could be brought to an "on scale" value and the remaining bromine determined from the reading of the indicator current. This is similar to the procedure used to determine chromates and vanadates using electrolytically generated cuprous ion, described in PART I of this thesis.

An experiment was tried in which bromine was electrolytically produced in a titration cell containing 45 ml. of a solution 0.4 formal in sodium bromide, 0.02 formal in cupric sulfate, and 0.6 formal in sulfuric acid. The indicator current due to the Br2-Br couple was off scale. Then the generator electrode was switched to cathode and the solution reduced. The reduction appeared to take place smoothly and the indicator current soon returned to an "on scale" reading. The experiment was repeated using a solution 0.2 formal in sodium bromide, 0.02 formal in cupric sulfate, and 0.6 formal in sulfuric acid. When this solution was reduced, cuprous bromide precipitated on the generator electrode. This indicated that the bromide ion concentration would have to be sufficiently high so that cuprous bromide would not precipitate from the solution, but would exist as the ion Cu Br2.

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Latimer<sup>(3)</sup> gives for the equilibrium constants of the reactions  $C \cup B_{R} = C \cup^{+} + B_{R}^{-}$   $K = 5.3 \times 10^{-9}$  $C \cup B_{R_{2}}^{-} = C \cup^{+} + \mathcal{E} B_{R}^{-}$   $K = 1.\mathcal{E} \times 10^{-6}$ 

Thus it is seen that in 0.2 formal sodium bromide Cu Br should not precipitate from the solution until the concentration of Cu Br<sub>2</sub><sup>-</sup> is approximately  $10^{-4}$  molal. The fact that precipitation was observed when the concentration of Cu Br<sub>2</sub><sup>-</sup> was approximately  $10^{-6}$  molal can probably be explained by the large local concentration of cuprous copper near the generator electrode when the system was cathodically reduced. Experiments indicated that 0.40 formal sodium bromide was a suitable value to prevent this precipitation.

Since both bromine and Cu  $Br_2^-$  give rise to indicator currents (due to the couples  $Br_2^- Br^-$  and Cu  $Br_2^- - C^{--}$ ), the indicator current had a minimum value, corresponding nearly to the equivalence point of the reaction

### $\mathcal{L}C_{U}B_{n_{2}}^{-} + B_{n_{2}} = \mathcal{L}C_{U}^{+} + 6 B_{n_{1}}^{-}$

Starting from the equivalence point, if the solution was cathodically reduced, Cu  $Br_2^-$  would be produced and the indicator current would rise. If the solution at the equivalence point was anodically oxidized,  $Br_2$  would be produced and again the current would rise. The phenomenon of a minimum indicator current in a system containing two ions which are present in reversible equilibrium and

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both of which produce indicator currents will be discussed more completely in PART IV of this thesis.

The presence of a minimum indicator current gave a convenient method of determining the equivalent generation times, since if the bromine was produced for a period of time T beginning from the minimum point, and after allowing the bromine to react for the desired period of time, the excess was reduced by generating Cu  $Br_2^{-}$ for time T'until the indicator current was again at the minimum value, the equivalent generation time would be T -T', and the necessity of using blank corrections would be eliminated.

When experiments were tried using this method for the determination of Bromine Numbers of cyclohexene, uniformly low results were obtained. By the bromide-bromate procedure carried out in glacial acetic acid, the Bromine Number of the sample of purified cyclohexene used was 181-182. By the electrolytic procedure described previously, using 50 percent acetic acid as the titration medium, the Bromine Number was 173-175. Using the solution containing sodium bromide, copper sulfate and sulfuric acid, and carrying out the procedure described above for determining the equivalent generation time, the Bromine Number was 136-145. When a 0.2 formal solution of sodium bromide in 0.6 formal sulfuric acid was used as the titration

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medium, instead of 50 percent acetic acid, the Bromine Numbers that were obtained were also very low. In order to determine if the cause of the low results was due to the medium in which the determinations were made, determinations of the Bromine Number of cyclohexene were carried out in an aqueous sodium bromide solution which was 0.6 formal in sulfuric acid using the bromidebromate procedure. The Bromine Numbers obtained were only about 70 percent as great as those using glacial acetic acid as the titration medium. The reason for the low results obtained when using an aqueous medium is probably due to the hydrolysis of the cyclohexene to cyclohexanol.

For those olefins which hydrolyze in water and which slowly add bromine, the electrolytic procedure cannot be used to determine the Bromine Number accurately since the electrolytic determination for slowly reacting olefins must be carried out in an aqueous medium. Bromine Numbers of olefins which do not hydrolyze can be determined electrolytically either by the procedure described using 50 percent acetic acid as the titration medium or by the use of a solution of sodium bromide, cupric sulfate and sulfuric acid as the titration medium. The medium to be used will depend upon the rate of addition of bromine to the olefin. If the rate of addition is very rapid, the 50 percent acetic acid medium can be used. If the

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rate of addition is not rapid, the cupric sulfatesodium bromide-dilute sulfuric acid medium must be used.

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8 5	netric	Bromine Number	167 168	164 167 168
umetric Bromine Number	Volur	Sample Size (milligrams)	a. 44.27 b. 44.27	a. 53.15 b. 53.15 c. 53.15
lectrolytic and Volu		Bromine Number	164 162 162	161 163 163 160 160
Comparison of <b>F</b>	Electrolytic	Generation Time (seconds)	87.1 85.8 86.1	102.5 103.5 103.6 101.5 101.6
		Sample Size (milligrams)	a. 0.4427 b. 0.4427 c. 0.4427	a. 0.5315 b. 0.5315 c. 0.5315 d. 0.5315 e. 0.5315 f. 0.5315
			н	Η

NT.17 f . -Table I 0 **•** +•• L 4 ŗ

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#### PART IV

AN AMPEROMETRIC METHOD FOR DETERMINING THE FORMAL POTENTIAL OF THE REACTION 2Cu<sup>++</sup>+ 7Br<sup>-</sup> = 2CuBr<sub>2</sub><sup>-</sup> + Br<sub>3</sub><sup>-</sup>

#### Introduction:

In the course of investigations with the cupric sulfate-sodium bromide system mentioned in PART III of this paper, it was noticed that a large initial indicator current was obtained from a solution containing cupric sulfate and sodium bromide. When the solution was electrolytically reduced, the indicator current at first decreased to a minimum value and then began to rise. When the generating system was changed to oxidation. the indicator current retraced its path, going through the same minimum value. The magnitude of the minimum indicator current was observed to be a function of the bromide ion concentration and of the cupric ion concentration. These observations indicated that the phenomenon was caused by an equilibrium between Cu Broand Brz-, since these are the ions responsible for the indicator current.

A mathematical analysis of the phenomenon was attempted, which led to a method by which the equilibrium constant for the reaction

### 2 Cut + 7 Br -> 2 Cu Br + Br3

could be calculated, using the observed minimum indicator current and indicator electrode sensitivities.

The indicator current was observed to be a linear function of the Cu  $Br_2^-$  and of the tri-bromide ion

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concentrations. Thus the indicator current should correspond to an expression

(1) 
$$\lambda = k, [C_{\nu} B_{n_2}] + k_{e} [B_{n_2}] + k_{3} [B_{n_3}]$$

where i represents the indicator current and  $k_1$ ,  $k_2$ ,  $k_3$  are constants. Both  $Br_2$  and  $Br_3^-$  are included since the bromine in solution existed in both forms at the concentrations of sodium bromide used. Latimer<sup>(1)</sup> gives for the reaction  $Br_2 + Br^- = Br_3^-$  K= 17. Both  $Br_2$  and  $Br_3^-$  will give indicator currents. Since

 $\begin{bmatrix} B_{R_2} \end{bmatrix} = \begin{bmatrix} B_{R_3} \end{bmatrix}, \begin{bmatrix} B_{R_2} \end{bmatrix}, \begin{bmatrix} B_{R_2} \end{bmatrix}$ can be eliminated from equation (1), giving
(2)  $\mathcal{L} = k \begin{bmatrix} C_{\nu} B_{R_2} \end{bmatrix} + \begin{pmatrix} k_2 + 17 k_3 \begin{bmatrix} B_{r-1} \end{bmatrix} \begin{bmatrix} B_{r-3} \end{bmatrix}$ The expression  $\begin{pmatrix} k_2 + 17 k_3 \begin{bmatrix} B_{r-1} \end{bmatrix}$  can be equated  $\begin{bmatrix} T_{r-1} B_{r-1} \end{bmatrix}$ 

to a new constant  $k_4$ , so equation (2) can be reduced to (3)  $\mathcal{L} = \mathcal{k} \cdot \left[ C \cup \beta n_2^{-1} \right] + \mathcal{k}_{\mathcal{H}} \cdot \left[ \beta n_3^{-1} \right]$ 

The equilibrium between  $Br_3^-$  and Cu  $Br_2^-$  can be expressed by the equation:

$$\mathcal{L}$$
  $\mathcal{L}_{1}$   $\mathcal{L}_{2}$  +  $\mathcal{L}_{13}$  =  $\mathcal{L}$   $\mathcal{L}_{1}$  + 7  $\mathcal{L}_{1}$  -

or by the expression:

$$\frac{\left[C_{u}^{\#}\right]^{2}\left[B_{n}\right]^{7}}{\left[C_{u}^{B_{n}}B_{n}\right]^{2}\left[B_{n}\right]^{3}} = K,$$

The cupric ion and bromide ion concentrations are essentially constant (the concentrations of Cu Br2and  $Br_3^-$  formed are of the order of  $10^{-6}$  formal, in solutions 0.02 formal in cupric ion and 0.4 formal in bromide ion), so the equilibrium constant can be simplified to

[Cu Bre-7" [Bra-7 = Ka (4)Solving equation (4) for the tri bromide ion concentration and substituting this value in equation (3) gives the indicator current as a function of the Cu Br2concentration.

 $\mathcal{L} = k_1 \left[ G_{u} B_{n_e}^{-} \right] + \frac{k_4 K_e}{\left[ G_{u} B_{n_e}^{-} \right]^e}$ (5)Differentiation of this expression with respect to time. and equating the differential to zero allows the concentration of Cu Br2 existing at the minimum indicator current to be expressed as a function of  ${\tt k_1}$  ,  ${\tt k_4}$  and  ${\tt K_2}$  .

$$\frac{di}{dt} = \left( \int_{\mathcal{R}_{1}}^{\mathcal{R}_{2}} - \frac{\partial}{\partial t} \int_{\mathcal{R}_{2}}^{\mathcal{R}_{2}} \int_{\mathcal{R}_{2}}^{\mathcal{R}_{2}} \int_{\mathcal{R}_{2}}^{\mathcal{R}_{2}} \int_{\mathcal{R}_{2}}^{\mathcal{R}_{2}} \frac{d}{dt} \left[ \int_{\mathcal{R}_{1}}^{\mathcal{R}_{2}} \int_{\mathcal{R}_{2}}^{\mathcal{R}_{2}} \int_{\mathcal{R}_{2}}^{\mathcal{R}_{2}} \int_{\mathcal{R}_{2}}^{\mathcal{R}_{2}} \frac{d}{dt} \left[ \int_{\mathcal{R}_{2}}^{\mathcal{R}_{2}} \int_{\mathcal{R}_{2}}^{\mathcal{R}_{2}} \int_{\mathcal{R}_{2}}^{\mathcal{R}_{2}} \int_{\mathcal{R}_{2}}^{\mathcal{R}_{2}} \frac{d}{dt} \left[ \int_{\mathcal{R}_{2}}^{\mathcal{R}_{2}} \int_{\mathcal{R}_{2}}^{\mathcal{R}_{2}} \int_{\mathcal{R}_{2}}^{\mathcal{R}_{2}} \int_{\mathcal{R}_{2}}^{\mathcal{R}_{2}} \int_{\mathcal{R}_{2}}^{\mathcal{R}_{2}} \frac{d}{dt} \left[ \int_{\mathcal{R}_{2}}^{\mathcal{R}_{2}} \int$$

$$\frac{\left[\operatorname{Gu}_{B_{12}}^{2}-\operatorname{J}^{3}\boldsymbol{k}_{1}^{2}-\boldsymbol{k}\cdot\boldsymbol{k}_{4}^{2}\boldsymbol{k}_{2}^{2}\right]}{\left[\operatorname{Gu}_{B_{12}}^{2}-\operatorname{J}^{3}\right]^{3}}=0$$

 $[(\mathcal{L}_{\mathcal{R}}, \mathcal{L}_{\mathcal{L}})] = \left( \begin{array}{c} \mathcal{L}_{\mathcal{L}} & \mathcal{L}_{\mathcal{L}} \\ \mathcal{L}_{\mathcal{L}} \end{array} \right)^{\frac{1}{3}} K_{\mathcal{L}}^{\frac{1}{3}}$  at minimum indicator current.

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Substitution of this value for the Cu  $Br_2^-$  concentration into equation (5) gives an expression for the minimum current (i min.).

$$l_{mun.} = R_{i} \left(\frac{2}{R_{i}}\right)^{\frac{1}{3}} K_{2}^{\frac{1}{3}} + \frac{k_{y}}{\left(\frac{2}{R_{i}}\right)^{\frac{2}{3}}} K_{2}^{\frac{2}{3}}$$

which can be reduced to  $lmin_{,} = \frac{3 k_{H}}{R^{3/3}} \frac{k_{R}}{K_{R}}^{3/3}$ 

Solving for 
$$K_2$$
  
(6)  $K_2 = \frac{4 (l_{min})^3}{27 k_1^2 k_4}$ 

The constants  $k_1$  and  $k_4$  can be evaluated by observing the change in indicator current per unit time when the concentration of one of the indicating ions is very small. Since  $\mathcal{A} = k_1 \left[ (\mathcal{U}_{k} \mathcal{B}_{r_{2}}^{-}) + k_4 \left[ \mathcal{B}_{r_{3}}^{-} \right] \right]$ 

$$k_{1} = \frac{di}{dt} \qquad [G_{1} B_{n_{2}}] \qquad [G_{1} B_{n_{2}}] >> [B_{n_{3}}]$$

and

 $k_{H} = \frac{di}{dt} [B_{n_{3}}] >> [C_{U} B_{n_{2}}]$ 

 $\begin{array}{l} \frac{di}{dt} & \text{is directly observable,} & \frac{d}{dt} \begin{bmatrix} \mathcal{L}_{u} & \mathcal{B}_{x_{g}}^{-} \end{bmatrix} & \text{and} \\ & \frac{d}{dt} \begin{bmatrix} \mathcal{B}_{x_{g}}^{-} \end{bmatrix} & \text{are given by the generation rates.} & \left( K_{g} \right) \end{array}$ 

Figure 1 shows the general nature of the indicator current in the vicinity of the minimum point. The experimental procedure used was to take the desired quantities of cupric sulfate, sodium bromide and sulfuric acid and dilute to 45.0 ml. Excess Cu Br2" was generated in the solution and then the generating system was reversed and Br3 was generated for intervals of two seconds each at a rate of  $1.03 \times 10^{-8}$  equivalents/second. The large indicator electrode was the cathode. The indicator current was read after each interval of generation and these values were plotted as a function of time. The change of indicator current vs. time  $\frac{du}{dt}$  was determined from the slope of the indicator current of each branch of the curve, which enabled  $k_1$  and  $k_4$  to be calculated as indicated above.

The equilbrium constant  $[G_{k}, B_{\lambda_{2}}^{-}]^{2} [B_{\lambda_{3}}^{-}] = K_{2}$ could then be calculated from equation (6) using the experimentally determined values of  $k_{1}$ ,  $k_{4}$  and i(min). If the value of  $K_{2}$  is divided by the square of the cupric ion concentration and the seventh power of the bromide ion concentration, the equilibrium constant for the reaction

 $\mathcal{E}$  Gu # + 7 Br<sup>-</sup> =  $\mathcal{E}$  Gu Br<sup>-</sup><sub>2</sub> + Br<sup>-</sup><sub>3</sub>

can be calculated

$$\frac{\left[\begin{array}{ccc} \Omega_{R_{2}} \end{array}\right]^{2} \left[\begin{array}{ccc} B_{R_{3}} \end{array}\right]^{7}}{\left[\begin{array}{ccc} \Omega_{u} \end{array}\right]^{2} \left[\begin{array}{ccc} B_{R_{3}} \end{array}\right]^{7}} = K$$

(7) 
$$K = \frac{K_{R}}{[G_{L}*]^{2}} [B_{T}^{-}]^{7}$$

By using the Nernst equation,  $E^{\circ} = \cdot \frac{059}{n} \log K$ , the formal potential of the reaction can be calculated. The formal potential of the reaction Cu  $Br_2^{-} = Cu^{++} + 2Br^{-} + e^{-}$ can be calculated approximately by subtraction of the formal potential of the reaction

 $\mathcal{R} C_{U}^{+} + 7 B_{\Lambda}^{-} = \mathcal{R} C_{U} B_{\Lambda_{2}}^{-} + B_{\Lambda_{3}}^{-}$ which was determined above, from the molal potential of  $3B_{\Lambda}^{-} = B_{\Lambda_{3}}^{-} + \mathcal{R}\mathcal{R}^{-}$ . This is given by Latimer(1) as E°= -1.051 v.

In Table I, the experimentally determined values of  $k_1$ ,  $k_4$  and  $i_{min}$  for experiments carried out at various cupric ion and bromide ion concentrations are tabulated, along with the values for  $K_2$  and K, calculated from equations (6) and (7). The potentials calculated with the Nernst equation and the half-cell potential of

 $C_{U} B_{n_{p}} = C_{U}^{\#} + e B_{n}^{+} + e^{-}$  are also tabulated.

Latimer(1) gives for the molal half-cell potential of the reaction  $\mathcal{R} Bn^- + C_U \rightarrow C_U Bn_e^- + e^- E^\circ = -0.05$ and for  $C_U \rightarrow C_U^+ + \mathcal{R}e^- = E^\circ = -0.3448$  Combining the two expressions, one obtains for the half-cell potential

 $C_U B_{h_2}^{-} = C_U^{+} + \mathcal{E} B_h^{-} + \mathcal{L}^{-} \quad \mathcal{E}^{\circ} = -.640$ The average formal half-cell potential calculated from amperometric date in this investigation is  $E^{\circ} = -.666$ , which is in fair agreement with the molal potential and which would agree even more closely if the activities of the ions were used instead of the concentrations.

It is of interest to note that the minimum indicator current in a solution containing cupric ion and bromide ion does not occur at the equivalence point, (i.e. when  $[B_{n_3}] = \frac{1}{2} [c_0 B_{n_2}]$ ). From equation (4), the concentration of Cu Br<sub>2</sub> at the equivalence point equals  $2^{\frac{N_3}{3}} \frac{N_2}{k_2}$  and the concentration of Br<sub>3</sub> equals  $\frac{N_2}{k_2}^{\frac{N_3}{3}}$ Substitution of these concentrations into equation (3) gives the indicator current at the equivalence point

(8) 
$$\mathcal{L}_{(2,p_{*})} = \frac{K_{R}^{3}}{R^{2/3}} \left[ R \cdot k_{1} + k_{2} \right]$$

The minimum indicator current has previously been determined to be imin. =  $3 \frac{K_2}{k_1} \frac{k_3}{k_1} \frac{k_3}{k_1} \frac{k_3}{k_2}$ 

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The minimum indicator current would correspond to the equivalence point only in a system in which the electron change of each half-cell involved in the equilibrium was equal, and when the areas of the indicating electrode were equal.

The shape of the indicator current curve in the vicinity of the minimum point can be predicted theoretically in the following manner. At the equivalence point  $\left[ Bn_3^{-1} \right] = \frac{1}{2} \left[ C_u Bn_2^{-1} \right]$ If the system is then cathodically reduced, the concentration of Cu Br<sub>2</sub><sup>-</sup> can be expressed as

## (9) $\left[ \operatorname{Gu} \operatorname{Br}_{2}^{-} \right] = K_{6} t + \mathcal{E} \left[ \operatorname{Br}_{3}^{-} \right]$

where  $K_{g_1}$  represents the generation rate and t represents the time of generation (t= 0 at the equivalence point). From equation (4)  $\begin{bmatrix} B_{\Lambda_3} \end{bmatrix} = \begin{bmatrix} K_2 \\ C_{u} & B_{\Lambda_3} \end{bmatrix} = \int_{a}^{K_2} \int_{a}^{a} f_{\lambda_3} \int_{a}^{a} f_{\lambda_3$ 

## (10) [ $\ln B_{n_2}^{-7}$ ] - $K_{G_1} t [ \ln B_{n_2}^{-7}]^2 - 2K_2 = 0$

This can be solved for (Cu  $Br_2$ -) for values of time t as soon as  $K_2$  has been determined from equation (6). Knowing the concentration of Cu  $Br_2$ -, one can determine the concentration of  $Br_3$ -. The substitution of these values into equation (3) will give the indicator current for that particular value of time used in solving for the concentration of Cu  $Br_2$ - in equation (9). The comparison of the calculated indicator current and the experimental value for that value of time depends upon determining the location of the equivalence point (i.e. t: 0) on the experimental curve. The indicator current at the equivalence point can be determined from equation (8). This indicator current then determines the position of t: 0 and allows a comparison to be made of the actual and theoretical indicator current for the generation of Cu Br<sub>2</sub><sup>-</sup>. For the generation of Br<sub>3</sub><sup>-</sup>, similar assumptions to those discussed above can also be made. At the equivalence point, t: 0, and  $[Br_3^-] = \frac{1}{g} [Cu Br_3^-]$ Upon anodic oxidation

## (11) $[B_{13}-] = K_{6_2} t + \frac{1}{p} [C_u B_{1p}-]$ Solving equation (4) for the concentration of Cu Br<sub>2</sub>and substitution of this value into equation (11), one

obtains a cubic equation in the concentration of  $Br_3^$ as a function of  $K_2$ ,  $K_{g2}$  and t, which can be solved for values of time t after the appropriate constants have been determined.

(12)  $\left[ Br_{3}^{-} \right]^{3} - \mathcal{R} K_{e_{2}} t \left[ Br_{3}^{-} \right]^{2} + K_{e_{2}}^{2} t^{2} \left[ Br_{3}^{-} \right] - \frac{K_{2}}{4} = 0$ 

In Figure 2, the theoretical indicator currents, calculated as indicated above, are plotted together with the experimentally determined indicator current vs. time curve. The solution was 0.0177 formal in Cu<sup>--</sup> and 0.88 formal in Br<sup>-</sup> and 0.7 formal in sulfuric acid. The agreement between the theoretical and experimental values is thought to be very good.

This amperometric method of determining equilibrium constants is directly applicable to few reactions. The conditions that are necessary in order that this method can be used on the instrument in its present condition are: (1) both half-cells involved in the equilibrium must establish reversible couples, (2) the concentration of the ions limiting the indicator current must be approximately  $10^{-6}$  formal. If the couple PtBr<sub>4</sub><sup>--</sup>+PtBr<sub>6</sub><sup>--</sup> is reversible, then it would be possible to determine amperometrically the equilibrium constant for the reaction PtBr<sub>6</sub><sup>--</sup>+Br<sup>--</sup>+PtBr<sub>4</sub><sup>--</sup> + Br<sub>3</sub><sup>-</sup>, since the potential of the half-cell PtBr<sub>4</sub><sup>--</sup>+2Br<sup>--</sup>+PtBr<sub>6</sub><sup>--</sup> te<sup>-</sup> = -0.60, has approximately the correct value to enable the reaction to be used on the instrument.

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	$k_4$	(),10 <sup>-6</sup> f.)	12.3	9.86	11.8	9.20	11.3	6.79	8.47	11.2	10.3	
	Γx	(μΑ/10 <sup>-6</sup> f.)	3.24	4.27	2.75	3.02	4.06	2.82	2.86	2.16	2.98	
T	imin.	(, MA.)	3.60	19.8	6.10	23.7	6.10	27.9	15.8	15.9	19.5	
Table	Br-	(formality)	0.40	0.80	0.40	0.80	0.40	0.80	0.88	0.88	0.88	
	cu++	(formality)	0.0177	0.0177	0.0354	0.0354	0.0531	0.0531	0.0177	0.0177	0.0177	
	Experiment		г	Q	Ю	4	ຸດ	υ	7	ĊĎ	თ	

		TADT		
nent	$\mathrm{K}_{2}$	L K	E° (volts)	E° (volts)
у. Х	= <u>4</u> (1 min) <sup>3</sup> 27 Je, <sup>2</sup> Je4	$K = \frac{\left[C_{u} B_{ne}\right]^{2} \left[B_{na}\right]^{2}}{\left[C_{u} + \right]^{2} \left[B_{n} - \right]^{2}}$	$c_{c} = c_{v} + 7 B_{v} = c_{c} C_{v} B_{v_{c}} + B_{v_{3}}$	lu Bre = Co + 2 Br + e -
	5.35x10-20	10.4x10 <sup>-14</sup>	-0.383	-0.668
	6.39x10-18	9.77x10-14	-0.384	-0.667
	3.77x10-19	18.4x10-14	-0.376	-0.675
	2.35x10 <sup>-17</sup>	9.00x10-14	-0.384	-0.667
	1.81x10-19	3.91x10-14	-0.395	-0.656
	4.98x10 <sup>-17</sup>	8.42x10-14	-0.386	-0.665
	8.45x10-18	6.65x10-14	-O.388	-0.663
r-1	1.5x10-18	9.00×10 <sup>-14</sup>	-0.384	-0.667
Ч	2.0x10 <sup>-18</sup>	9.40×10 <sup>-14</sup>	-0.384	-0.667

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Table I (continued)

Exp





Figure 2. Indicator Current

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