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THE CATHODIC REDUCTION OF BROMATE IONS ON MERCURY
IN NEUTRAL AND BASIC SOLUTIONS

by

JAW-SHIN CHANG, 1944-

A

THESIS

submitted to the faculty of
UNIVERSITY OF MISSOURI-ROLLA

in partial fulfillment of the requirements for the
Degree of

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

Rolla, Missouri

1970

Approved by


(Adviser)





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THE CATHODIC REDUCTION OF BrO_3^- ON Hg
IN NEUTRAL AND BASIC SOLUTIONS

Jaw-Shin Chang

Department of Chemical Engineering
and the
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Rolla, Missouri, U.S.A.

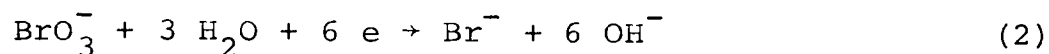
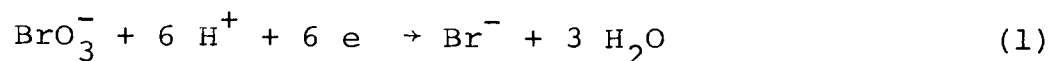
Abstract

The reduction of BrO_3^- was studied in neutral and basic solutions on a stationary Hg surface under activation controlled conditions. Coulombic efficiency studies showed that BrO_3^- was reduced to Br^- with high efficiencies. The polarization measurements lead to a proposed reaction scheme which is consistent with the experimental observations.

Introduction

The reduction of BrO_3^- has been previously studied primarily on a dropping Hg cathode. Factors affecting the diffusion-controlled reaction have been well investigated.¹⁻⁴ The total diffusion current observed

corresponds to one of the following net electrode reactions:



The purpose of this investigation was to study the reduction on a stationary Hg surface under activation-controlled conditions to obtain more information about the electrochemical reaction kinetics. The investigation included studies of the efficiency of BrO_3^- reduction and the polarization behavior.

Experimental

The electrolysis cell had two co-axial compartments separated by a fritted-glass disc. The inner compartment (50 ml capacity) contained a Pd anode and the outer compartment (250 ml capacity) a Hg pool cathode with a surface area of 0.82 cm^2 . All solutions employed analytical grade chemicals and distilled water. Pre-purified nitrogen was bubbled through the electrolyte to provide an inert atmosphere and for stirring.

The studies were made in neutral and basic solutions with BrO_3^- concentrations ranging from 0.05 to 0.2 M and at $25 \pm 0.1^\circ\text{C}$ except as stated. The amount of Br^- produced during the electrolyses was used as the basis of

the efficiency determinations, except for a few experiments which were based on the BrO_3^- consumption.

The polarization behavior was determined potentiostatically except as noted. A normal calomel electrode (NCE) at 25°C was used as the reference electrode. A salt bridge containing the same electrolyte as the electrolysis cell was employed to prevent contamination by the reference electrode. All reported potentials are referred to the standard hydrogen electrode (SHE) at 25°C.

Results

Efficiency Measurements. The efficiencies of the BrO_3^- reduction to Br^- are summarized in Tab. I. It can be seen that the efficiencies are generally quite high. The efficiencies in the $\text{KBr-KBrO}_3\text{-KOH}$ electrolytes were based on the BrO_3^- consumption* during an electrolysis and were subject to more experimental error than the Br^- production** in solutions initially containing no Br^- . In the electrolytes which originally contained Br^- , the anolyte became pale yellow after several hours of electrolysis due to Br_2 production from Br^- oxidation at the anode.

*Analysis by the Iodometric Method.

**Analysis by Mohr's method.

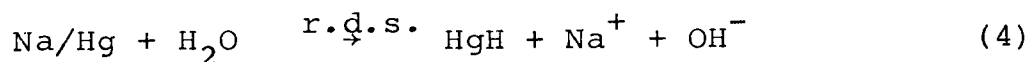
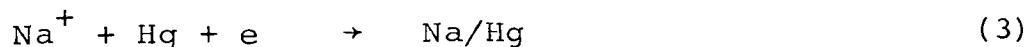
Polarization Measurements. The polarization measurements were carried out with the same electrolytes used for the efficiency measurements. Semi-logarithmic plots of V vs. i are shown in Fig. 1. They contain linear Tafel sections with slopes ranging from 0.100 to 0.125 V. The rest potentials, Tafel slopes, and electrolyte pH's are summarized in Tab. II. There were no significant currents until the potentials were lowered to about 0.7 V below the rest potentials. The polarization behavior in 0.2 M KBrO_3 -1.0 M KOH was also studied galvanostatically. As also seen in Fig. 1, the galvanostatic and potentiostatic data are essentially the same. Only very slight effects were noted with Br^- additions.

Discussion

The high efficiencies for the conversion of BrO_3^- to Br^- (84-102%) indicate this reaction to be the predominant, if not exclusive, reaction occurring at the Hg cathode under the conditions of this study. The reduction took place in the potential region -1.10 to -1.55 V(SHE). The charge on the cathode during the reduction is an important consideration as it determines the type of interaction between the electrode surface and species in solution. The potential of zero charge (pzc) on Hg in the presence of KBrO_3 -KBr solutions can be estimated to be between -0.2 and -0.4 V and to be pH independent.⁵ Thus, it

follows that BrO_3^- is being reduced at a cathode that has a relatively high negative charge. Since repulsive forces exist between the BrO_3^- and the surface at which it is being reduced, one of the first points that must be considered is the method by which the electron transfer between the two takes place.

One type of reaction scheme that might be suggested is an indirect one in which some neutral species or cations in the solutions (i.e., H^+ , K^+ , or H_2O) is first reduced to a reactive intermediate which remains in or goes into solution and in turn reduces the BrO_3^- . This would circumvent the necessity of contact of the anion with the negatively charged surface for electron transfer. The hydrogen ions are at such low concentrations ($\text{pH} = 13$) that they are not considered. The discharge of K^+ to give an amalgam (K/Hg) or water to give $\text{H}^\cdot(\text{ads})$ still leaves the reactive intermediate on the negatively charged surface and does not fit into this category. However, if H^\cdot were desorbed, it could be the reactive intermediate. Hydrogen evolution on Hg in alkaline solutions purportedly occurs through an initial discharge of the alkali metal ion which subsequently reacts with water. The mechanism in 0.1 N NaOH at 20°C has been given as^{6,7}





The Tafel relation was given as

$$\eta = -1.45 - 0.100 \log i \quad (6)$$

In the absence of similar information for KOH, it could be reasonably assumed that K^+ behaves similarly to Na^+ and that the overpotential equations are related in a manner similar to the equilibrium potentials, i.e.,

$\eta_{\text{KOH}} - \eta_{\text{NaOH}} = E_{\text{K}^+, \text{K}} - E_{\text{Na}^+, \text{Na}} = -0.21 \text{ V}$. This gives for the KOH solution

$$\eta = -1.66 - 0.100 \log i \quad (7)$$

Expressing this in terms of potentials on the normal hydrogen scale (pH = 13) gives

$$V = E_{\text{H}^+/\text{H}_2} - 1.66 - 0.100 \log i \quad (8)$$

$$= -2.43 - 0.100 \log i \quad (9)$$

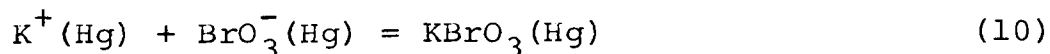
For hydrogen to be evolved (or in this case H^* to be deposited) at a rate equivalent to BrO_3^- reduction (10^{-4} - 10^{-1} amp·cm⁻²) would require potentials of -2.0 to -2.3 V. These are sufficiently negative to the potential region for BrO_3^- reduction that H^* (sol) can be eliminated from consideration as an intermediate. It also does not appear possible that any soluble reactive intermediate would be formed from either K^+ or water.

It is possible that a reactive intermediate on the Hg surface is participating in the reduction, although the problem with repulsive forces would still be present. The h.e. mechanism mentioned above eliminates H^* (ads) and/or KH (potassium hydride) as being intermediates, but K/Hg yet remains a possibility. There was some evidence of amalgam formation because after polarizations for long periods of time at high c.d.'s were terminated, hydrogen could be seen slowly evolving from the cathode. No specific information regarding K/Hg was found, but Pourbaix⁸ gives the reversible potential for the formation of Na/Hg as -1.6 V (pH independent). As sodium is slightly more electropositive than potassium (0.21 V), the potential for the formation of K/Hg would probably be in the vicinity of -1.8 V. This potential is generally more negative than that for BrO_3^- reduction, so it appears that amalgam formation is a parallel reaction that becomes appreciable only at high current densities. The efficiency data (Tab. I) show a slight indication of this. The high reduction efficiencies in themselves are also evidence against such a reaction intermediate.

Another reaction scheme that is feasible involves the combination of BrO_3^- and a cation (or cations) into a neutral or positively charged intermediate that can come into contact with the negatively charged cathode. The high coulombic efficiency for conversion to Br^- indicates

the bromate to be held at the cathode until the entire reduction reaction has reached or neared completion. A mechanism involving $K_Y BrO_3^{z+}$ cations has been proposed by Orlemann and Kolthoff.^{3,4} A similar mechanism is offered here which explains the experimental observations and differs from the Orlemann-Kolthoff mechanism only in that $KBrO_3$ is proposed as the intermediate species and that its formation is a result of ionic association phenomena.

It is well known that cation concentrations increase greatly above that of the bulk solution at negatively charged Hg surfaces. Data for KBr and $KBrO_3$ are not available but some estimations can be made from data for NaF solutions (see Tab. III). The radii of potassium ions are considerably larger than those of sodium ions (1.33 compared to 0.97 Å) causing the attractive forces between K^+ and the cathode to be less than those between Na^+ and the cathode. Though this would result in a lesser surface (or double layer) concentration for K^+ , it would still be expected to be on the order of 5 to 10 times the bulk value. Under these circumstances, there would be a significant amount of ionic association. As a first approximation, the extent of association could be treated as an equilibrium phenomenon, i.e.,



and

$$\theta_{\text{KBrO}_3} = K \theta_{\text{K}^+} \theta_{\text{BrO}_3^-} \quad (11)$$

From Tab. III, it can be seen that for NaF solutions, $\theta^+\theta^-$ is approximated by C^+C^- . Assuming this to be true also for KBrO_3 solutions,

$$\theta_{\text{KBrO}_3} = K C_{\text{K}^+} C_{\text{BrO}_3^-} \quad (12)$$

If this concept of the reaction is true, then at a given potential the current should be proportional to the surface concentration of KBrO_3 , or

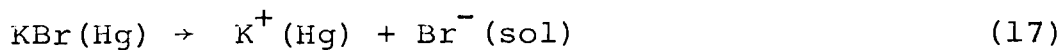
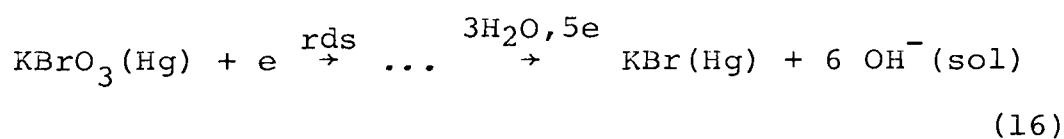
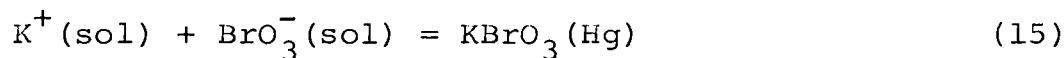
$$(i)_V = k' \theta_{\text{KBrO}_3} \quad (13)$$

Substituting eq. (12),

$$(i)_V = k' (K C_{\text{K}^+} C_{\text{BrO}_3^-}) = k C_{\text{K}^+} C_{\text{BrO}_3^-} \quad (14)$$

Fig. 2 shows log-log plots of current density versus C_{K^+} , $C_{\text{BrO}_3^-}$, and $C_{\text{K}^+} C_{\text{BrO}_3^-}$ which give 1.1, 0.7 and 1.0 for the respective reaction orders. Considering the approximations, this is considered to agree acceptably with the proposed mechanism. This scheme also is consistent with the small effect of temperature since the transfer of electrons would be more dependent on the electrode potential

as it affects the surface concentrations than on the energy of the reacting species. This information, along with the Tafel slopes of $2.3RT/\alpha F^*$, which indicate the first electron transfer to be rate determining, leads to the following reaction scheme:



The higher solubility of KBr as compared with $KBrO_3$ (657.8 gm KBr and 72.4 gm $KBrO_3$ per liter of 0.1 N KOH at 25°C, respectively)^{**} facilitates the transfer of Br^- from the double layer back to the bulk solution.

* Assuming $\alpha = 0.5$

** Determined experimentally

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TABLE I

A SUMMARY OF THE EFFICIENCIES OF BrO_3^- REDUCTION
ON Hg AT 25°C

Electrolyte gmol·liter ⁻¹	Efficiency, percent					
	Current density x 10 ³ , amp·cm ⁻²					
	7.32	12.2	24.4	36.6	48.8	73.2
0.1 KBrO ₃		94	98	99	95	
0.05 KBrO ₃ -1.0 KOH			99			94
			96			
0.1 KBrO ₃ -1.0 KOH			102			
0.2 KBrO ₃ -1.0 KOH			99			96
0.2 KBrO ₃ -0.1 KOH			98			
0.1 KBrO ₃ -0.1 KBr -1.0 KOH	86		90			84

TABLE II

REST POTENTIALS, TAFEL SLOPES, AND ELECTROLYTE pH'S
FOR THE REDUCTION OF BrO_3^- ON Hg AT 25°C

Electrolyte	Initial pH	Rest Potential	Tafel Slope
$\text{gmol}\cdot\text{liter}^{-1}$		volts (SHE)	volts
0.1 KBrO_3	7.1	0.370	0.125
0.05 KBrO_3 -1.0 KOH	13.2	0.046	0.100
0.1 KBrO_3 -1.0 KOH	13.2	0.048	0.110
0.2 KBrO_3 -1.0 KOH	13.2	0.048	0.110
0.2 KBrO_3 -0.1 KOH	12.2	0.084	0.120
0.1 KBrO_3 -0.1 KBr -1.0 KOH	13.1	0.035	0.110

TABLE III*

CONCENTRATIONS OF Na⁺ AND F⁻ IN THE PLANE OF CLOSEST APPROACH
FOR NaF SOLUTIONS IN CONTACT WITH Hg AT 25°C

Potential	Na ⁺ Concentration		F ⁻ Concentration		C ⁺ C ⁻	θ ⁺ θ ⁻
	C ⁺ ,bulk	θ ⁺ ,surface	C ⁻ ,bulk	θ ⁻ ,surface		
volts (SHE)	gmol/liter		gmol/liter			
-1.07	0.01	6.04	0.01	1.63x10 ⁻⁵	10 ⁻⁴	0.985x10 ⁻⁴
	0.1	7.03	0.1	1.42x10 ⁻³	10 ⁻²	0.998x10 ⁻²
	1.0	9.62	1.0	1.04x10 ⁻¹	1	1
-1.47	0.01	13.1	0.01	7.62x10 ⁻⁶	10 ⁻⁴	0.998x10 ⁻⁴
	0.1	14.8	0.1	6.76x10 ⁻⁴	10 ⁻²	10 ⁻²
	1.0	18.1	1.0	5.52x10 ⁻²	1	1

* Paul Delahay, Double Layer and Electrode Kinetics, p. 46.

CAPTIONS FOR FIGURES

1. Polarization curves for the reduction of BrO_3^- on Hg at 25°C.
2. Effect of K^+ and BrO_3^- concentrations on the reduction of BrO_3^- on Hg at -1.37 V(SHE) at 25°C.

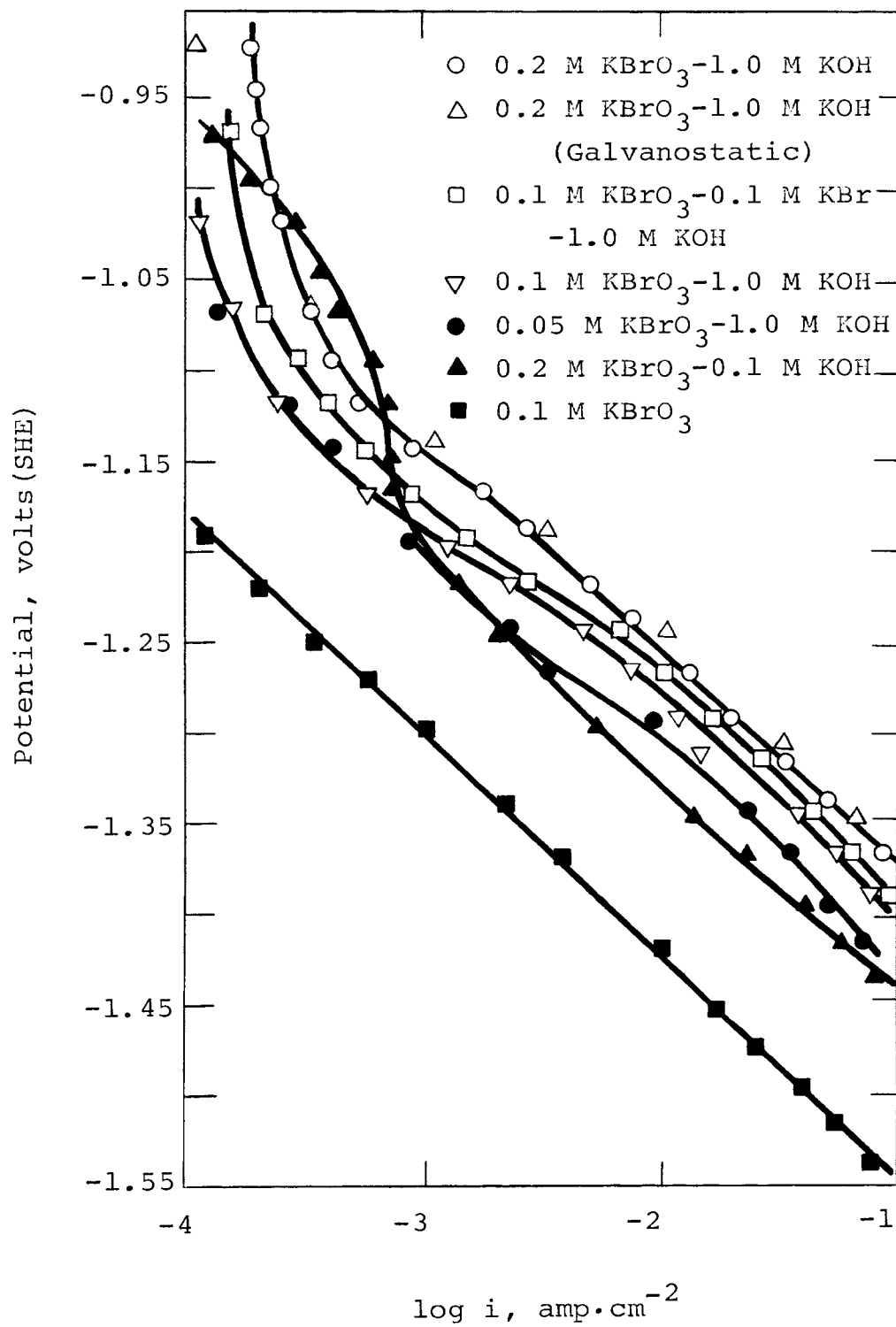


Fig. 1

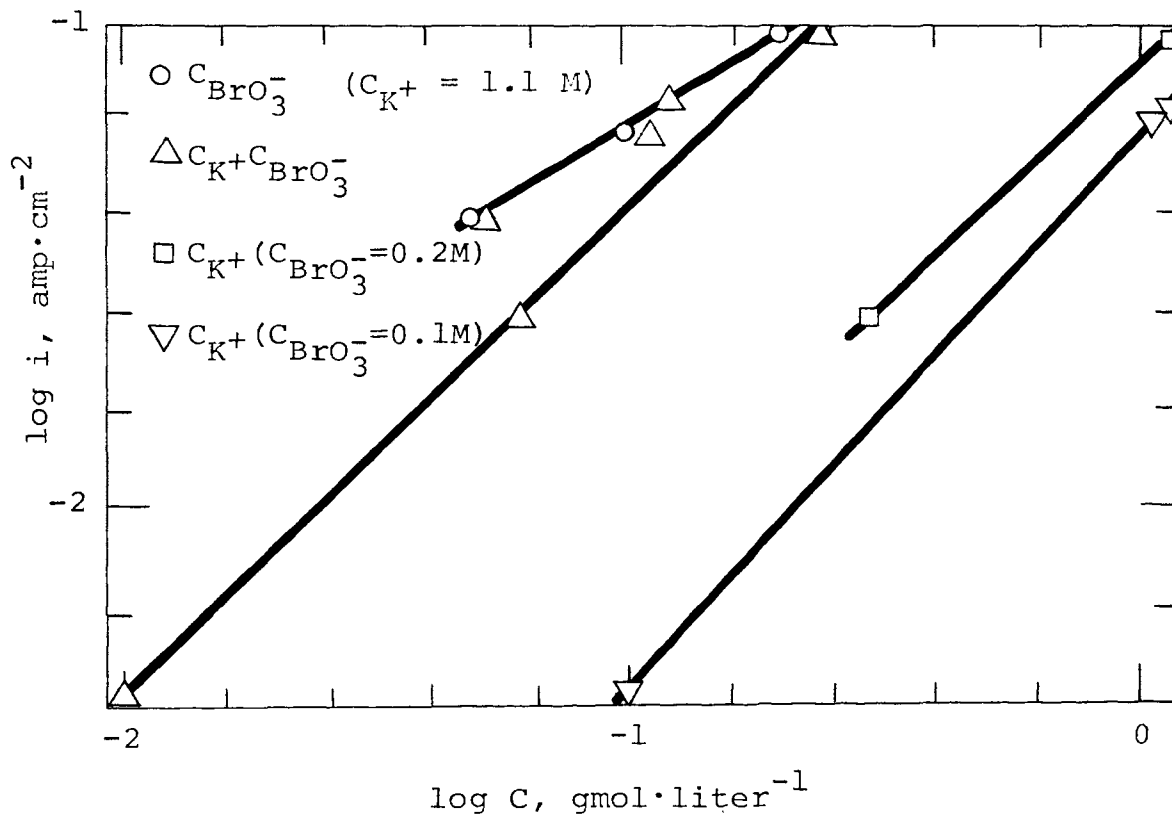


Fig. 2

APPENDICES

APPENDIX A

MATERIALS

The following is a list of the major materials and reagents used in this investigation. Detailed specifications or analyses of the reagents may be obtained from the chemical catalogues of the respective suppliers.

1. Acetic Acid. Reagent grade, meets ACS specifications. Mallinckrodt Chemical Works, St. Louis, Mo.

2. Mercury. Triple distilled, meets ACS specifications. Bethlehem Instruments, Hellertown, Pa.

3. Mercurous Chloride. Reagent grade, meets ACS specifications. Mallinckrodt Chemical Works, St. Louis, Mo.

4. Molybdenum Hydroxide. Reagent grade, meets ACS specifications. Merck & Co., Rahway, N.J.

5. Nitrogen. Prepurified grade, Matheson Co., East Rutherford, N.J.

6. Potassium Bromate. Reagent grade, meets ACS specifications. Fisher Scientific Co., Fairlawn, N.J.

7. Potassium Bromide. Reagent grade, meets ACS specifications. Fisher Scientific Co., Fairlawn, N.J.

8. Potassium Chromate. Reagent grade, meets ACS specifications. Fisher Scientific Co., Fairlawn, N.J.

9. Potassium Hydroxide. Reagent grade, meets ACS specifications. Fisher Scientific Co., Fairlawn, N.J.

10. Potassium Permanganate. Reagent grade, meets ACS specifications. Fisher Scientific Co., Fairlawn, N.J.

11. Silver Nitrate. Reagent grade, meets ACS specifications. Fisher Scientific Co., Fairlawn, N.J.

12. Sodium Hydroxide. Reagent grade, meets ACS specifications. Fisher Scientific Co., Fairlawn, N.J.

13. Sodium Thiosulfate. Reagent grade, meets ACS specifications. Fisher Scientific Co., Fairlawn, N.J.

14. Starch. Ordinary Corn Starch.

APPENDIX B
EQUIPMENT

The following is a list of the principal equipment components used in this investigation.

1. Milliammeter. Model 931, Ser. No. 1697, Weston Electric Instruments Corp., Newark, N.J.
2. Power Supply. Model Sorensen QRB 40-.75, Ser. No. 775, Raytheon Company, South Norwalk, Conn.
3. Recorder. Type VOM-5, Bausch & Lomb Co., Inc., Dover, N.H.
4. Current Regulator. Materials Research Center, University of Missouri, Rolla, Mo.
5. Potentiostat. Wenking 66 TS 1, Gerhard Bank Elektronik Gottingen, West Germany.
6. Electrometer. Model 610 C, Ser. No. 63779, Keithley Instruments Inc., Cleveland, Ohio.
7. Torsion Balance. Style RX-1, Ser. No. 16680 & 16687, The Torsion Balance Co., New York.
8. Semi-micro Balance. Type 26 04, Ser. No. 121211, Sartorius Werks AG., Gottingen, West Germany.
9. Micro-burette. Shelback, 10 ml, 0.05 ml graduations, Fisher Scientific Co., Pittsburgh, Pa.
10. pH Meter. Model 19, Ser. No. 1596, Fisher Scientific Co., Pittsburgh, Pa.

APPENDIX C
ANALYTICAL

A. Bromide Ion Determination (Mohr's Method).

The amounts of bromide ion were determined by precipitating them as silver bromide with a known quantity of AgNO_3 containing excess Ag (Mohr's method). The excess Ag was determined using a chromate indicator. It was found that a neutralized indicator served better because it did not change the pH of the titrated solution. In this investigation the potassium chromate solution (0.52 N or 5%) was neutralized with dilute nitric acid.

Anions which do not form complex silver ions or which form relatively soluble silver salts do not interfere with the analysis. Although bromate ions were present in the test solution, they do not interfere. The allowable pH range for the titration was checked and found to be 6.5-10.5. In acid medium, chromate ions combine with hydrogen ions:



to greatly reduce the sensitivity of the indicator. On the other hand, if the solution is too alkaline (pH > 10.5), silver hydroxide may precipitate before silver chromate. For pH adjustments, dilute acetic acid or sodium bicarbonate was used.

1. Preparation of 0.1 N silver nitrate standard solution. Dry analytical-reagent grade silver nitrate at 120°C for two hours and then cool in a dessicator. Weight out 16.978 gm of the dried silver nitrate and dissolve in distilled water, dilute to 1 liter.

2. Titration of bromide with standard silver nitrate solution.

Step 1. Transfer the reacted electrolyte into a beaker. Rinse the cell twice with distilled water and collect in the same beaker.

Step 2. Measure the pH of the solution in the beaker, and if not in the range of 6.5-10.5, adjust to this value with sodium bicarbonate or dilute acetic acid.

Step 3. The volume of the solution from Step 2 was measured and 60 ml withdrawn as a sample for the titration.

Step 4. Add one ml of neutralized potassium chromate indicator to the sample.

Step 5. Titrate the solution from Step 4 with 0.1 N AgNO_3 with constant swirling until the first permanent reddish-brown color is reached.

Step 6. Repeat titration (Steps 3-5) three times.

Step 7. Carry out blank titration with unreacted electrolyte as in Steps 2-6 for the reacted solutions. This difference is the amount of AgNO_3 used for the precipitation of bromide ions.

A flow chart of the bromide ion determination is shown in Table IV.

3. Sample calculations. Consider a 0.1 M KBrO_3 electrolyte that has undergone reduction for which the following were obtained:

Total volume of the reacted solution = 300 ml

Volume of sample = 60 ml

Volume of AgNO_3 used for the titration = 7.02 ml

Volume of AgNO_3 used for the blank titration = 0.10 ml

Net amount of AgNO_3 used = 6.92 ml

From the equation $W = V N E$, we know that the titer value is:

$$1 \text{ ml } \text{AgNO}_3 = 7.9916 \text{ mg } \text{Br}^-$$

Therefore, for this sample there are

$$(6.92)(7.9916) = 55.4 \text{ mg } \text{Br}^-$$

The total amount of bromide produced is

$$(55.4/1000)(300/60) = 0.277 \text{ gm}$$

B. Bromate Ion Determination (Iodometric Method).

Iodide exerts a reducing action upon strongly oxidizing systems with the formation of an equivalent amount of iodine. Therefore, when iodide is added in excess to a solution containing bromate, iodine is liberated according to the equation:

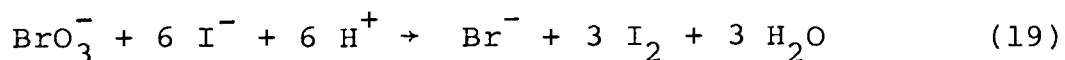
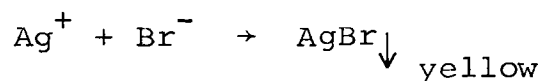
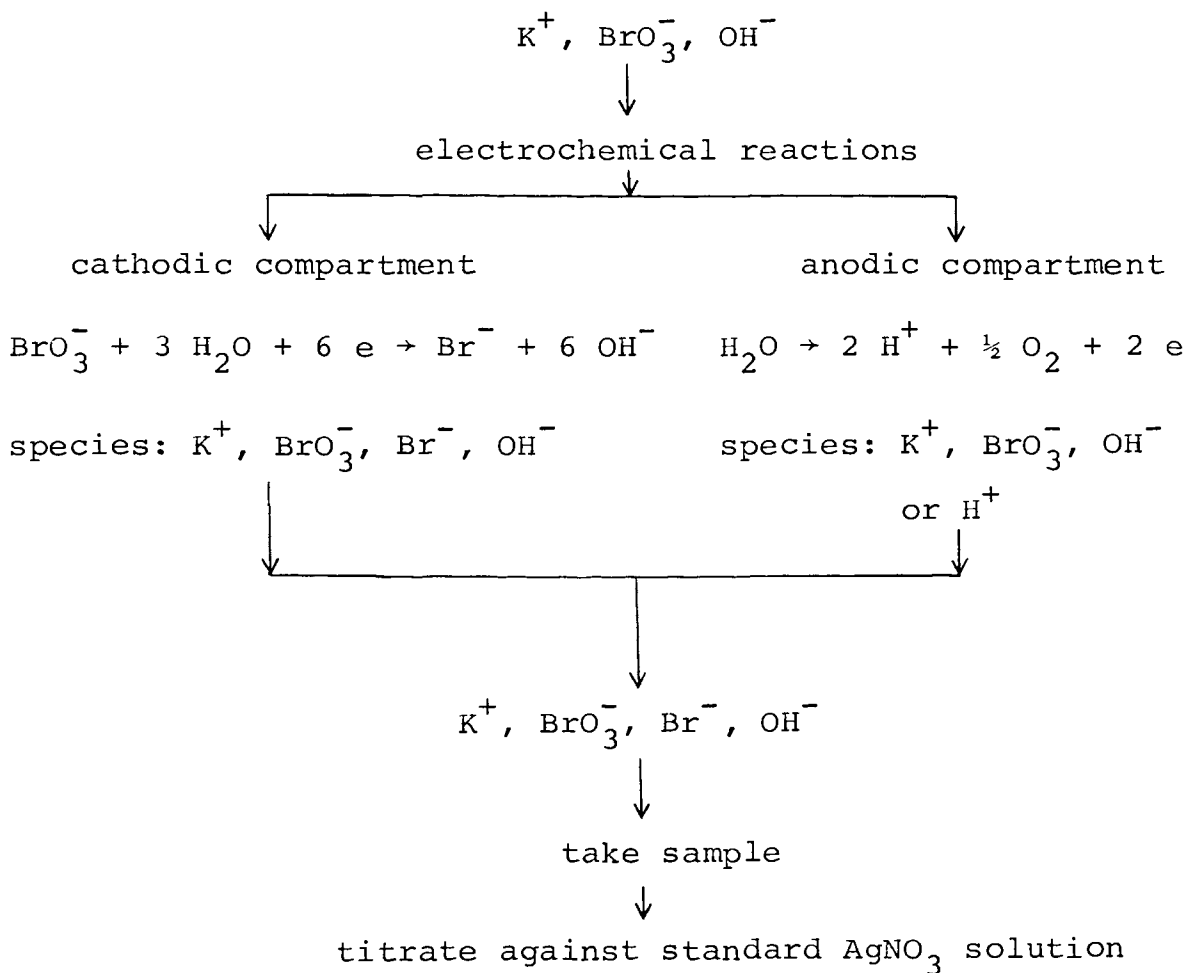


TABLE IV

FLOW CHART FOR THE DETERMINATION OF Br^-

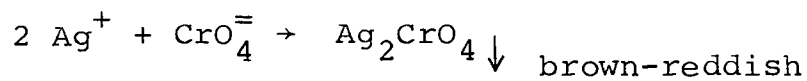
Electrolyte: 0.1 M KBrO_3 -n M KOH, n = 0, 0.05, 0.1, 0.2



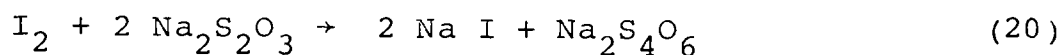
indicator: 5% (0.52 N) neutralized K_2CrO_4

end point: color change of ppt.

yellow → brown-reddish



The iodine liberated can be titrated against standard sodium thiosulfate solution and the bromate ion concentration is determined from the volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution used,



The starch used as the indicator should not be added until the yellow color due to the iodine has become very pale. The end point is taken as the sharp color change from blue to colorless. A blank titration is unnecessary.

1. Preparation of 0.1 N sodium thiosulfate solution.

Dissolve 15 gm of anhydrous sodium thiosulfate or 25 gm of sodium thiosulfate pentahydrate in conductivity water and dilute to 1 liter. This solution is titrated against the standard potassium bromate solution mentioned below.

2. Standardization of sodium thiosulfate with potassium bromate.

Step 1. To 10 ml of standard bromate solution, add 2 gm of potassium iodide and 10 ml of 1 N sulfuric acid.

Step 2. Titrate the solution from Step 1 with sodium thiosulfate standard solution prepared in part 1. When the color of the liquid has become pale yellow, add a few drops of starch solution and continue the titration until the color changes from blue to colorless.

Step 3. The titration is carried out at least three times. From the amount of bromate used and the volume of sodium thiosulfate solution required for the titration, the concentration of the thiosulfate solution is calculated.

4. Determination of bromate ion concentration of the electrolyte. The bromate ion present in the electrolyte prior to electrolysis is determined as in part 3. For the titration of electrolyte after the electrolysis, the procedure is as follows:

Step 1. The bromine produced in anodic compartment must be removed to prevent its further interference with the titration. To do this, collect the anolyte in a beaker and evaporate nearly to dryness.

Step 2. Transfer the catholyte to the same beaker, mix well and dilute to 300 ml.

Step 3. Pipet 10 ml of the liquid from Step 2 to a beaker and add 2 gm of KI and 15 ml of 1 N sulfuric acid. Proceed with the titration as described in part 3.

A flow chart of this analysis is shown in Table V.

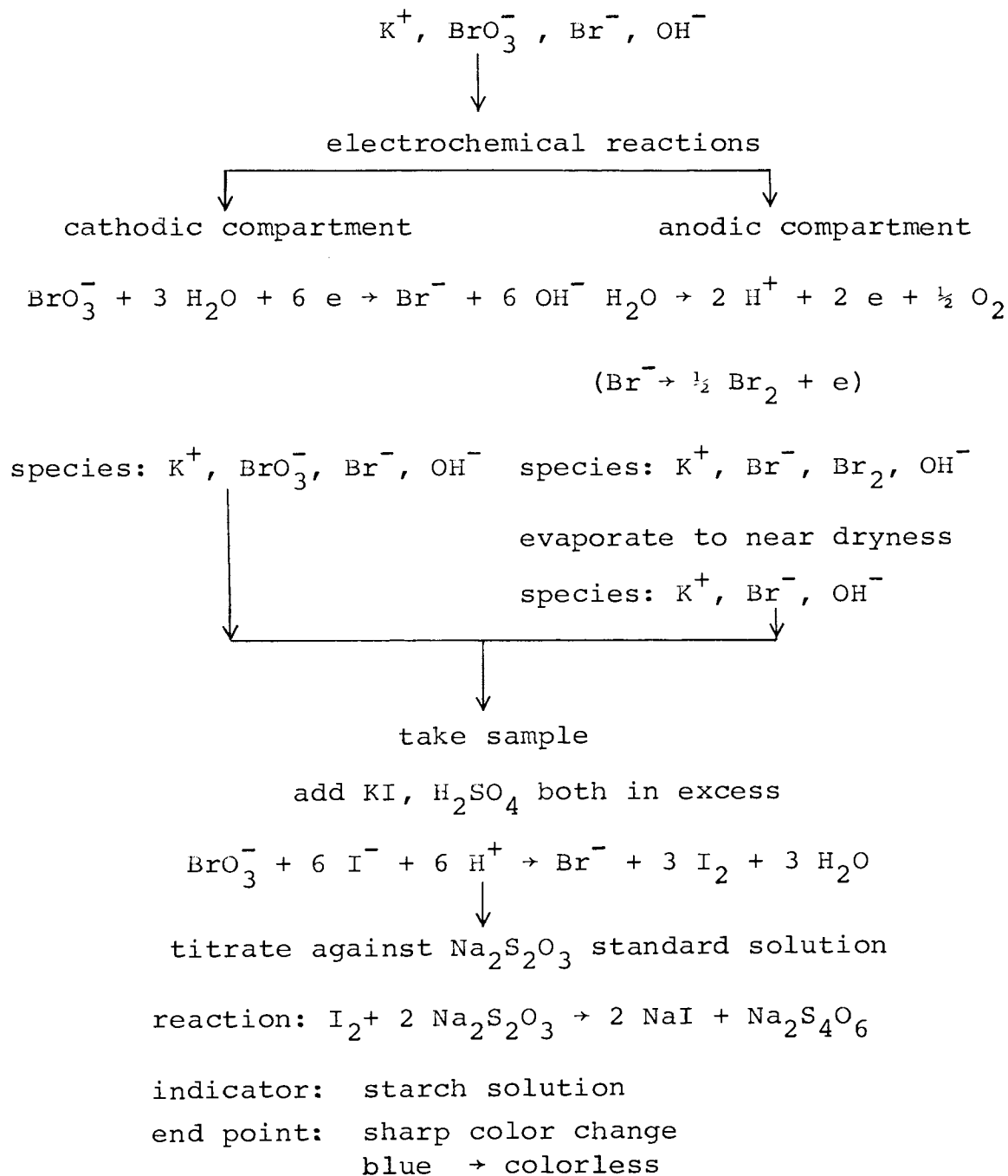
5. Sample Calculations. Consider 300 ml of the 0.1 M KBrO_3 -0.1 M KBr -1.0 M KOH solution that has been electrolyzed:

Before the reaction: total volume = 300 ml
volume of sample = 10 ml

TABLE V

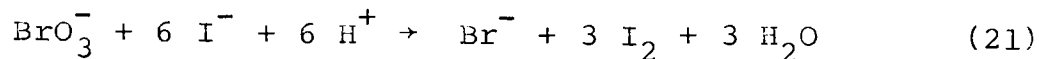
FLOW CHART FOR THE DETERMINATION OF BrO_3^-

Electrolyte: 0.1 M KBrO_3 - 0.1 M KBr - 1.0 M KOH

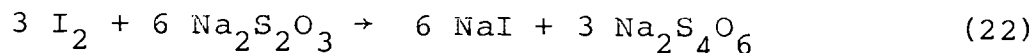


Na₂S₂O₃ used for the titration =
60.5 ml

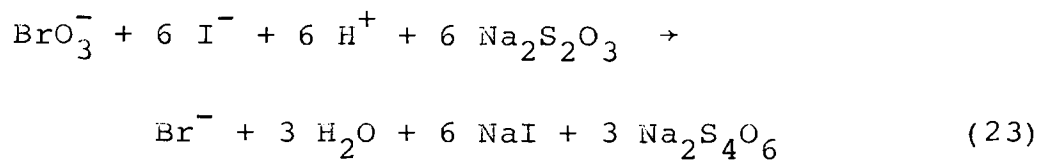
From the equations



and



we get



thus

$$1 \text{ ml of } 0.10 \text{ N Na}_2\text{S}_2\text{O}_3 = 2.132 \text{ mg BrO}_3^-$$

From this titer value, the amount of bromate present in the 10 ml sample was,

$$(60.5)(2.132) = 128.99 \text{ mg} = 0.129 \text{ gm}$$

In 300 ml of the solution, the amount of bromate was

$$(0.129)(300/10) = 3.87 \text{ gm}$$

After the reaction: total volume = 300 ml

volume of sample = 10 ml

Na₂S₂O₃ required for the
titration = 47.4 ml

From the titer value, the amount of bromate present was

$$(47.4) (2.132/1000) (300/10) = 3.032 \text{ gm}$$

APPENDIX D
EXPERIMENTAL DATA

Tables VI - VII Efficiency Studies Data
Tables VIII - XV Polarization Studies Data
Tables XVI - XVII Activation Energy Studies Data

Abbreviations used in tables:

W_t - Theoretical weight of bromide produced, gm
 W_e - Experimental weight of bromide produced, gm
 M_t - Theoretical weight of bromate reacted, gm
 M_1 - Weight of bromate before the electrolysis, gm
 M_2 - Weight of bromate after the electrolysis, gm
 M_e - Experimental weight of bromate reacted, gm
 I - Current, amp
 i - Current density, $\text{amp}\cdot\text{cm}^{-2}$

TABLE VI

DATE FOR THE EFFICIENCIES OF BrO_3^- REDUCTION ON Hg AT 25°C

Electrolyte	$i \times 10^3$	Polarization time	W_t	W_e	Efficiency
gmols·liter	amp·cm ⁻²	hours	gm	gm	percent
0.1 KBrO ₃	12.2	82.2	0.4087	0.3844	94
	24.4	28.4	0.2820	0.2770	98
	36.6	20.0	0.2985	0.2975	99
	48.8	21.8	0.4330	0.4095	95
0.05 KBrO ₃ -1.0 KOH	24.4	34.0	0.3385	0.3370	99
0.1 KBrO ₃ -1.0 KOH	24.4	40.0	0.3975	0.4050	102
	7.32	95.5-114.5	0.285-0.340	0.3015	106-89
0.2 KBrO ₃ -1.0 KOH	24.4	34.4	0.3420	0.3400	99
	73.2	12.0	0.3580	0.3408	96
0.2 KBrO ₃ -1.0 KOH	24.4	41.0	0.4080	0.4000	98

cathode area = 0.82 cm²

TABLE VII

DATA FOR THE EFFICIENCIES OF BrO_3^- REDUCTION ON Hg AT 25°C
 (BrO_3^- AS A BASIS OF EFFICIENCY DETERMINATIONS)

Electrolyte	$i \times 10^3$	Polarization time	M_t	M_1	M_2	M_e	Efficiency
gmols·liter	amp·cm ⁻²	hours	gm	gm	gm	gm	percent
0.05 KBrO_3	24.4	68.5	1.088	1.970	0.927	1.043	96
-1.0 KOH	73.2	20.0	0.955	1.970	1.074	0.860	94
0.1 KBrO_3	7.32	147.0	0.702	3.870	3.268	0.602	86
-0.1 KBr	24.4	67.0	1.067	3.870	2.910	0.960	90
-1.0 KOH	73.2	21.0	1.003	3.870	3.032	0.837	84

Cathode area = 0.82 cm²

TABLE VIII

THE CURRENT-POTENTIAL RELATIONSHIP FOR THE REDUCTION OF
 BrO_3^- ON Hg IN 0.1 M KBrO_3 AT 25°C

V_m	V	$I \times 10^3$	$i \times 10^3$
volts (NCE)	volts (SHE)	amp	amp·cm ⁻²
1.300	-1.018	0.040	0.049
1.400	-1.118	0.050	0.061
1.475	-1.193	0.104	0.137
1.500	-1.218	0.180	0.220
1.525	-1.243	0.310	0.378
1.550	-1.268	0.510	0.622
1.580	-1.298	0.940	1.147
1.620	-1.338	1.900	2.320
1.650	-1.368	3.400	4.150
1.700	-1.418	9.200	11.220
1.725	-1.443	15.000	18.300
1.750	-1.468	22.600	27.570
1.775	-1.493	35.000	42.700
1.800	-1.513	49.000	59.780
1.825	-1.543	68.000	82.960

TABLE IX

THE CURRENT-POTENTIAL RELATIONSHIP FOR THE REDUCTION OF
 BrO_3^- ON Hg IN 0.05 M KBrO_3 -1.0 M KOH AT 25°C

V_m	V	$I \times 10^3$	$i \times 10^3$
volts (NCE)	volts (SHE)	amp	amp·cm ⁻²
1.100	-0.818	0.105	0.128
1.250	-0.968	0.111	0.135
1.350	-1.068	0.130	0.159
1.400	-1.118	0.243	0.296
1.425	-1.143	0.35	0.427
1.450	-1.168	0.51	0.622
1.475	-1.193	0.76	0.927
1.500	-1.218	1.25	1.525
1.525	-1.243	2.00	2.440
1.550	-1.268	2.90	3.540
1.575	-1.293	8.35	10.187
1.600	-1.318	13.7	16.714
1.625	-1.343	21.2	25.864
1.650	-1.368	32.0	39.04
1.675	-1.393	44.5	54.30
1.700	-1.418	62.0	75.64

TABLE X

THE CURRENT-POTENTIAL RELATIONSHIP FOR THE REDUCTION OF
 BrO_3^- ON Hg IN 0.1 M KBrO_3 -1.0 M KOH AT 25°C

V_m	V	$I \times 10^3$	$i \times 10^3$
volts (NCE)	volts (SHE)	amp	amp·cm ⁻²
1.300	-1.018	0.107	0.130
1.350	-1.068	0.140	0.171
1.400	-1.118	0.22	0.268
1.450	-1.168	0.50	0.61
1.475	-1.193	1.15	1.40
1.500	-1.218	2.20	2.68
1.525	-1.243	4.25	5.19
1.550	-1.268	6.7	8.17
1.575	-1.293	10.4	12.68
1.600	-1.318	13.0	15.80
1.625	-1.343	35.0	42.70
1.650	-1.368	51.0	62.20
1.675	-1.393	69.0	84.18

TABLE XI

THE CURRENT-POTENTIAL RELATIONSHIP FOR THE REDUCTION OF
 BrO_3^- ON Hg IN 0.2 M KBrO_3 - 1.0 M KOH AT 25°C

V_m	V	$I \times 10^3$	$i \times 10^3$
volts (NCE)	volts (SHE)	amp	amp.cm ⁻²
1.100	-0.818	0.082	0.100
1.200	-0.918	0.164	0.200
1.225	0.943	0.178	0.217
1.250	-0.968	0.185	0.226
1.275	-0.993	0.204	0.249
1.300	-1.018	0.23	0.268
1.350	-1.068	0.29	0.354
1.375	-1.093	0.35	0.427
1.400	-1.118	0.48	0.585
1.425	-1.143	0.78	0.952
1.450	-1.168	1.57	1.92
1.470	-1.188	2.4	2.93
1.500	-1.218	4.5	5.49
1.520	-1.238	6.8	8.30
1.550	-1.268	12.2	14.88
1.575	-1.293	17.5	21.35
1.600	-1.318	31.0	37.82
1.620	-1.338	42.0	51.22
1.650	-1.368	80.0	97.6

TABLE XII

THE CURRENT-POTENTIAL RELATIONSHIP FOR THE REDUCTION OF
 BrO_3^- ON Hg IN 0.2 M KBrO_3 -1.0 M KOH AT 25°C
 BY THE GALVANOSTATIC METHOD

V_m	V	$I \times 10^3$	$i \times 10^3$
volts (NCE)	volts (SHE)	amp	amp·cm ⁻²
1.200	-0.918	0.1	0.122
1.350	-1.068	0.3	0.366
1.420	-1.138	1.0	1.22
1.470	-1.188	3.0	3.66
1.525	-1.243	10.0	12.2
1.590	-1.308	30.0	36.6
1.630	-1.348	60.0	73.2

TABLE XIII

THE CURRENT-POTENTIAL RELATIONSHIP FOR THE REDUCTION OF
 BrO_3^- ON Hg IN 0.2 M KBrO_3 -0.1 M KOH AT 25°C

V_m	V	$I \times 10^3$	$i \times 10^3$
volts (NCE)	volts (SHE)	amp	amp·cm ⁻²
1.250	-0.968	0.117	0.143
1.275	-0.993	0.160	0.195
1.300	-1.018	0.250	0.305
1.325	-1.043	0.320	0.390
1.350	-1.068	0.385	0.470
1.375	-1.093	0.550	0.670
1.400	-1.118	0.585	0.714
1.425	-1.143	0.62	0.756
1.450	-1.168	0.63	0.769
1.500	-1.218	1.25	1.525
1.525	-1.243	1.80	2.196
1.550	-1.268	3.0	3.66
1.575	-1.293	4.8	5.86
1.625	-1.343	13.1	15.98
1.650	-1.368	20.5	25.01
1.675	-1.393	35.0	42.70
1.700	-1.418	51.0	62.20
1.720	-1.438	73.0	89.06

TABLE XIV

THE CURRENT-POTENTIAL RELATIONSHIP FOR THE REDUCTION OF
 BrO_3^- ON Hg IN 0.1 M KBrO_3 -0.1 M KBr -1.0 M KOH
 AT 25°C (RUN 1)

V_m	V	$I \times 10^3$	$i \times 10^3$
volts (NCE)	volts (SHE)	amp	amp·cm ⁻²
1.150	-0.868	0.082	0.100
1.250	-0.968	0.142	0.173
1.350	-1.068	0.193	0.235
1.375	-1.093	0.27	0.329
1.400	-1.118	0.35	0.427
1.425	-1.143	0.50	0.610
1.450	-1.168	0.80	0.976
1.475	-1.193	1.40	1.708
1.500	-1.218	2.40	2.928
1.525	-1.243	5.98	7.33
1.550	-1.268	9.50	11.59
1.575	-1.293	15.2	18.54
1.600	-1.318	24.5	29.89
1.625	-1.343	39.0	47.58
1.650	-1.368	57.0	69.54
1.675	-1.393	83.0	101.26

TABLE XV

THE CURRENT-POTENTIAL RELATIONSHIP FOR THE REDUCTION OF
 BrO_3^- ON Hg IN 0.1 M KBrO_3 -0.1 M KBr -1.0 M KOH AT 25°C
 (RUN 2)

V_m	V	$I \times 10^3$	$i \times 10^3$
volts (NCE)	volts (SHE)	amp	amp·cm ⁻²
1.250	-0.968	0.071	0.086
1.300	-1.018	0.130	0.158
1.350	-1.068	0.185	0.226
1.400	-1.118	0.36	0.439
1.450	-1.168	1.02	1.24
1.475	-1.193	2.00	2.44
1.500	-1.218	3.4	3.93
1.550	-1.268	9.8	11.90
1.600	-1.318	23.0	28.06
1.625	-1.343	36.5	44.53
1.650	-1.368	51.0	62.2
1.675	-1.393	72.0	87.8

TABLE XVI

THE CURRENT-TEMPERATURE RELATIONSHIP FOR THE REDUCTION OF
 BrO_3^- ON Hg IN 0.1 M KBrO_3 -1.0 M KOH

(A) $V = -1.20$ volts (SHE)

Temperature	$I \times 10^3$	$i \times 10^3$
$^\circ\text{C}$	amp	$\text{amp} \cdot \text{cm}^{-2}$
25	2.8	3.42
30	2.8	3.42
35	2.7	3.3
40	2.8	3.42
45	2.8	3.42

(B) $V = -1.30$ volts (SHE)

Temperature	$I \times 10^3$	$i \times 10^3$
$^\circ\text{C}$	amp	$\text{amp} \cdot \text{cm}^{-2}$
20	15.0	18.3
25	15.0	18.3
30	16.3	19.8
35	16.4	20.0
40	16.4	20.0
45	16.5	20.1

TABLE XVII

THE CURRENT-TEMPERATURE RELATIONSHIP FOR THE REDUCTION OF
 BrO_3^- ON Hg IN 0.1 M KBrO_3 -0.1 M KBr -1.0 M KOH

(A) $V = -1.20$ volts (SHE)

Temperature	$I \times 10^3$	$i \times 10^3$
$^{\circ}\text{C}$	amp	$\text{amp} \cdot \text{cm}^{-2}$
20	3.1	3.78
25	3.3	4.03
30	3.4	4.15
35	3.6	4.38
40	3.8	4.63

(B) $V = -1.30$ volts (SHE)

Temperature	$I \times 10^3$	$i \times 10^3$
$^{\circ}\text{C}$	amp	$\text{amp} \cdot \text{cm}^{-2}$
20	22	26.8
25	22.2	27.1
30	22.4	27.3
35	22.8	27.8
40	22.9	28
45	23	28.1

VITA

Jaw-Shin Chang was born on November 21, 1944, in Chiayi, Taiwan. He graduated from I-Lan High School in June, 1962.

He entered Cheng Kung University in September, 1962, and graduated in June, 1966, with a B.S. degree in Chemical Engineering. After graduation, he served in the Chinese Army for one year of military service as a Second Lieutenant. He joined the Asia Cement Corporation in Taipei from August, 1967, to July, 1968.

He came to the United States and enrolled in the Graduate School of the University of Missouri-Rolla in September, 1968.