1970

The cathodic reduction of maleic acid

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Recommended Citation

Hsieh, Show Yih, "The cathodic reduction of maleic acid" (1970). *Doctoral Dissertations*. 2289.
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THE CATHODIC REDUCTION OF MALEIC ACID

by

SHOW YIH HSIEH, 1940-

A DISSERTATION

Presented to the Faculty of the Graduate School of the

UNIVERSITY OF MISSOURI - ROLLA

In Partial Fulfillment of the Requirements for the Degree

DOCTOR OF PHILOSOPHY

in

CHEMICAL ENGINEERING

1970

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ABSTRACT

The electrochemical reduction of maleic acid (0.0003 to 0.3 M) was studied on Hg, 0.5% Bi(Hg) amalgam, 5.0% Bi(Hg) amalgam, and Bi cathodes in 1 N H_2SO_4-K_2SO_4-KOH electrolytes (pH 0.3 to 4.0) at 60°C. The maleic acid was converted to succinic acid with high efficiencies (86 to 100%) on all cathodes. Polarization curves with linear Tafel sections were found. All the cathodes had similar kinetic parameters which were:

$$\partial V/\partial \log i = -2.3RT/F$$

$$\partial \log i/\partial pH = -1$$

$$\partial \log i/\partial \log C_M = 1$$

The empirical rate equation is

$$i = k\, C_M\, C_{H^+} \exp(-FV/RT)$$

where, i = current density, amp/cm^2

V = potential, volts(SHE)

C_M = undissociated maleic acid concentration, gmol/liter

C_{H^+} = hydrogen ion concentration, gmol/liter

R = gas constant

T = absolute temperature

F = Faraday's constant

k = rate constant

A reaction mechanism consistent with the experimental observations is proposed as being

$$M(sol) \rightleftharpoons M(ads)$$

$$M(ads) + e \rightleftharpoons M^-(ads)$$

$$M^-(ads) + H^+(sol) \xrightarrow{rds} MH(ads)$$

$$MH(ads) \xrightarrow{H^+,e} \cdots \longrightarrow MH_2(sol)$$

ACKNOWLEDGEMENTS

The author wishes to thank Dr. J. W. Johnson, Professor of Chemical Engineering, and Dr. W. J. James, Director of the Graduate Center for Materials Research, University of Missouri-Rolla, for their guidance, support, and encouragement during the course of this investigation.

He is also grateful for the financial assistance received from the Department of Chemical Engineering and the Graduate Center for Materials Research, and for a Fellowship from the American Chemical Society - Petroleum Research Fund, without which, this study would not have been possible.

The author is deeply indebted to his wife and parents for their encouragements while pursuing advanced studies in the United States.

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I. INTRODUCTION

Electrode kinetics have been studied since the turn of the century. However, until 1947, the studies were primarily limited to the hydrogen ion discharge (hydrogen evolution) and, to a lesser extent, the oxygen evolution reactions. In recent years, interest in fuel cell research has stimulated a great deal of work in the electrochemical oxidation of organic compounds. The electrochemical reduction of organic compounds has not yet received a great deal of attention, especially from the mechanistic viewpoint.

The objective of this investigation was to establish a reaction mechanism for the cathodic reduction of maleic acid in aqueous solutions on mercury, bismuth, and bismuth-mercury amalgams. It is hoped that studies such as these will lead to a better understanding of this category of cathodic reactions, i.e., hydrogenation of unsaturated hydrocarbons.

II. LITERATURE REVIEW

Maleic acid is the cis-isomer of butendioic acid. Its formula is HOOC-CH=CH-COOH and the formula weight is 116.1. It crystallizes as colorless, monoclinic prisms and has a melting point of 130.5°C.[1]

Maleic acid has been chemically reduced to succinic acid ($HOOC\text{-}CH_2\text{-}CH_2\text{-}COOH$) with various catalysts.[2] In the presence of Raney nickel, for example, aqueous solutions of maleic acid have been reduced with gaseous hydrogen at 100°C and 2,500 psi.[2] The same reaction occurs at room temperature with a colloidal palladium catalyst.[2]

Numerous reports are available on the electrochemical reduction of maleic acid[3-15], mostly concerning polarographic analyses or current efficiencies. Some limited information concerning kinetic studies can be found. These, as well as the hydrogenation of similar compounds and the hydrogen evolution reaction, will be reviewed briefly in this section.

A. Current Efficiency Studies

Pomilio[3] was probably the first to carry out the reduction of maleic acid electrochemically. He reported that the reduction took place at a nickel cathode in both alcoholic and aqueous solutions of sulfuric acid. Later Norris and Gumming[4] obtained over 90 percent yields of succinic acid at a lead cathode in sulfuric acid solution. Swann, Wanderer, Schaffer, and Streaker[5] made an extensive study with cathodes of copper, zinc, cadmium, mercury, aluminum, tin, lead, bismuth, iron, cobalt, and nickel. Tajima, Seki, and Mori[6] obtained current efficiencies of 99 percent at a titanium cathode. Kanakam, Pathy, and Udupa[7] obtained 95 and 99 percent current efficiencies on a stationary and a rotating lead cathode, respectively.

Larger scale reductions of maleic acid have also been reported. Yatani[8] recovered succinic acid from maleic anhydride which was present in the waste gas from a naphthalene oxidation process. Watabe[9] reported a continuous process of electrochemical manufacturing of succinic acid by passing maleic acid solution through four electrolytic cells connected in series.

Results of the preceeding works are summarized in Table I.

TABLE I

SUMMARY OF CURRENT EFFICIENCY STUDIES OF THE ELECTROCHEMICAL REDUCTION OF MALEIC ACID

Ref	Cathode	Sulfuric acid conc	Maleic acid conc	Current density	Temp	Current eff*
		Wt percent	Wt percent	ma/cm^2	$^\circ C$	percent
4	Pb	10	20	30-70	-	90
5	Cu	30	8	50	28-30	17
	Zn	30	8	50	28-30	22
	Cd	30	8	50	28-30	22
	Hg	30	8	50	28-30	86
	Al	30	8	50	28-30	15
	Sn	30	8	50	28-30	14
	Pb	30	8	50	28-30	33
	Bi	30	8	50	28-30	24
	Fe	30	8	50	28-30	35
	Co	30	8	50	28-30	27
	Ni	30	8	50	28-30	33
	Cu	30	8	50	65-70	49
	Zn	30	8	50	65-70	61
	Cd	30	8	50	65-70	66
	Hg	30	8	50	65-70	98
	Al	30	8	50	65-70	52
	Sn	30	8	50	65-70	69
	Pb	30	8	50	65-70	75
	Bi	30	8	50	65-70	35
	Fe	30	8	50	65-70	68
	Co	30	8	50	65-70	29
	Ni	30	8	50	65-70	71

TABLE I (CONT'D)

Ref	Cathode	Sulfuric acid conc	Maleic acid conc	Current density	Temp	Current eff*
		Wt percent	Wt percent	ma/cm^2	^{o}C	percent
6	Ti	50	20	76	80	99
7	Pb	5	7	100	70-75	95
	Pb**	5	7	100	70-75	99
8	Pb	18	-	40	80	-

* Average value if more than two values were reported.

**Rotating electrode.

B. Polarographic Studies

The polarographic reduction of maleic acid has been studied for nearly as long as the science of polarography has been known. In 1928, Herasymenko[10] reported that maleic acid was reduced to succinic acid at a dropping mercury electrode. He also reported that the undissociated acid was the reacting species.

Later, Vopicka[11] found that at a constant pH, the half-wave potential ($E_{\frac{1}{2}}$) of the polarographic reduction of maleic acid was constant and independent of the concentration of the acid. In 0.1 N $CaCl_2$ solution, he observed two waves in the polarographic reduction of maleic acid. He attributed the first wave to the reduction of the undissociated acid and the second to the reduction of its anions. Herasymenko[12] derived an equation for the dependence of the $E_{\frac{1}{2}}$ on pH assuming that the undissociated maleic acid was the reacting species. Values of $E_{\frac{1}{2}}$ calculated from the equation were compared with the experimental data of Vopicka. The comparison was satisfactory in the pH range 0 to 5.

In 1949, Elving and Teitibaum[13] conducted an extensive investigation over a pH range from 2 to 9. Two waves were observed in a solution of low buffering capacity. By increasing the buffer concentration, the two waves gradually merged into one. They concluded that the two waves did not represent the successive reduction of the undissociated acid and its anions.

In 1954, Elving and Rosenthal[14] reexamined the polarographic reduction of maleic acid for solutions whose pH ranged from 0.7 to 12. Only one wave was observed from pH 0.7 to 5. At pH 5, the height of the wave began to decrease and, simultaneously, a second more negative wave appeared. The second wave began to decrease in size at pH 8 and disappeared at pH 10. The equation derived by Herasymenko was used to explain the effect of pH on the half-wave potential.

C. Kinetic Studies

1. Maleic acid. Manzhilei[15] studied the reduction of 0.2 M maleic acid in 0.1 N H_2SO_4 on platinized-platinum and mercury-plated cathodes. The mercury-plated electrode was prepared by coating platinum foil in a solution of Hg_2SO_4 in 0.1 N H_2SO_4. The polarization measurements were made galvanostatically from 0.5 to 50 ma using a steady state method. Plots of log i (current) versus V (potential) were linear over 1.5 to 2.5 decades of current.

With the platinized-platinum cathode, the Tafel slopes were close to -2.3RT/F (-50 to -70 mv) at 12, 20, and 40°C and occurred over the potential range +0.3 to 0 volts(SHE). The apparent activation energy at 0.15 v was reported as 15.5 Kcal.

With the mercury cathode, the polarization curves at 24 and 48°C almost coincided, indicating that temperature had a very small effect. The Tafel slopes were about -100 mv and ocurred over the potential range -0.45 to -0.6 v.

No pH or maleic acid concentration effect on the polarization behavior was reported.

2. Acrylic acid (CH_2=CHCOOH). Manzhilei[15] also obtained polarization curves for the reduction of acrylic acid on platinized-platinum and mercury-plated cathodes at temperatures ranging from 10 to 50°C. The electrolyte was 0.2 M acrylic acid in 0.1 N H_2SO_4. Similar to maleic acid, the reduction of acrylic acid involves the saturation of a double bond.

For the platinized-platinum cathode, the Tafel slopes were close to -2.3RT/F. The apparent activation energies were 8.0, 7.4, and 6.8 Kcal at potentials of 0.2, 0.15, and 0.1 v(SHE), respectively. The change of activation energy with potential was 12 Kcal/volt.

The Tafel slopes with the mercury-plated cathode were about -110 mv at both 20 and 40°C. The temperature effects were again insignificant.

3. Ethylene. Kuhn[16] studied the reduction of ethylene in 1.0 and 0.1 N H_2SO_4 and in 1.0 and 0.1 N NaOH on platinum cathodes at ethylene partial pressures of 1.0, 0.1, and 0.01 atm. Ethane was found to be the reduction product. The following kinetic parameters were obtained:

$$\partial V/\partial \log i = -2(2.3RT/F)$$

$$\partial \log i_o/\partial pH = 0$$

$$\partial \log i/\partial \log p > 0$$

The following mechanism was proposed:

$$R \rightleftharpoons R(ads)$$

$$R(ads) + e \xrightarrow{rds} R^-(ads)$$

$$R^-(ads) + H^+ \longrightarrow RH(ads)$$

$$RH(ads) + e \longrightarrow RH^-(ads)$$

$$RH^-(ads) + H^+ \longrightarrow RH_2(ads)$$

$$RH_2(ads) \longrightarrow RH_2$$

D. Hydrogen Evolution Reaction (h.e.r.)

The h.e.r. is undoubtedly the most extensively studied cathodic reaction. The polarization behavior is strongly dependent on the nature of the electrode. For example, platinized-platinum can be used for making a reversible hydrogen electrode because its overpotential is so small. On the other hand, an overpotential greater than one volt is usually required to evolve hydrogen from mercury.

Metals have been qualitatively classified into three groups according to their overpotential or exchange current for the h.e.r.[17] Metals such as mercury, lead, thallium, and cadmium exhibit low hydrogen chemisorption and have very low exchange currents; metals from the platinum group adsorb hydrogen well and have high exchange currents; and metals such as molybdenum, tungsten, copper, and nickel exhibit strong hydrogen adsorption and have medium exchange currents.

In general, the following three steps have been considered for the h.e.r.[17]

I. Discharge reaction:

$$H^+(sol) + e \rightleftharpoons H(ads)$$

II. Ion+atom reaction:

$$H^+(sol) + H(ads) + e \rightleftharpoons H_2(sol)$$

III. Combination reaction:

$$H(ads) + H(ads) \rightleftharpoons H_2(sol)$$

Kinetic equations have been derived for various combinations of these and the theoretical values of the resulting parameters tabulated in most textbooks of electrode kinetics.[18,19] The Tafel slopes for both low and high coverages of adsorbed hydrogen are summarized in Table II.

On mercury cathodes, numerous researchers have proposed that reaction I is the rate determining step. This was suggested by the following findings:[20]

1. Tafel slope = $-2(2.3RT/F)$
2. $\partial \log i/\partial pH = -1$ (in acidic solution)
3. Both electrocapillary and differential capacity measurements have indicated that the atomic hydrogen coverage on a polarized surface is unmeasurably low, which indicates that the removal of adsorbed hydrogen is fast in comparison with the step of hydrogen ion discharge.

The mechanism on platinum depends on the pretreatment as well as the state of the metal surface. With platinized-platinum electrodes, the Tafel slope is $-2.3RT/2F$ at low current densities. A limiting current (Tafel slope = $-\infty$) is reached at higher overpotentials.[18] From Table II, it appears that the combination reaction must be rate determining with the H coverage changing from 0 (at low currents) to 1 (at high currents). This coverage-current

TABLE II

THEORETICAL TAFEL SLOPES* FOR THE HYDROGEN EVOLUTION REACTION

Mechanism	Rate Determining Step	Tafel Slope	
		$\theta \rightarrow 0$	$\theta \rightarrow 1$
Discharge and Combination	Discharge	-2(2.3RT/F)	-2(2.3RT/F)
	Combination	-2.3RT/2F	$-\infty$
Discharge and Ion + Atom	Discharge	-2(2.3RT/F)	-2(2.3RT/F)
	Ion+Atom	-2(2.3RT/3F)	-2(2.3RT/F)

---

* The symmetry factor α has been assumed to be 0.5.

dependence has been confirmed with both charging curves and pseudocapacity studies on platinum.[21] When current densities are further increased, the Tafel slope changes to -2(2.3RT/F) which suggests that the rate determining step changes to reaction II (ion+atom reaction).

On metals with medium exchange currents such as nickel and copper, the observed Tafel slope of -2(2.3RT/F) suggests either a slow discharge or a slow ion+atom reaction. From hydrogen/tritium separation factor measurements[22], the latter has been shown to be rate determining.

The results of h.e.r. on mercury and bismuth are summarized in Table III. No mechanism has been discussed for bismuth. Mathews[23] has, however, classified bismuth with the group with medium exchange currents, for which the ion+atom reaction is likely the rate determining step.

TABLE III

EXCHANGE CURRENTS AND SYMMETRY FACTORS FOR THE HYDROGEN EVOLUTION REACTION ON Hg AND Bi CATHODES*

Electrode	Solution	Exchange Current amp/cm^2	α**
Hg	0.1 N H_2SO_4	2×10^{-13}	0.51
	0.2 N H_2SO_4	6×10^{-12}	0.52
	0.25N H_2SO_4	8×10^{-13}	0.50
	1.0 N H_2SO_4	5×10^{-13}	0.50
	1.0 N H_2SO_4	1×10^{-12}	0.49
	5 N H_2SO_4	9×10^{-13}	0.50
Bi	1 N HCl	10^{-8}	0.4
	1 N HCl	10^{-7}	0.6

---

* References 24 and 25.

**Assuming the Tafel slope = $2.3RT/\alpha F$.

III. EXPERIMENTAL

Four different cathodes (mercury, 0.5 percent bismuth amalgam, 5 percent bismuth amalgam, and bismuth) were used in this investigation of the electrochemical reduction of maleic acid to succinic acid. All were liquid within the temperature range of the study (50 to 75°C) with the exception of bismuth which was solid. The following studies were performed on each cathode:

(1) Current-potential studies. Polarization curves were obtained for electrolytes of various maleic acid concentration and pH. The maleic acid concentration ranged from 0.0003 to 0.3 M and pH from 0.3 to 4. The electrolyte pH was controlled by using varying ratios of H_2SO_4, K_2SO_4, and KOH in which the sulfate normality was held constant at unity to insure good conductance.

(2) Current-temperature studies. The temperature dependence of the current was studied from 50 to 75°C at various constant potentials within the linear Tafel region.

(3) Faradaic efficiency studies. The efficiency of conversion of maleic acid to succinic acid was studied galvanostatically at 0.03 M maleic acid concentration and various pH's and current densities.

A complete discussion of each of the studies, including materials, apparatus, procedure, and results follows in the remainder of this section.

A. Current-Potential Studies

1. Materials. A list of materials used in this investigation is given in Appendix A. All the chemicals were Fisher "certified" grade except the maleic acid which was Matheson "superior". Conductivity water was used in preparing the solutions. The mercury used was Bethlehem's triple-distilled instrument grade and the bismuth was ESPI 6N grade (99.9999 percent purity).

2. Apparatus. The major apparatus consisted of an electrolysis cell, a potentiostat, an electrometer, and a recorder arranged as shown in Figure 1. A list of equipment is given in Appendix B. The potentiostat was used to maintain a constant potential on the cathode. The potential was monitored with the electrometer. The rest (open circuit) potential and current were recorded from the potentiostat output. The cell was immersed in a thermostated water-bath.

a. Cells. The cell used for the liquid cathodes (mercury and amalgams) is shown schematically in Figure 2.

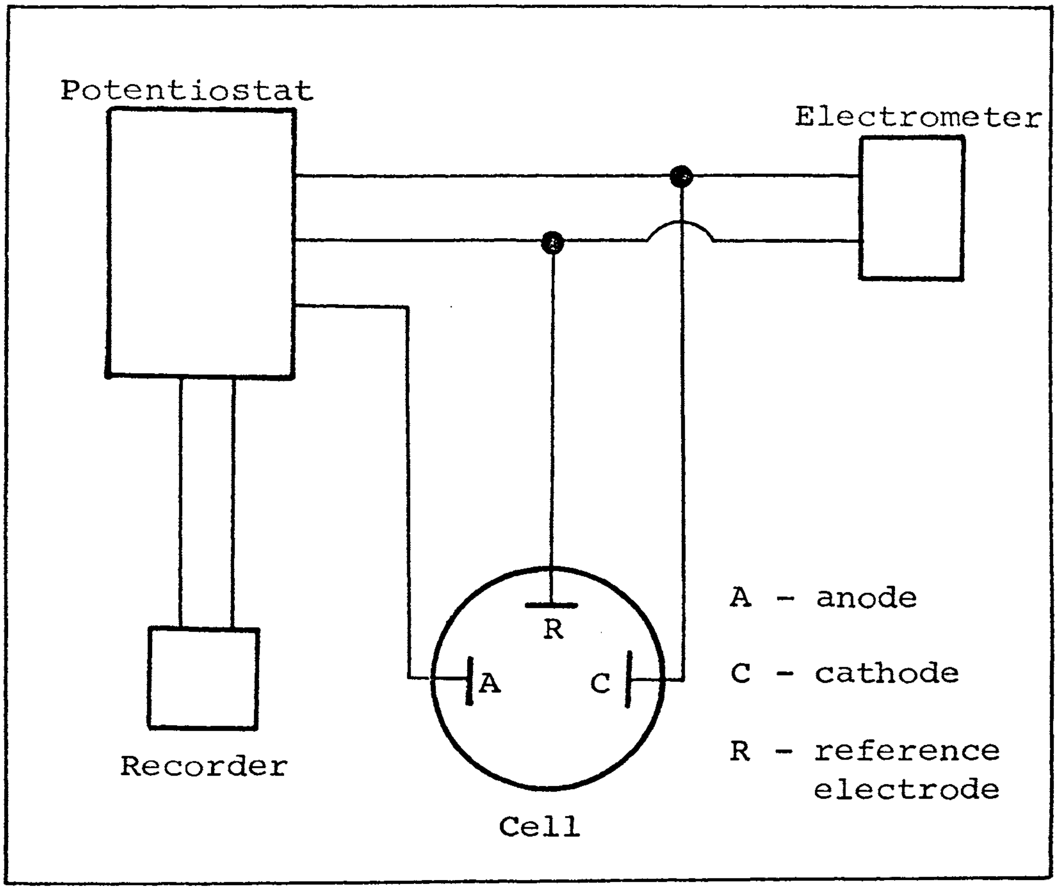
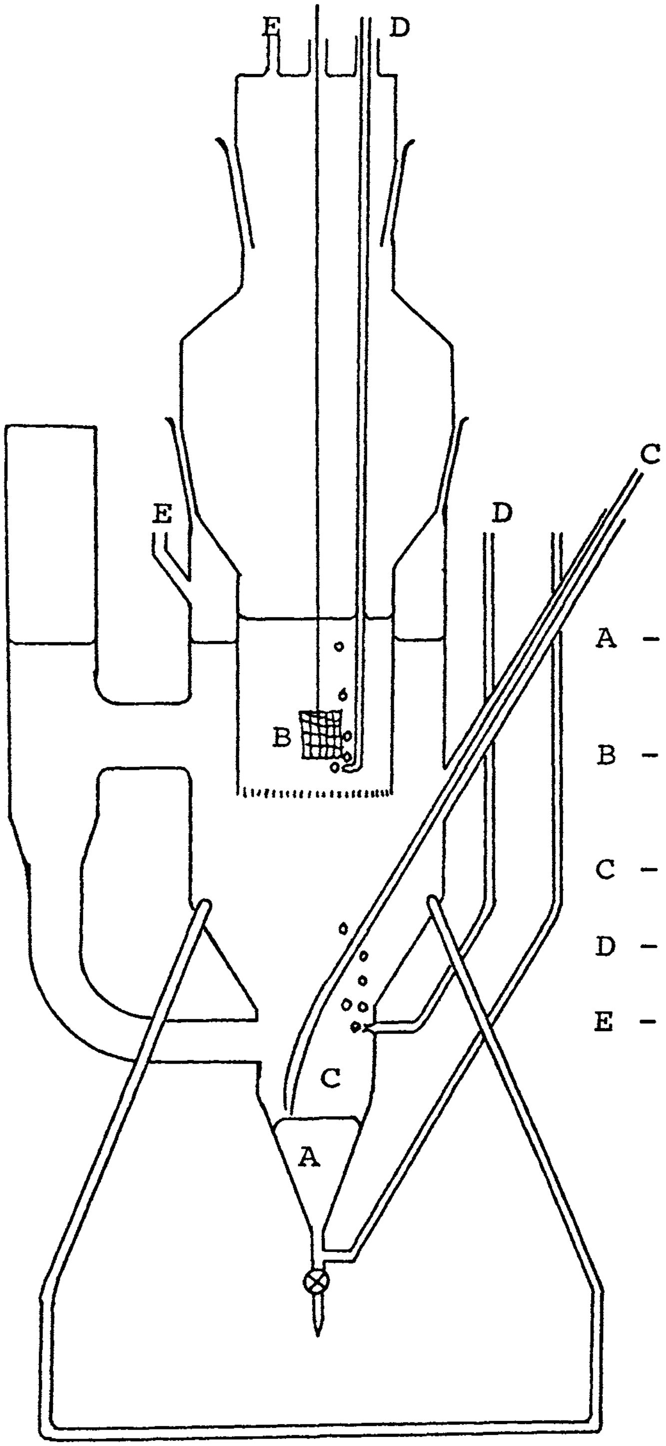


Figure 1. Diagram of the apparatus used for the potentiostatic studies of the cathodic reduction of maleic acid.



A - Mercury or amalgam cathode

B - Platinized-platinum anode

C - Luggin capillary

D - Nitrogen inlets

E - Nitrogen outlets

Figure 2. Electrolysis cell used with the liquid cathodes for studies of the cathodic reduction of maleic acid.

It was constructed of pyrex glass. The lower (cathodic) compartment had a capacity of 1,100 ml. It had a conical base which, when filled with mercury or amalgam, served as the cathode. The area of the cathode could be varied from 2 to 23 cm^2 by varying the amount of mercury or amalgam in the base. The upper (anodic) compartment had a capacity of 300 ml. A glass frit separated the two compartments. Both had inlets and water-sealed outlets for nitrogen purging and stirring.

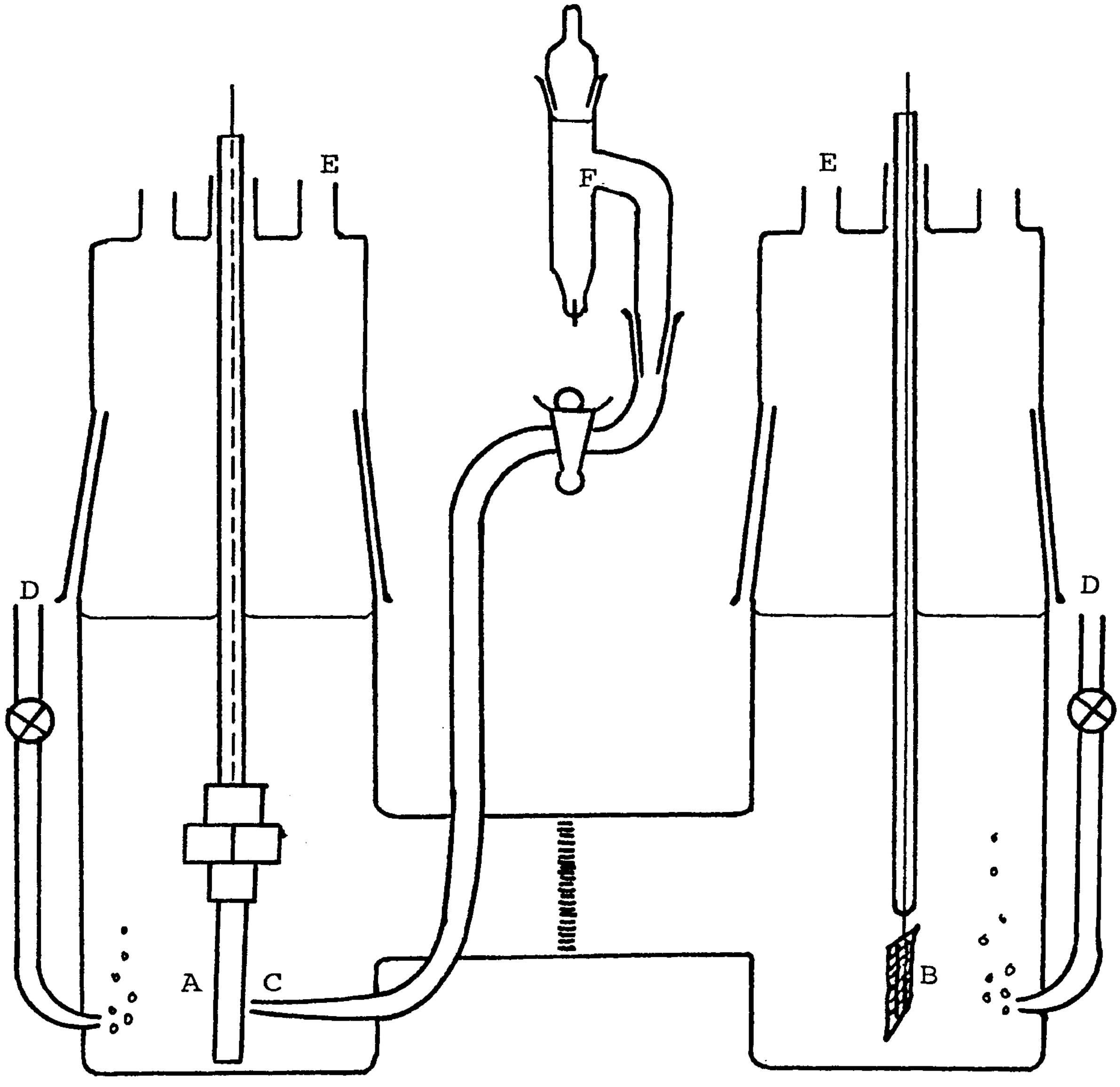
The usual pyrex H-cell was used with the solid (bismuth) cathode. The anodic and cathodic compartments (each 250 ml capacity) were also separated by a glass frit. A schematic diagram of this cell is shown in Figure 3.

b. Electrodes.

(1) Anode. The platinized-platinum anode was fabricated by folding a piece of platinum wire gauze on a platinum wire frame. It had a geometric area of 15 cm^2. The platinum wire lead was sealed in a glass tube. The electrode was platinized in a chloroplatinic acid solution to which a trace of lead acetate had been added.

(2) Cathodes.

(a) Mercury cathode. Triple-distilled instrument grade mercury was used as the cathode.



A - Bismuth cathode

B - Platinized-platinum anode

C - Luggin capillary

D - Nitrogen inlets

E - Nitrogen outlets

F - Reference electrode

Fifure 3. Electrolysis cell used with the solid cathode for studies of the cathodic reduction of maleic acid.

(b) Amalgam cathode. The amalgams were prepared by dissolving bismuth metal in mercury with slight heating (75°C) in a drying oven for 24 hours.

(c) Bismuth cathode. The side of a bismuth rod (0.75 cm diameter) was machined to give a flat surface of 3 cm^2. The surface was polished, then mounted in a teflon fitting which served as a holder. A diagram of the electrode is shown in Figure 4.

(3) Reference electrode. The reference electrode was connected to the cathodic compartment of the cells through a water-sealed stopcock and a Luggin capillary. It was a Hg/Hg_2SO_4 (1.0 N H_2SO_4) electrode (0.617 volt, SHE at 60°C) and was at room temperature.

3. Procedures.

a. Electrode activation.

(1) Solid electrode. The bismuth electrode was activated before each experiment by a cathodic polarization in 1 N H_2SO_4 along with a platinized-platinum anode at a current of 4 amperes for 4 minutes. The electrode usually became black upon passing the current. It was polished with a piece of paper towel until bright, then rinsed thoroughly with conductivity water and transferred into the cell.

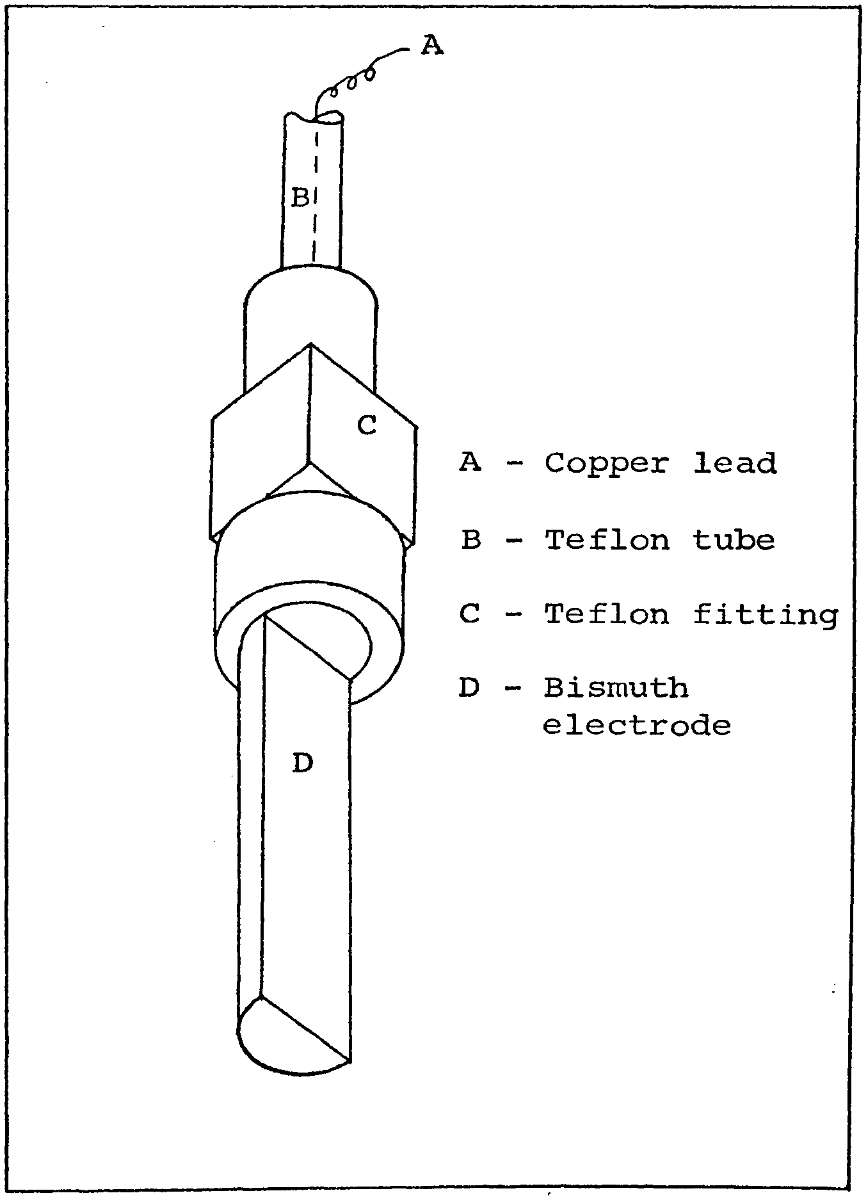


Figure 4. The bismuth electrode.

(2) Liquid electrode. Fresh mercury or amalgam was used for each experiment without further activation.

b. Potentiostatic experiments. Nitrogen purging was begun as soon as the cell was charged with solution. The distance between the cathode and the Luggin capillary tip was adjusted to a minimum to reduce the ohmic overpotential. The cathode potential was allowed to reach a steady state with no current flowing (rest potential), after which a predetermined potential (more negative than the rest potential) was applied and held constant by means of the potentiostat. When the current reached a steady state (less than 10 percent change per hour), the potential was decreased again by 20 to 200 mv as needed. This procedure was continued until a limiting value of current was reached.

4. Data and results. Current-potential relations were determined in electrolytes of various maleic acid concentration and pH as shown in Table IV. The electrolytes were solutions of H_2SO_4 and/or K_2SO_4 with the exception of the solution of pH 4 to which a small amount of KOH was added. The total sulfate concentration was held constant at 1.0 N. All pH's were measured at 60^oC.

TABLE IV

SOLUTIONS AND ELECTRODES USED IN THE INVESTIGATION OF THE CATHODIC REDUCTION OF MALEIC ACID

Electrode	Maleic acid concentration, gmole/liter				
	pH				
	0.3	1.1	1.8	2.7	4.0
Hg	0.03 0.01 0.003 0.001 0.0003	0.03	0.03	0.03	0.03
0.5% Bi(Hg)	0.03 0.003 0.0003		0.03	0.03	
5.0% Bi(Hg)	0.03 0.003 0.0003		0.03	0.03	
Bi	0.3 0.03 0.003 0.0003		0.03	0.03	

The rest potentials were usually obtained within 1 to 2 hours at open circuit. They were approximately 0.51 and 0.13 volts(SHE) for the mercury and bismuth-containing cathodes, respectively. The pH and maleic acid concentration had no noticeable effect on the rest potential.

The current-potential data have been tabulated in Appendix C and plotted in Figures 5 to 12. In each curve, there are three distinguishable regions: a residual current, a linear Tafel, and a limiting current region. The limiting currents were proportional to the maleic acid concentrations (see Figure 13). The residual currents with amalgams were dependent on the amount of dissolved bismuth (see Figure 14). The bismuth cathode had relatively large residual currents that were subtracted from subsequent currents to give corrected values. These results (i.e., the corrected current-potential relations) are shown in Figures 15 and 16.

On all cathodes, the Tafel slopes ($\partial V/\partial \log i$) were close to -2.3RT/F (-60 to -90 mv). The effect of maleic acid concentration at pH 0.3 was obtained by plotting log i against log C at constant potential. A linear relationship was obtained with a slope close to unity (see Figure 17).

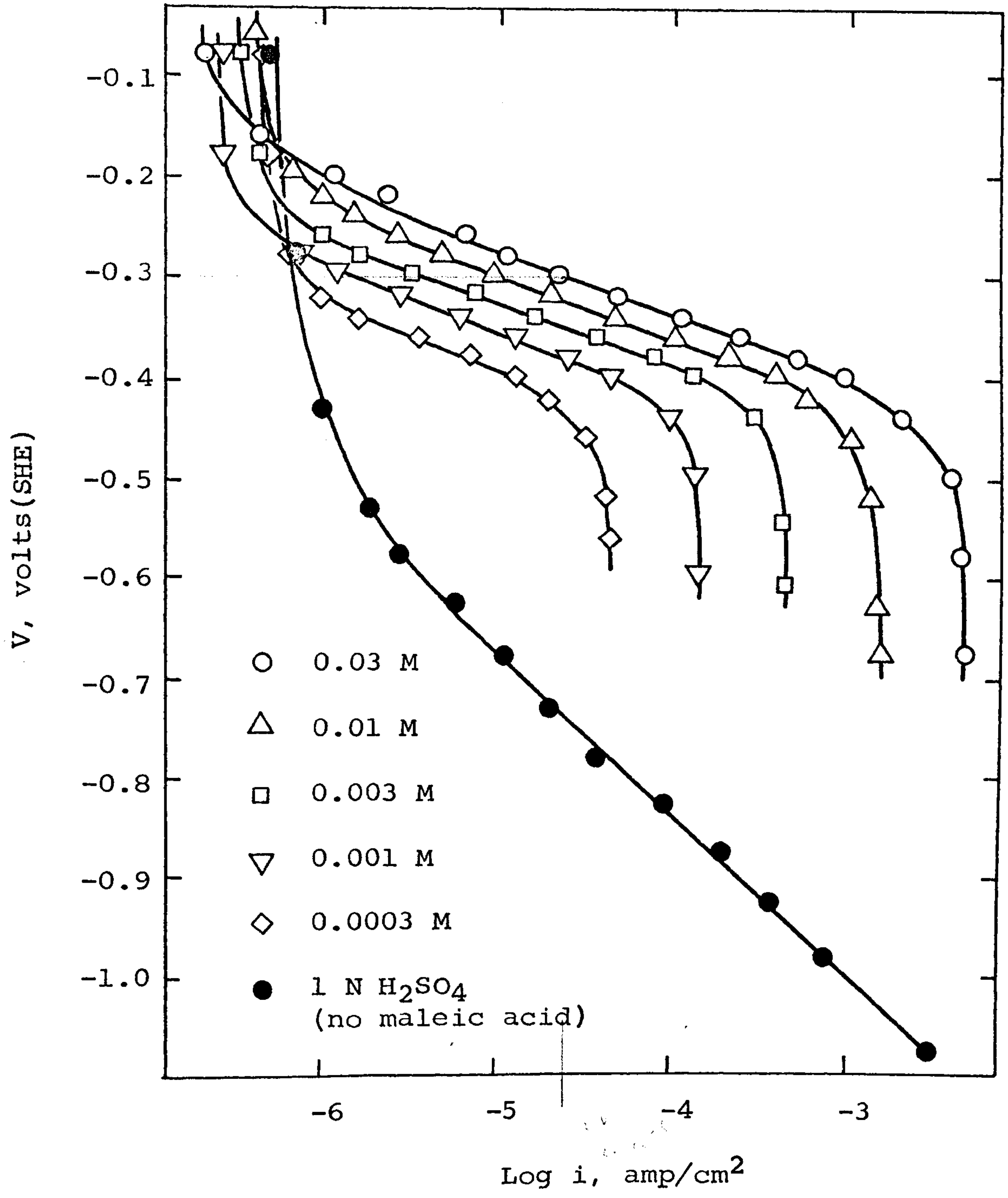


Figure 5. Polarization curves for the cathodic reduction of maleic acid on a Hg cathode at 60°C in 1 N H_2SO_4 (pH=0.3).

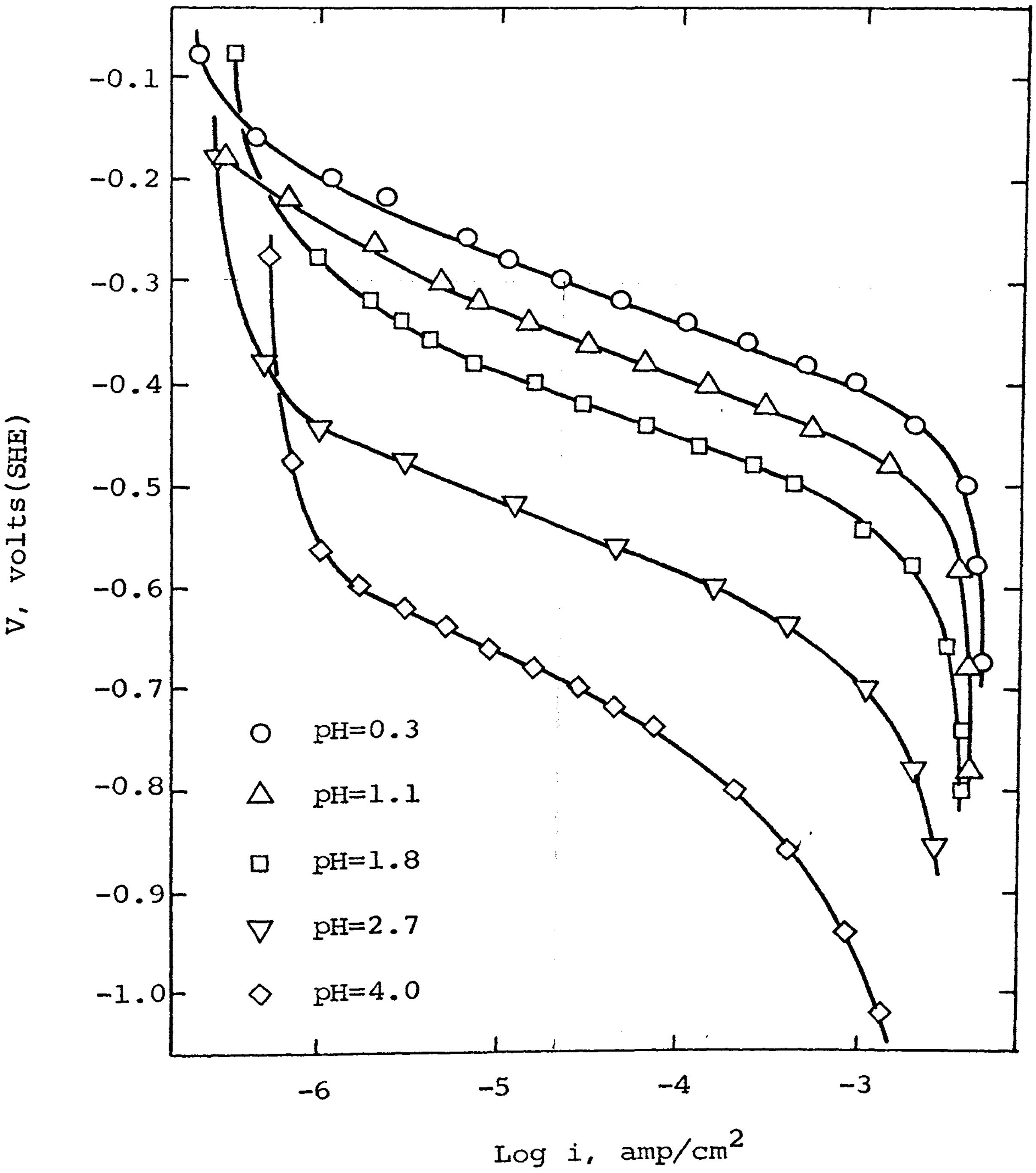


Figure 6. Polarization curves for the cathodic reduction of 0.03 M maleic acid on a Hg cathode at 60°C.

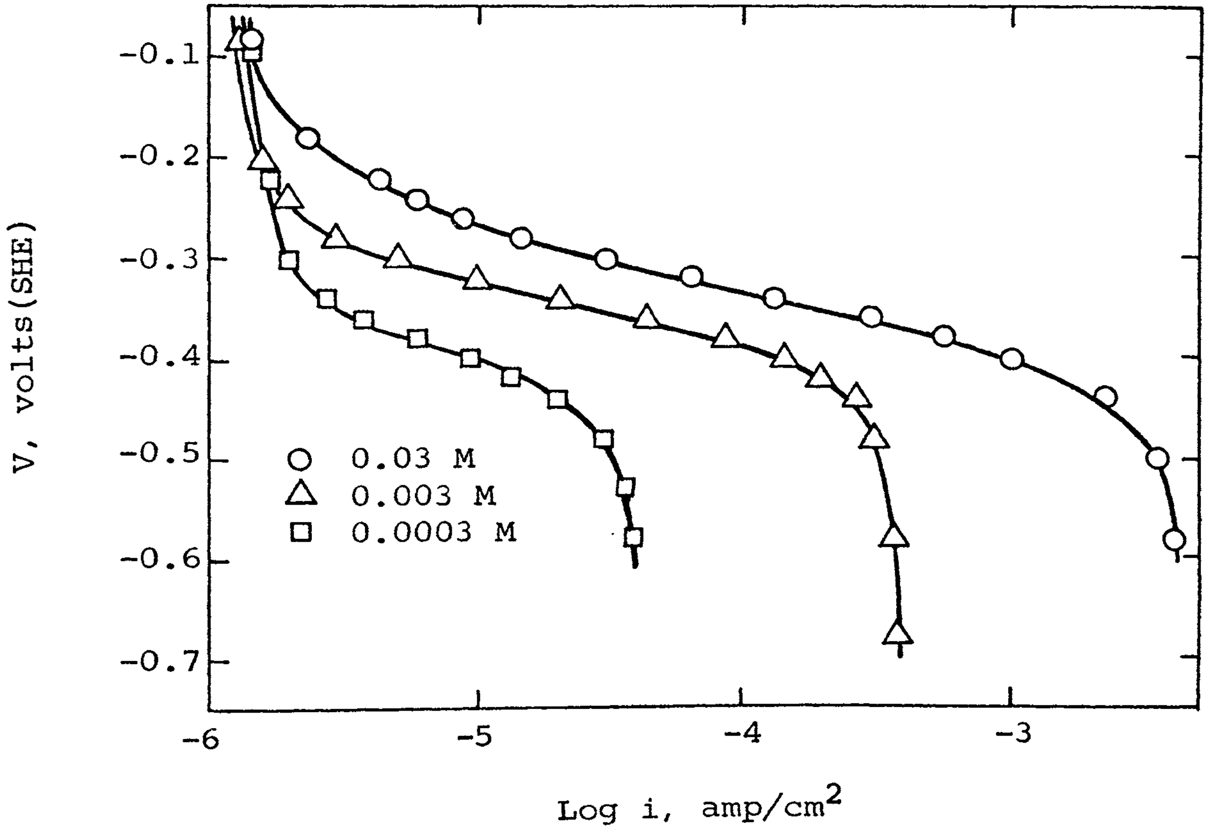


Figure 7. Polarization curves for the cathodic reduction of maleic acid on a 0.5% Bi(Hg) cathode at 60°C in 1 N H_2SO_4 (pH=0.3).

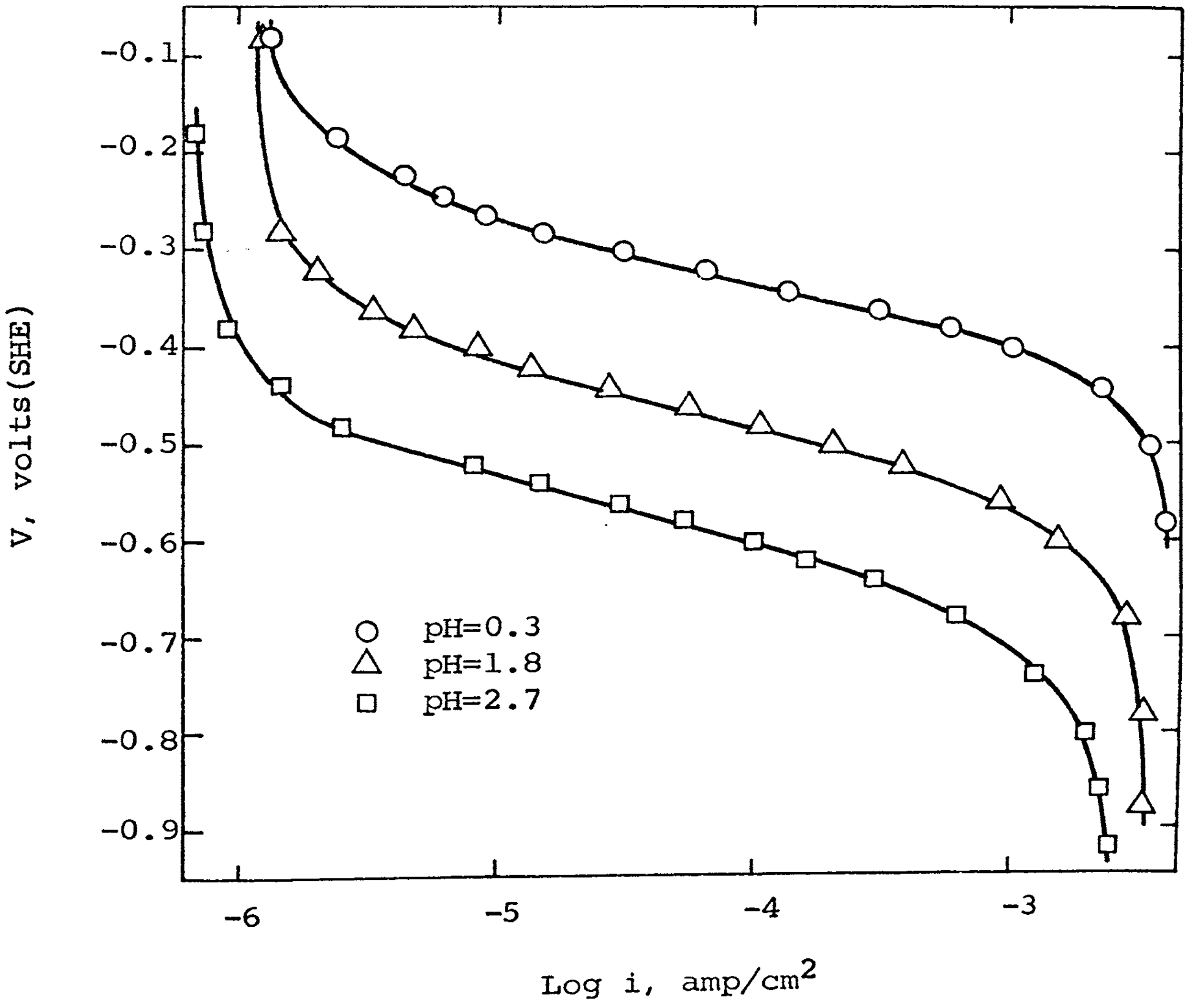


Figure 8. Polarization curves for the cathodic reduction of 0.03 M maleic acid on a 0.5% Bi(Hg) cathode at 60^{o}C.

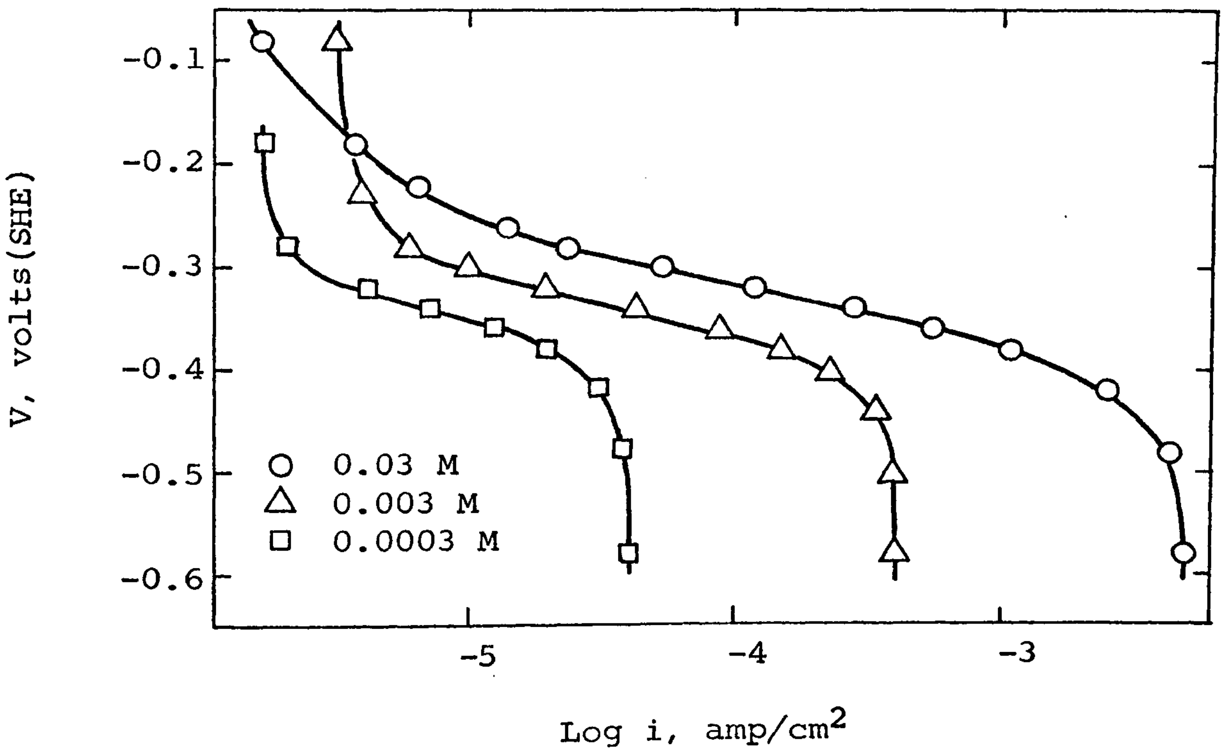


Figure 9. Polarization curves for the cathodic reduction of maleic acid on a 5% Bi(Hg) cathode at 60°C in 1 N H_2SO_4 (pH=0.3)

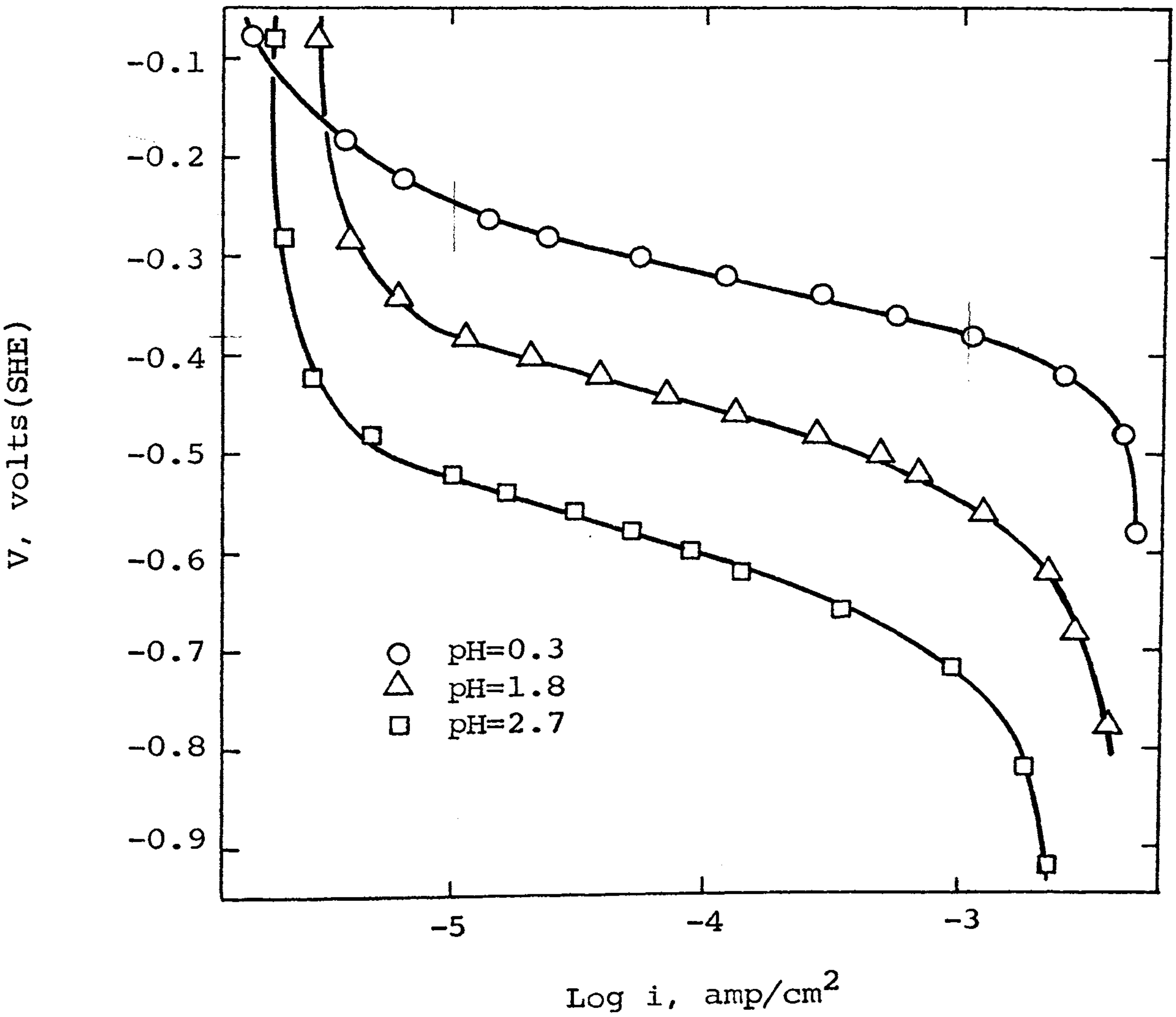


Figure 10. Polarization curves for the cathodic reduction of 0.03 M maleic acid on a 5% Bi(Hg) cathode at 60°C.

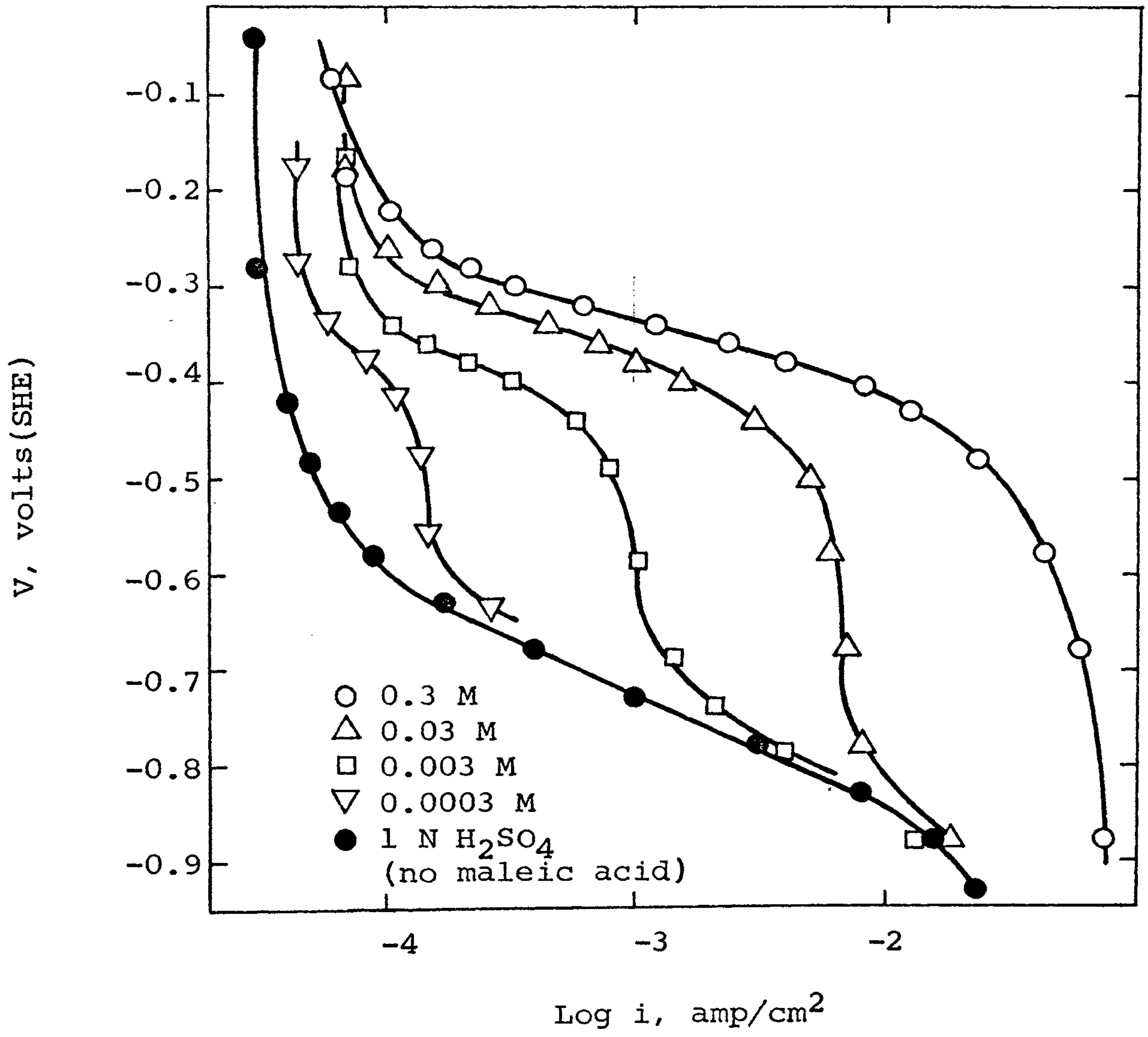


Figure 11. Polarization curves for the cathodic reduction of maleic acid on a Bi cathode at 60°C in 1 N H_2SO_4 (pH=0.3)

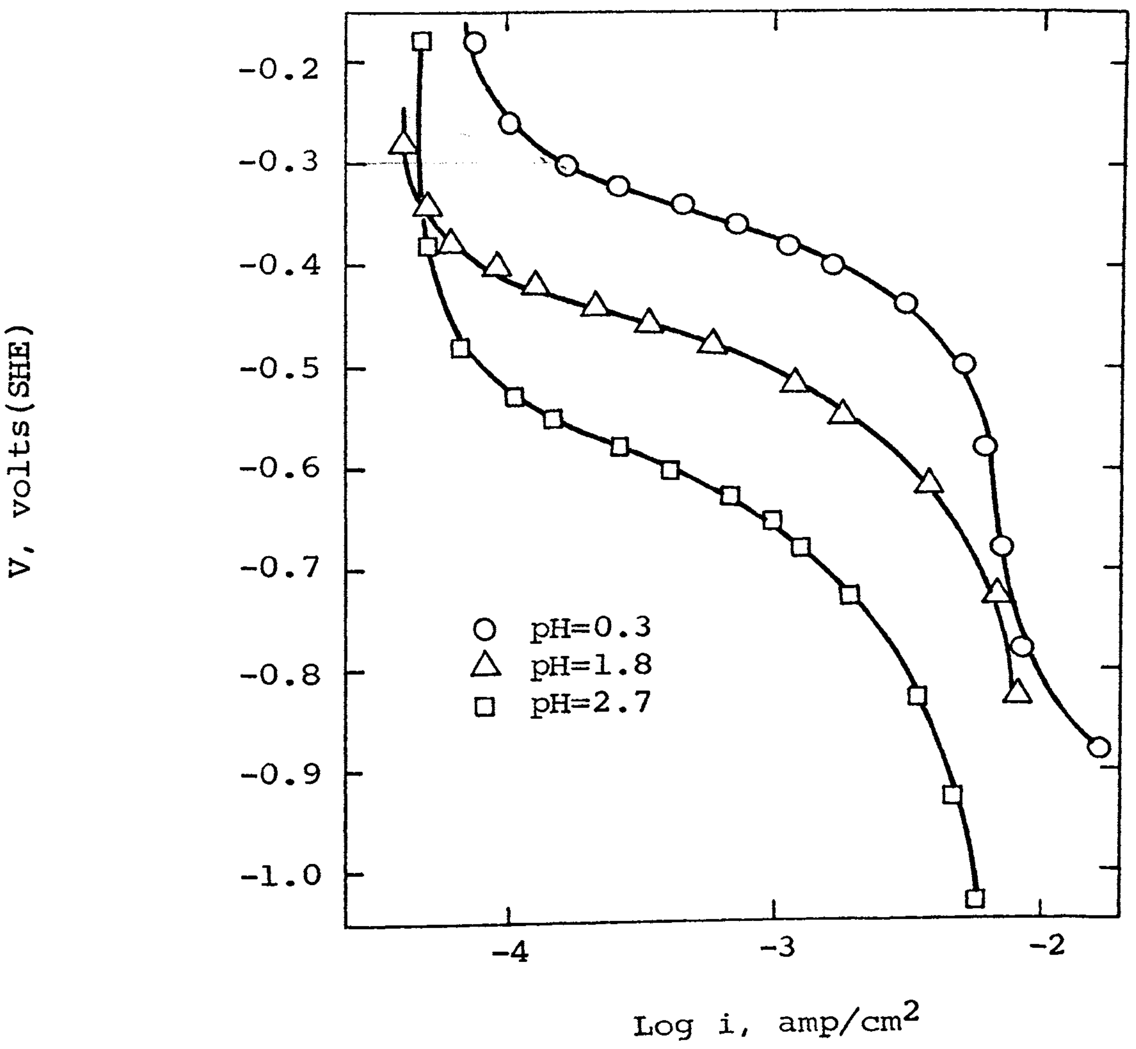


Figure 12. Polarization curves for the cathodic reduction of 0.03 M maleic acid on a Bi cathode at 60°C

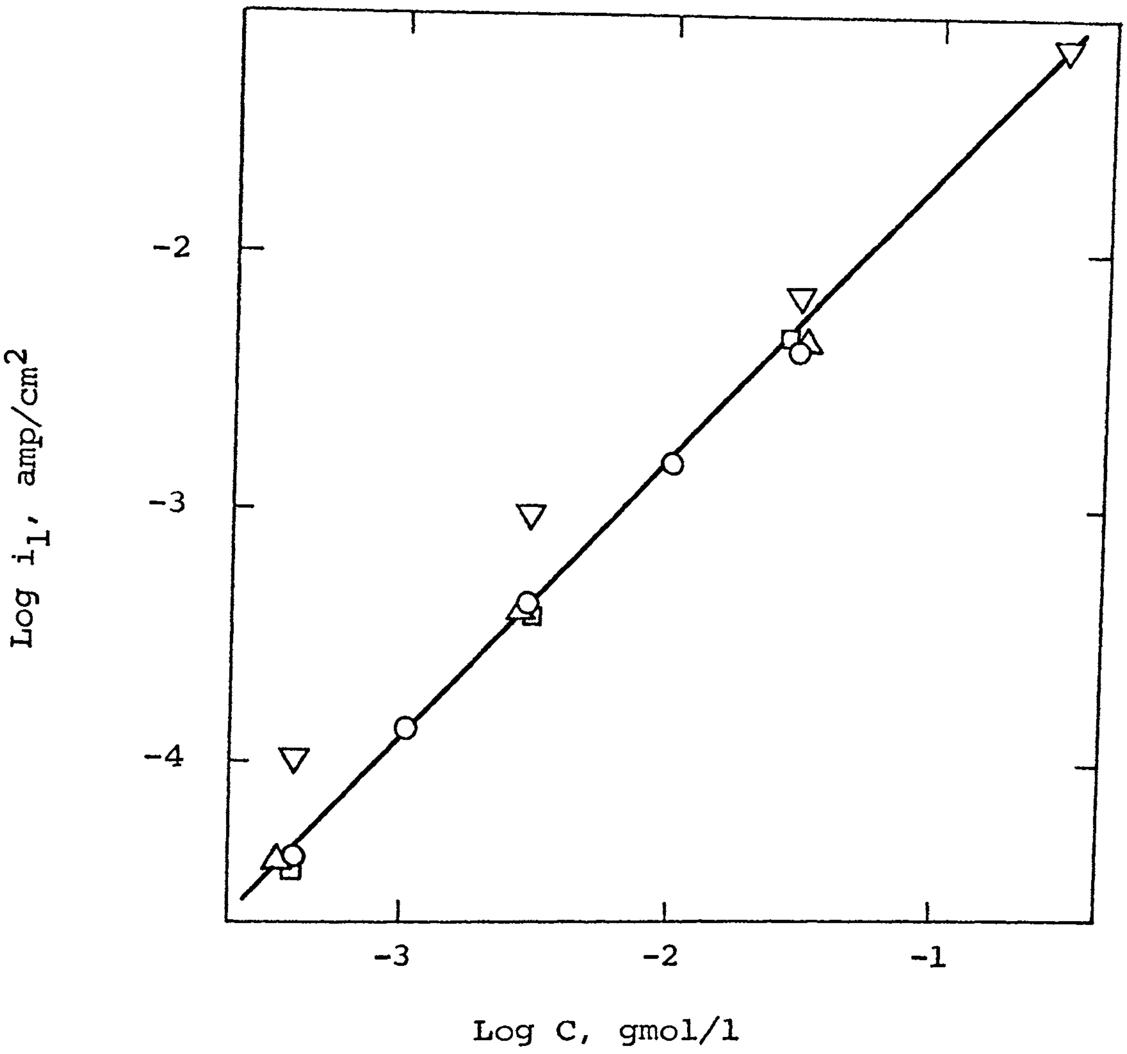


Figure 13. Relations between limiting current and maleic acid concentration for the cathodic reduction of maleic acid at 60°C in 1 N H_2SO_4 (pH=0.3) (○, Hg; △, 0.5% Bi; □, 5% Bi; ▽, Bi).

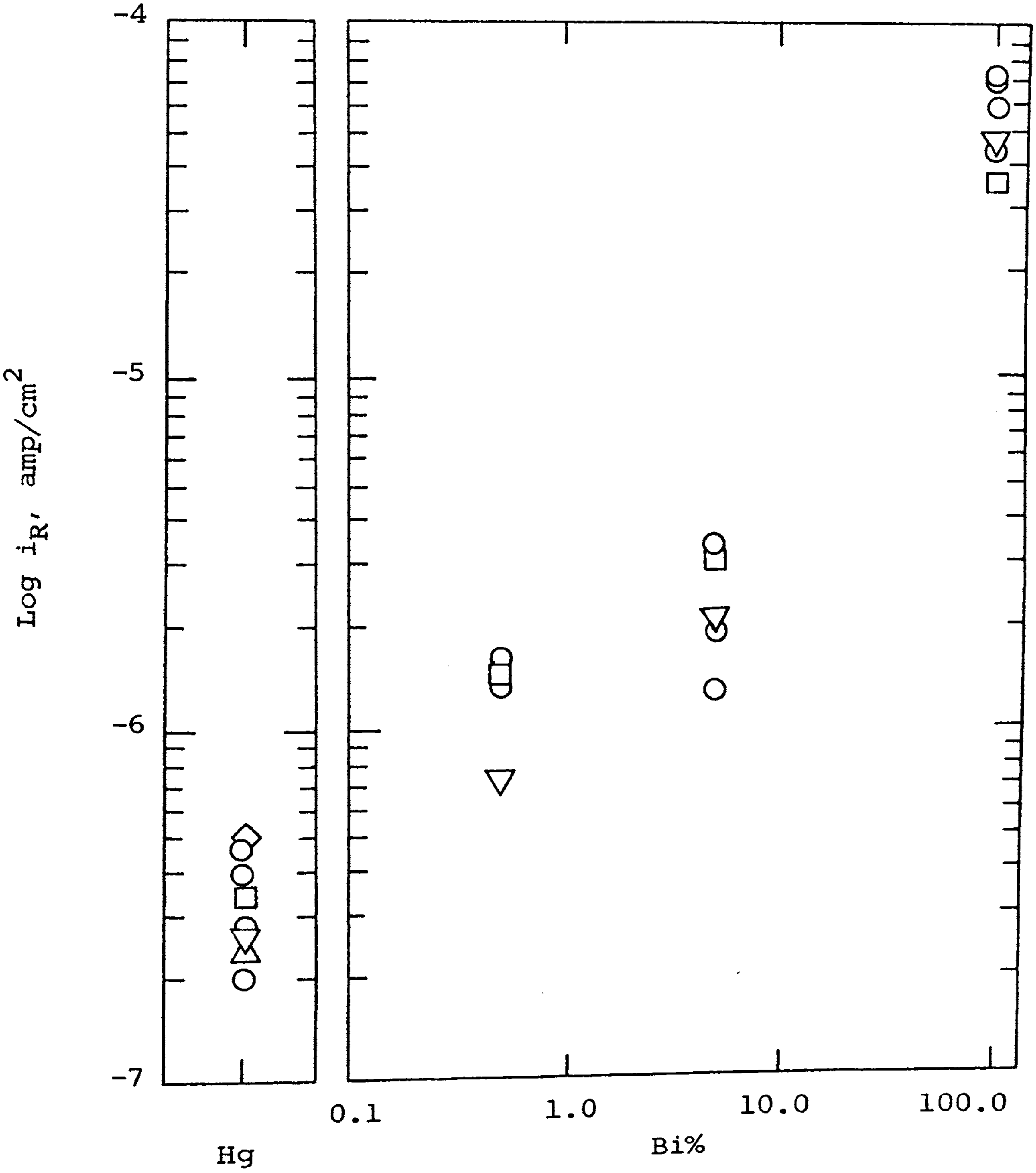


Figure 14. Relationships between the residual current and the amount of dissolved bismuth in the cathode for the reduction of maleic acid at 60°C. (○, pH=0.3; △, pH=1.1; □, pH=1.8; ▽, pH=2.7; ◇, pH=4.0)

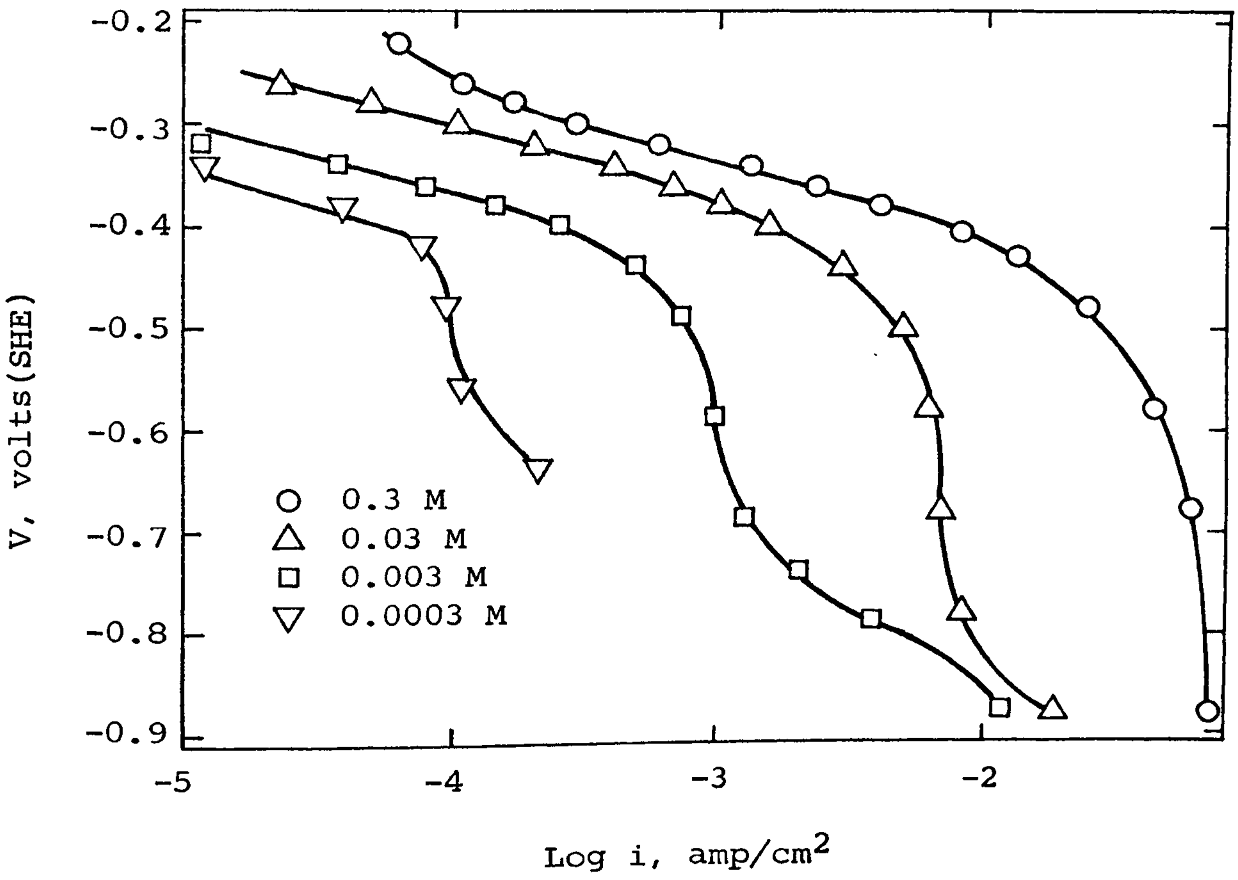


Figure 15. Corrected polarization curves for the cathodic reduction of maleic acid on a Bi cathode at 60°C in 1 N H_2SO_4 (pH=0.3).

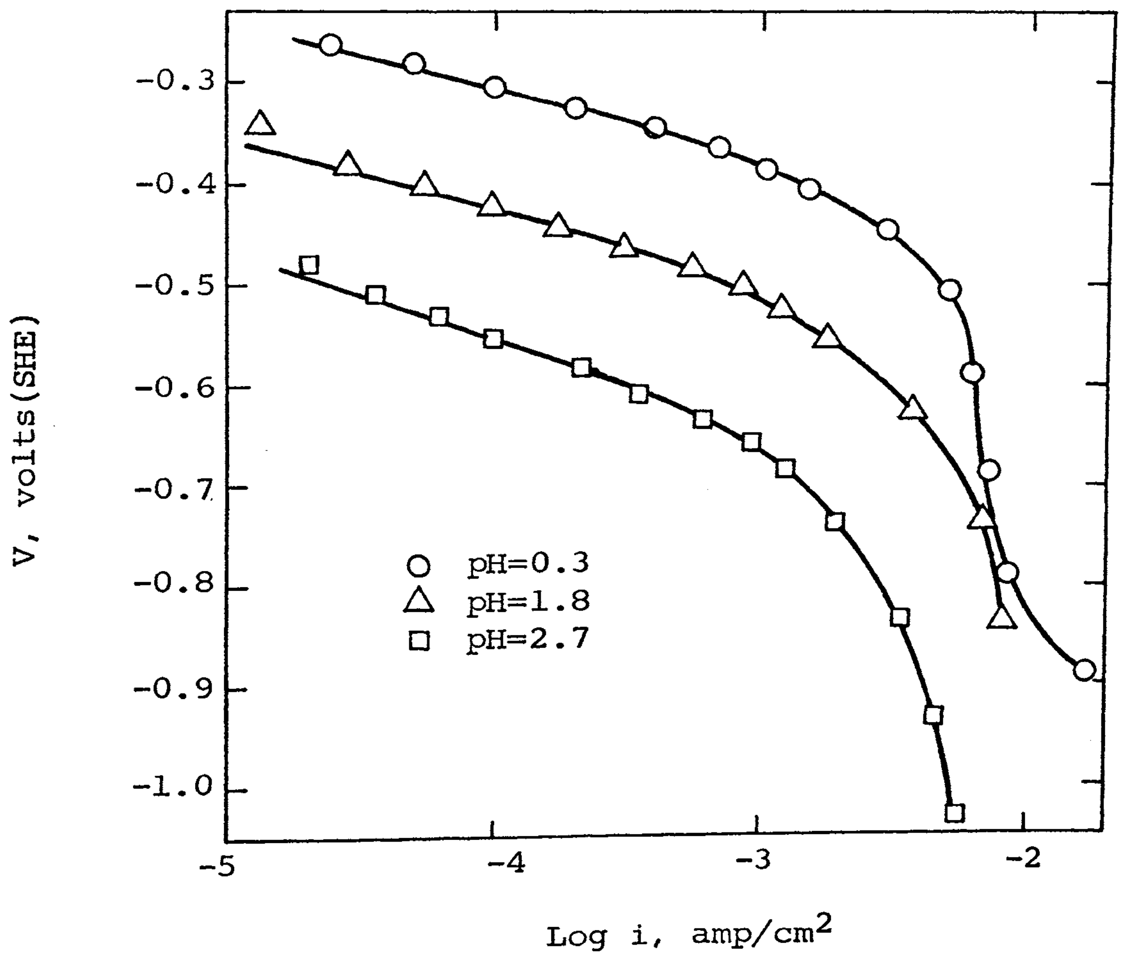


Figure 16. Corrected polarization curves for the cathodic reduction of 0.03 M maleic acid on a Bi cathode at 60°C.

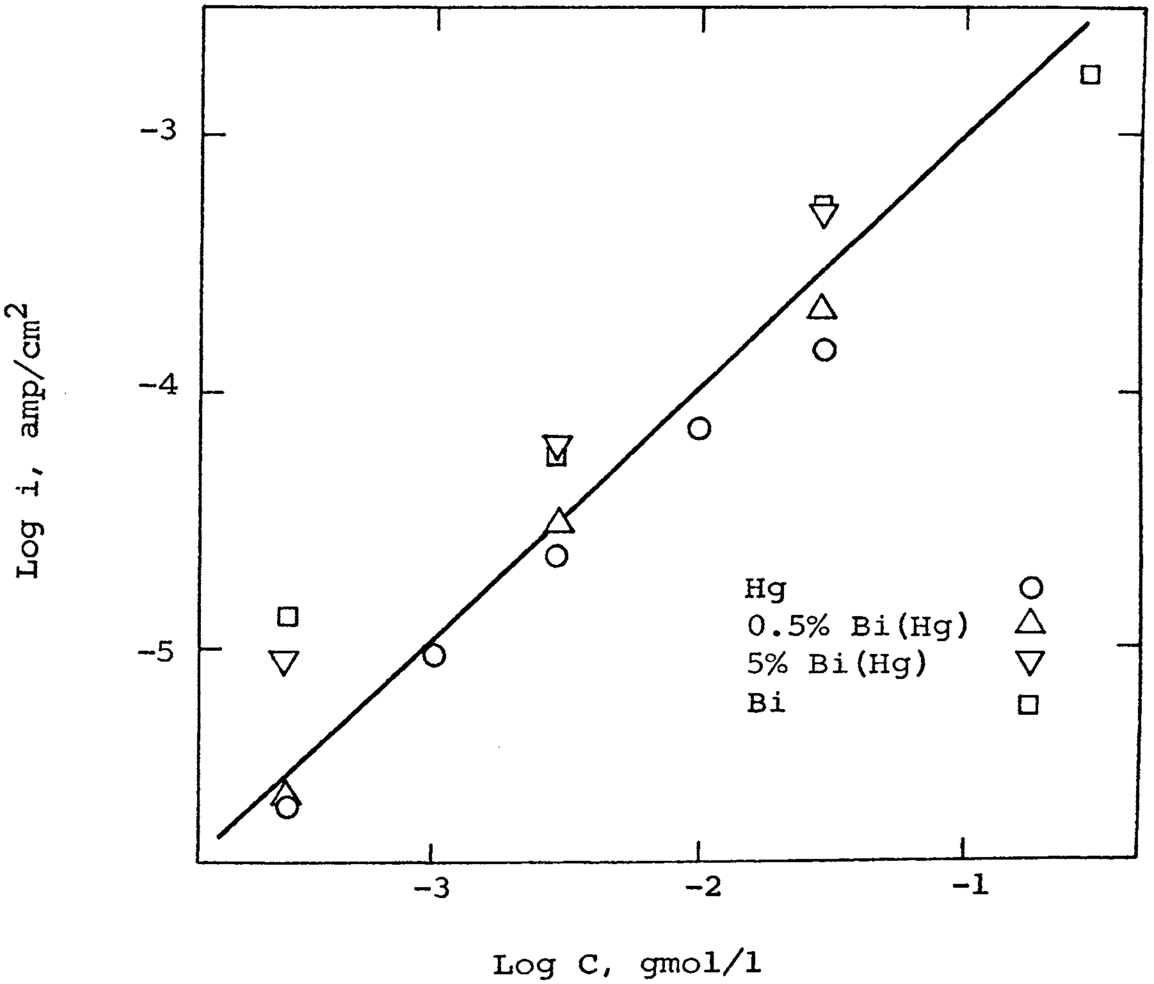


Figure 17. Effect of maleic acid concentration on current for the cathodic reduction of maleic acid at -0.35 volts(SHE) and 60°C in 1 N H_2SO_4 (pH=0.3).

The pH effect on the reaction rate was negative, i.e., $\partial \log i/\partial \mathrm{pH} < 0$. A quantitative interpretation of these relationships will be given in the discussion section.

B. Current-Temperature Studies

1. Materials and apparatus. The materials and apparatus used in this section were the same as those in the current-potential studies.

2. Procedure. The procedure followed was the same as used in the current-potential studies except that temperature instead of potential was the variable. The temperature was first held constant with the cathode polarized at a given potential within the linear Tafel region. When the current had reached a steady value, the temperature was decreased by 5 C°. The temperature was varied from 75 to 50°C in this manner.

3. Data and results. Three temperature studies were made for each electrode, two at pH 0.3 and one at pH 2.7. The data are tabulated in Appendix C. Arrhenius plots were prepared and are shown in Figures 18 to 21. The resulting apparent activation energies are given in Table V and have been plotted in Figure 22 as a function of potential. The variation of activation energy with potential was about 28 Kcal/volt.

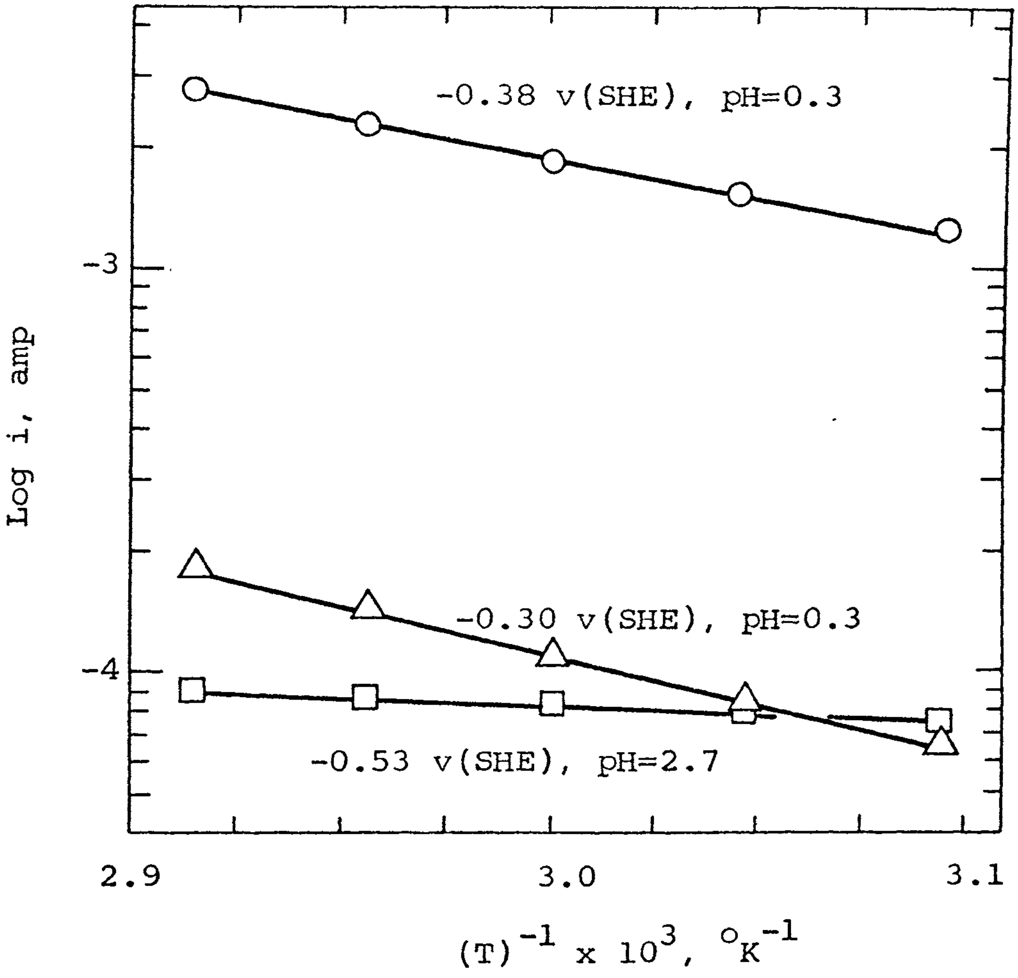


Figure 18. Arrhenius plots for the cathodic reduction of 0.03 M maleic acid on a Hg cathode.

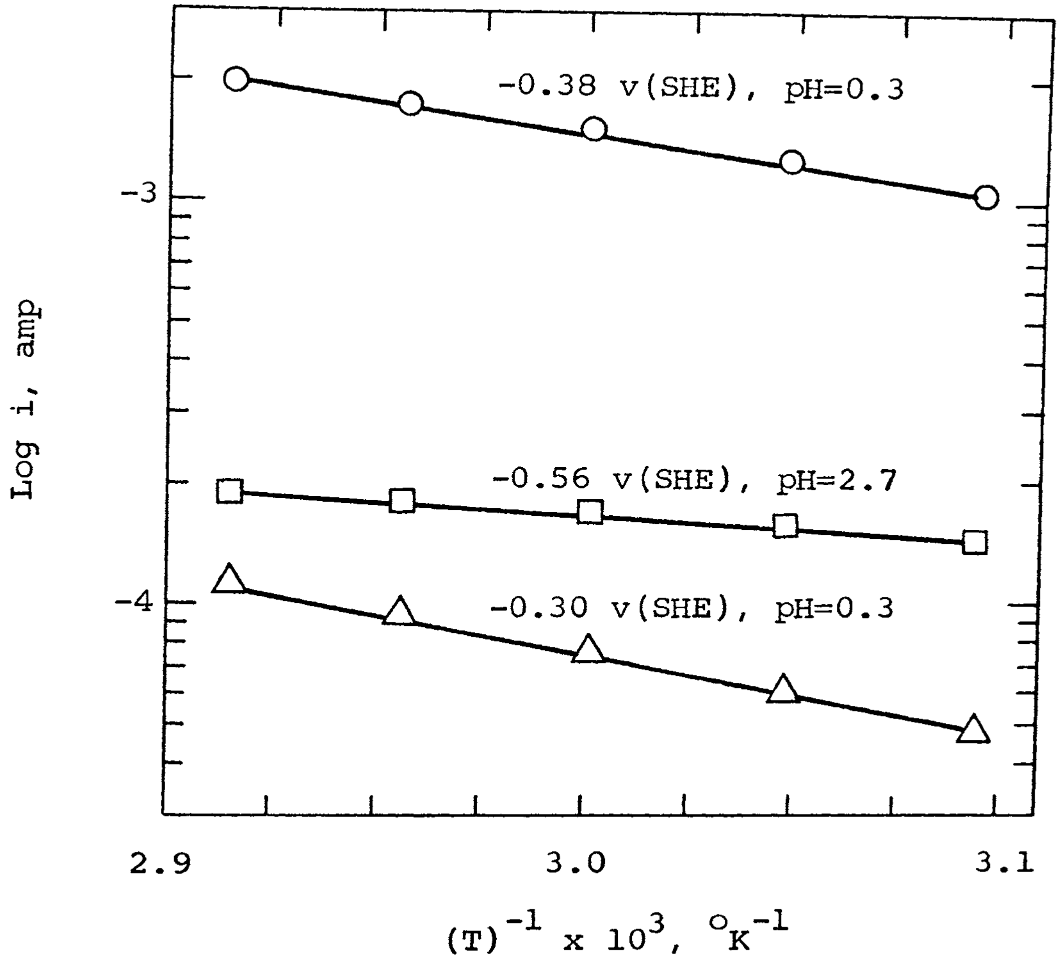


Figure 19. Arrhenius plots for the cathodic reduction of 0.03 M maleic acid on a 0.5% Bi(Hg) cathode.

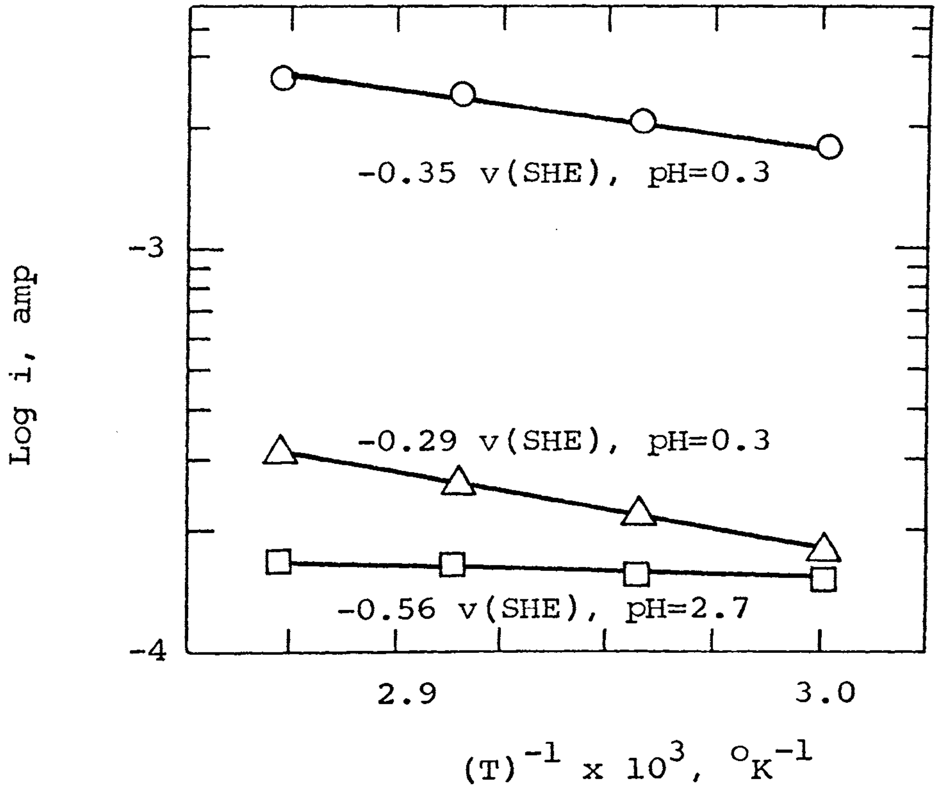


Figure 20. Arrhenius plots for the cathodic reduction of 0.03 M maleic acid on a 5% Bi(Hg) cathode.

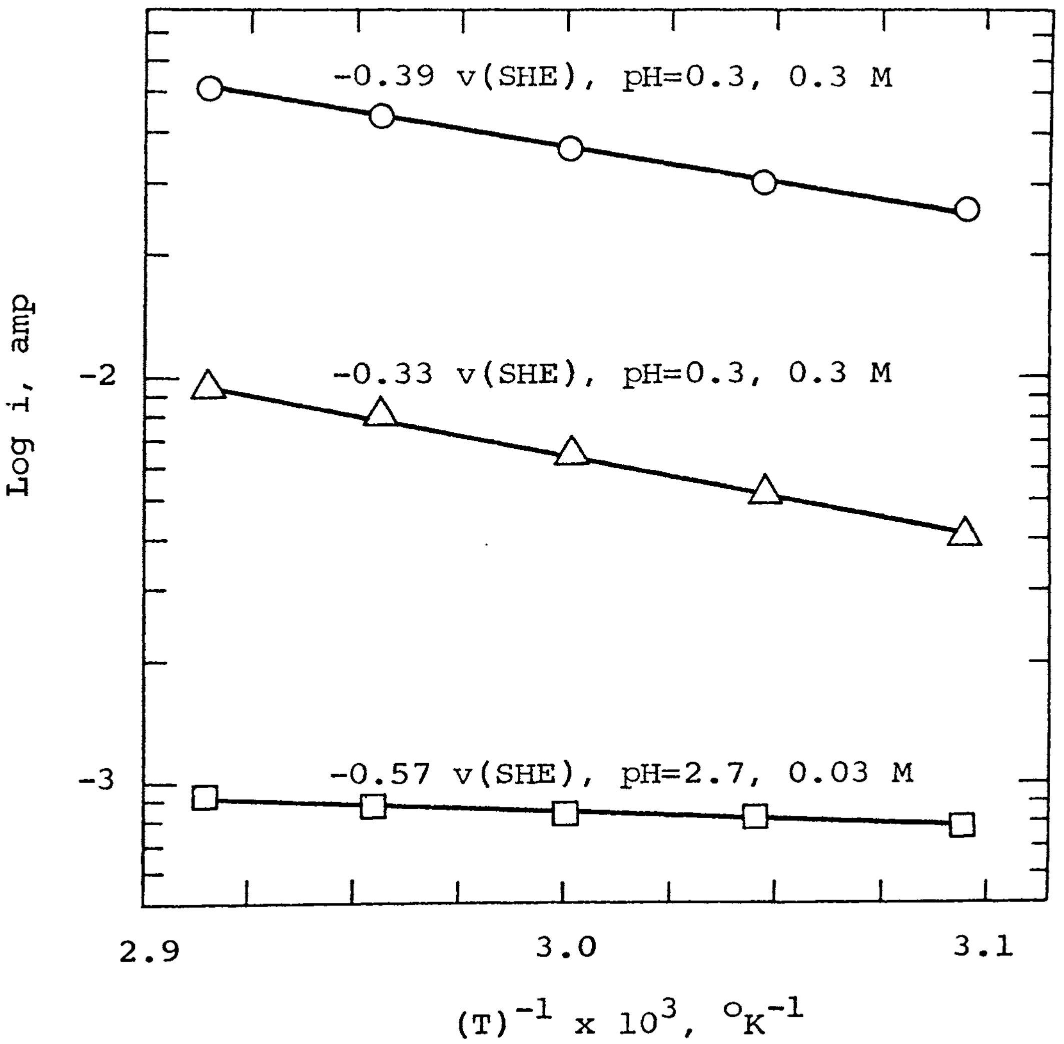


Figure 21. Arrhenius plots for the cathodic reduction of maleic acid on a Bi cathode

TABLE V

APPARENT ACTIVATION ENERGIES FOR THE CATHODIC REDUCTION OF MALEIC ACID

Electrode	Maleic acid conc	pH	Potential	Apparent activation energy
	gmol/l		volts(SHE)	Kcal
Hg	0.03	0.3	-0.30	10.9
Hg	0.03	0.3	-0.38	8.7
Hg	0.03	2.7	-0.53	2.2
0.5% Bi(Hg)	0.03	0.3	-0.30	9.6
0.5% Bi(Hg)	0.03	0.3	-0.38	7.3
0.5% Bi(Hg)	0.03	2.7	-0.56	2.8
5% Bi(Hg)	0.03	0.3	-0.29	9.0
5% Bi(Hg)	0.03	0.3	-0.35	6.0
5% Bi(Hg)	0.03	2.7	-0.56	1.6
Bi	0.30	0.3	-0.33	9.3
Bi	0.30	0.3	-0.39	7.5
Bi	0.03	2.7	-0.57	2.0

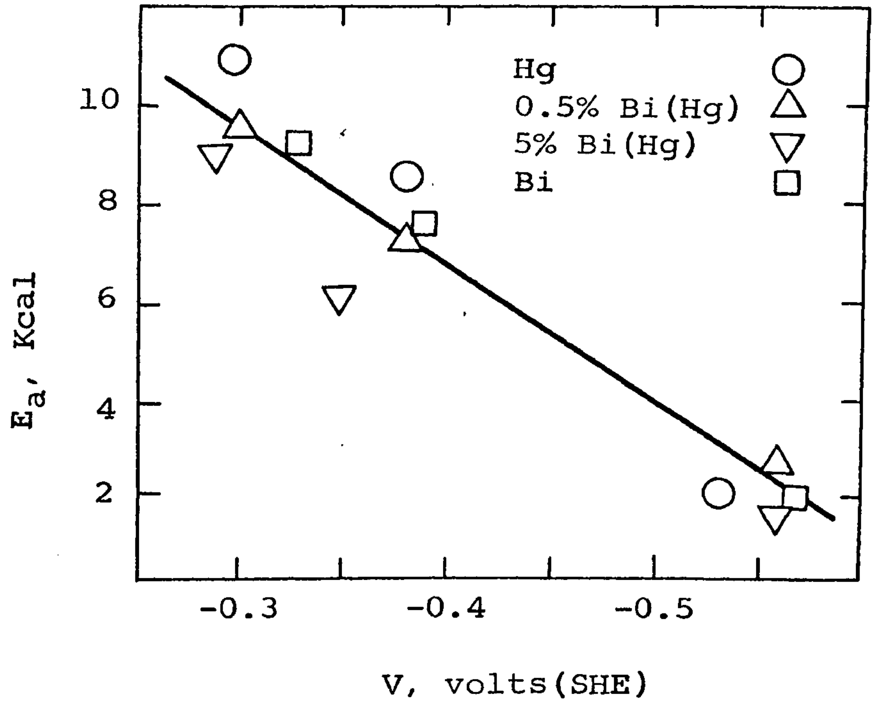


Figure 22. The effect of potential on apparent activation energy for the cathodic reduction of maleic acid at 60°C.

C. Faradaic Efficiency Studies

1. Materials. The materials used in this section were the same as described previously.

2. Apparatus. The apparatus consisted of an electrolysis cell, a d.c. power supply, a variable resistor, an ammeter, a recorder, and an electrometer. A diagram illustrating the arrangement is shown in Figure 23. A list of the equipment is included in Appendix B.

Figure 24 shows the cell used with liquid cathodes. The cathodic compartment was a glass jar of about 350 ml volume. It had a nitrogen inlet, a water-sealed gas outlet, and was fitted with a Luggin capillary. A platinum wire sealed in a glass tube was immersed into the cathode at the bottom of the compartment and served as a lead. The anodic compartment was a pyrex immersion filter tube with a fritted-glass disc on the bottom.

Figure 25 shows the cell used with the bismuth cathode. The cathodic compartment was a 80 ml test tube sealed with a teflon-lined cork. The anodic compartment was a gas dispersion tube which had a fritted-glass bottom.

A platinized-platinum anode was used with both cells. The anodic compartments were continuously purged with nitrogen during the experiments. The water-bath tempera-

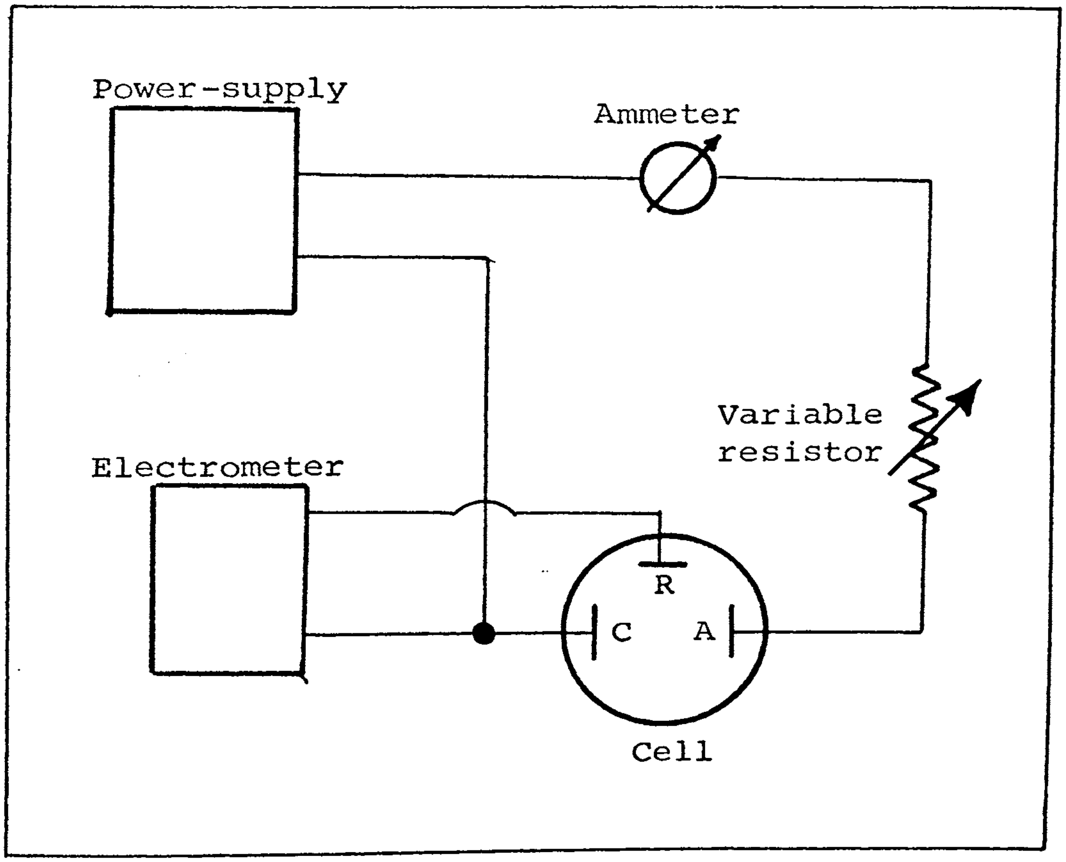
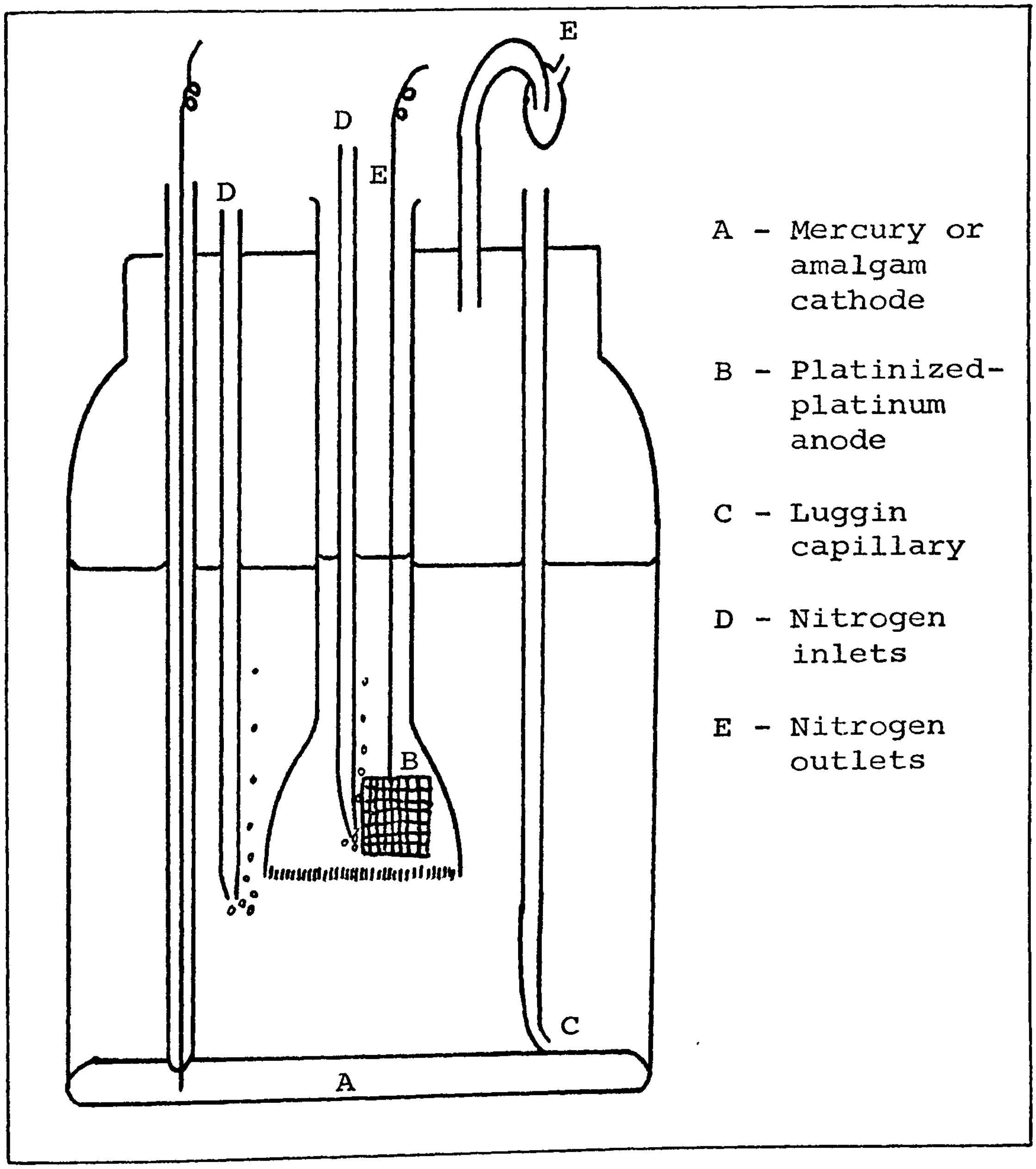


Figure 23. Diagram of the apparatus used for the faradaic efficiency studies of the cathodic reduction of maleic acid.



A - Mercury or amalgam cathode

B - Platinized-platinum anode

C - Luggin capillary

D - Nitrogen inlets

E - Nitrogen outlets

Figure 24. Electrolysis cell used with the liquid cathodes for the faradaic efficiency studies of the cathodic reduction of maleic acid.

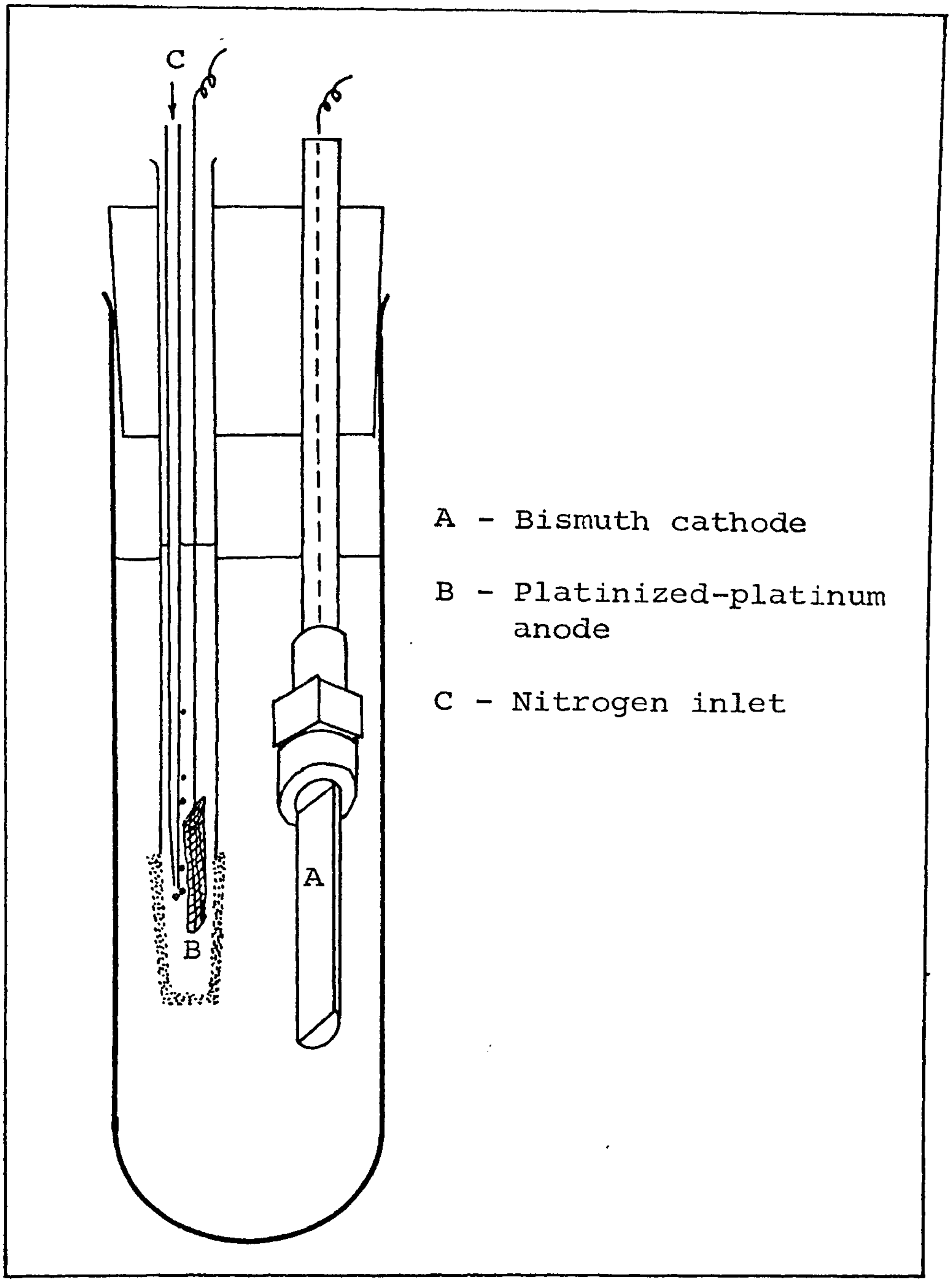


Figure 25. Electrolysis cell used with a solid cathode for the faradaic efficiency studies of the cathodic reduction of maleic acid.

ture was controlled at 60 ± 0.2°C.

3. Procedure. The initial portion of the experiments were the same as for the potentiostatic experiments. To begin an electrolysis, the power-supply was turned on and the current adjusted to a desired value by varying the applied voltage and/or the variable resistor. The current was kept constant by keeping the total resistance of the circuit much larger than that of the cell. After a predetermined time interval had elapsed, the current was stopped and the electrolyte analyzed for succinic acid.

Geopfert's[26] method was used to determine the quantity of succinic acid formed during the electrolysis. With this procedure, the remaining maleic acid was oxidized with $KMnO_4$ and the resulting succinic acid extracted with ether. After extraction, the residual aqueous phase was discarded and some distilled water added to the ether phase. The succinic acid was quantitatively transferred into the aqueous solution by heating to remove the ether. The pH of the solution was then adjusted to 6.5-7.0 and an excess (known) amount of $AgNO_3$ added. The succinic acid was precipitated as silver succinate and the excess silver ion titrated with NH_4SCN according to the Volhard method.[27] A detailed procedure is given in Appendix D. Based on the analysis of eight known samples, the accuracy of the analysis was 100 ± 5 percent.

4. Data and results. The faradaic efficiencies were determined for a maleic acid concentration of 0.03 M at pH's of 0.3 and 2.7 for each cathode. The results are reported in Table VI. All studies were made at potentials in the upper portion of the linear Tafel region at 60°C. The efficiency was defined as the ratio of the actual amount of succinic acid produced to the theoretical amount according to the following reaction:

$$\mathrm{HOOC{-}CH{=}CH{-}COOH} + 2\mathrm{H}^+ + 2e \rightleftharpoons \mathrm{HOOC{-}CH_2{-}CH_2{-}COOH}$$

The theoretical amount produced during an electrolysis was calculated using Faraday's law

$$W = \frac{I\ t\ A}{z\ F}$$

where, W = amount of succinic acid produced, gm

I = current, amp

t = time, sec

A = formula weight of succinic acid = 118

z = electrons transferred = 2

F = Faraday's constant = 96,500 coul/g-equiv

The analytical data and sample calculations are given in Appendix D.

TABLE VI

EFFICIENCY STUDIES FOR THE CATHODIC REDUCTION OF MALEIC ACID (0.03 M) TO SUCCINIC ACID AT 60°C

Electrode	pH	I x 10^3	Time	Efficiency
		amp*	hrs	percent
Hg	0.3	5.5	32.13	97
Hg	2.7	2.5	66.50	89
0.5% Bi(Hg)	0.3	10.0	18.13	100
0.5% Bi(Hg)	2.7	3.5	50.80	87
5.0% Bi(Hg)	0.3	14.5	13.48	97
5.0% Bi(Hg)	2.7	3.5	52.25	89
Bi	0.3	7.0	5.35	102
Bi	2.7	4.0	9.50	86

* The cathode area was 33 cm^2 for liquid cathodes and 3 cm^2 for the solid cathode.

IV. DISCUSSION

In this section, the experimental results are discussed and a reaction mechanism consistent with the experimental observations is proposed. It consists of two parts: (1) summary and analysis of the experimental results, and (2) establishment of the reaction mechanism.

A. Summary and Analysis of the Experimental Results

1. Faradaic efficiencies. The faradaic efficiencies on all cathodes were close to 100 and 90 percent at pH's of 0.3 and 2.7, respectively (see Table VI). The efficiency appears to have a pH dependence that would indicate the formation of some by-products at pH 2.7. After several electrolyses, the electrolytes were analyzed with a flame-ionization gas chromatograph and only two peaks, corresponding to maleic and succinic acids, were found. No gas evolution was observed at the cathodes, although it is possible for appreciable hydrogen to be evolved with no visual evidence due to its solubility. The low currents (at the corresponding potentials) in solutions containing no maleic acid also indicate hydrogen evolution not to be responsible. (Any role of maleic acid as a depolarizer would probably also produce succinic acid and not reduce

the efficiency.) The absence of gas evolution from the cathode after electrolyses indicated that no K^+ ions were being discharged to form an amalgam. Thus, since the predominate (or possibly exclusive) product is succinic acid, the overall reaction will be represented as

$$HOOC\text{-}CH{=}CH\text{-}COOH + 2H^+ + 2e \rightleftharpoons HOOC\text{-}CH_2\text{-}CH_2\text{-}COOH$$

2. Residual current. The residual currents were thought to result from the reduction of impurities in the electrolyte. It was observed that their magnitudes with the amalgam cathodes were dependent on the bismuth concentration and were considerably higher than those with the mercury cathodes (see Figure 14). This suggested that some bismuth may have been dissolved while the rest potential was being established and later reduced to give the rather high residual currents. The presence of dissolved bismuth was confirmed when black free bismuth was formed upon treating several solutions with sodium stannite.[28]

3. Reversible potential, exchange current, and rest potential.

a. Reversible potentials. The reversible potentials are the ones that should be exhibited when the net current is zero. At this condition, the electrode reactions are at equilibrium and thermodynamic equations are applicable. The reaction concerned in this investigation was

$$C_4H_4O_4\ (aq) + 2H^+\ (aq) + 2e \rightleftharpoons C_4H_6O_4\ (aq) \qquad (1)$$

The standard free energies of formation at 25°C for maleic acid and succinic acid are reported as:[29]

Maleic acid (c)	-149.40 Kcal
Succinic acid (c)	-178.80 Kcal
Succinic acid (aq)	-178.51 Kcal

No data are available for maleic acid (aq). However, assuming that the free energy of formation of maleic acid (aq) is approximately equal to that of maleic acid (c) (as in the case for succinic acid), the standard reversible potential at 25°C can be calculated as

$$E^o_{298} = \frac{-\Delta G^o}{nF} \approx \frac{-178-(-149)}{(2)(23.06)} = 0.63 \text{ volts(SHE)}$$

The standard reversible potential at 60°C can be determined by

$$E^o_{333} = E^o_{298} + \Delta T(\partial E^o/\partial T) = E^o_{298} + \Delta T(\Delta S^o_{298}/nF)^*$$

The standard entropy of the reaction at 25°C, ΔS^o_{298}, is obtained from the relation

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

Using heat of combustion data[30], the standard heats of

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* Assuming that ΔS^o (or $\partial E^o/\partial T$) is constant over the temperature range 25-60°C.

formation at 60°C of maleic acid (c) and succinic acid (c) are calculated as -188.18 and -225.56 Kcal/mole, respectively. Assuming that the heats of solution of maleic and succinic acids are about equal or negligible as compared with their heats of formation, then

$$\Delta H^{o}_{298} = -225.56-(-188.18) = -37.38 \text{ Kcal}$$

$$\Delta S^{o}_{298} = \frac{\Delta H^{o} - \Delta G^{o}}{T} = \frac{-37.38-(-29)}{298} = -0.0285 \text{ Kcal}/{}^{o}\text{K}$$

Therefore

$$\partial E^{o}/\partial T = \Delta S^{o}/nF = \frac{-0.0285}{(2)(23.06)} = -0.0006 \text{ volt}/{}^{o}\text{K}$$

and

$$E^{o}_{333} = 0.63 + (35)(-0.0006) = 0.61 \text{ volt(SHE)}$$

The reversible potential can now be obtained with the Nernst equation

$$E = E^{o}_{333} - \frac{RT}{nF} \ln \frac{a_S}{a_M \, a^2_{H^+}}$$

$$= 0.61 + 0.033 \log a_M - 0.066 \text{ pH} - 0.033 \log a_S$$

where, a_M = activity of maleic acid
$\approx$ concentration of maleic acid

a_S = activity of succinic acid
$\approx$ concentration of succinic acid

At pH=0.3, a_M=0.03, and a_S ranging from 10^{-8} to 10^{-3}, the corresponding potentials are 0.80 to 0.64 volts(SHE).

b. Exchange currents. The exchange current is normally defined as the current density at the reversible potential assuming linear Tafel behavior in the potential region under consideration. By extrapolating the linear portion of the V-log i plots to the reversible potential, the exchange currents were determined to be 10^{-21} to 10^{-18} amp/cm^2.

c. Rest potentials. Barring any complicating factors, the rest potential for a reaction should be the same as the reversible potential. In this investigation, it was found that the rest potentials were approximately 0.51 and 0.13 volts(SHE) for the mercury and bismuth-containing cathodes, respectively. The difference between the rest and reversible values is probably due to the low exchange current of the maleic acid reduction reaction. Its smallness would allow many other reactions, including those involving impurities, to determine the potential. With the bismuth-containing cathodes, it should be noted that the observed rest potentials were in the vicinity of the reversible potential of the reaction[31]

$$Bi^{+3} + 3e \rightleftharpoons Bi$$

for which,

$$E^{o} = 0.215 + 0.197 \log(a_{Bi^{+3}}) \qquad \text{(at } 25^{o}\text{C)}$$

4. Tafel slopes. Current values in the Tafel region could be reproduced within 10 and 20 percent with the solid and liquid cathodes, respectively. The lengths of the linear regions depended on the magnitudes of the residual current, pH, and maleic acid concentration as indicated in Figures 5 to 12. On all cathodes, the Tafel slopes were close to -2.3RT/F (-60 to -90 mv).

5. Maleic acid concentration effect. Tafel curves for various maleic acid concentrations (0.0003 to 0.3 M) in 1 N H_2SO_4 are shown in Figures 5, 7, 11, and 15. Since H_2SO_4 is a considerably stronger acid than maleic, the pH of the electrolyte was not affected by the latter. For this case (pH=0.3), the dissociation of maleic acid over the entire maleic acid concentration range is essentially constant as indicated by the following equilibrium relation:*

$$\frac{(H^{+})\ (M^{-})}{(M)} = K_1$$

or

$$\frac{(M^{-})}{(M)} = \frac{K_1}{H^{+}} = \text{constant} \qquad (3)$$

Therefore, the same slopes ($\partial \log i/\partial \log C$) should result from log-log plots of current against either undissociated,

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* The second dissociation can be neglected at this pH.

dissociated, or the total maleic acid concentration. Such a plot involving the total maleic acid concentration is shown in Figure 17 which has a slope close to unity.

6. pH effect. With data from Figure 6 for the mercury cathode, the log-log plot of current versus pH at constant potential and total maleic acid concentration is not linear and has a slope changing from approximately -1 to -2 (see Figure 26). This nonlinearity can be resolved by taking the dissociation of maleic acid into account. It indicates the reacting species to be either the undissociated or dissociated acid whose concentrations are different from the total maleic acid concentration, especially at pH's greater than 0.3 (see Table VII).

To determine the pH effect, an indirect method which utilized the following rate expression was used:

$$i = k\ C_M^m\ C_{H^+}^n \exp(-FV/RT) \tag{4}$$

where, i = current density, amp/cm^2

k = rate constant

C_M = reacting maleic acid species concentration, gmol/l

m = reaction order of reacting maleic acid species = 1*

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* Determined in previous section.

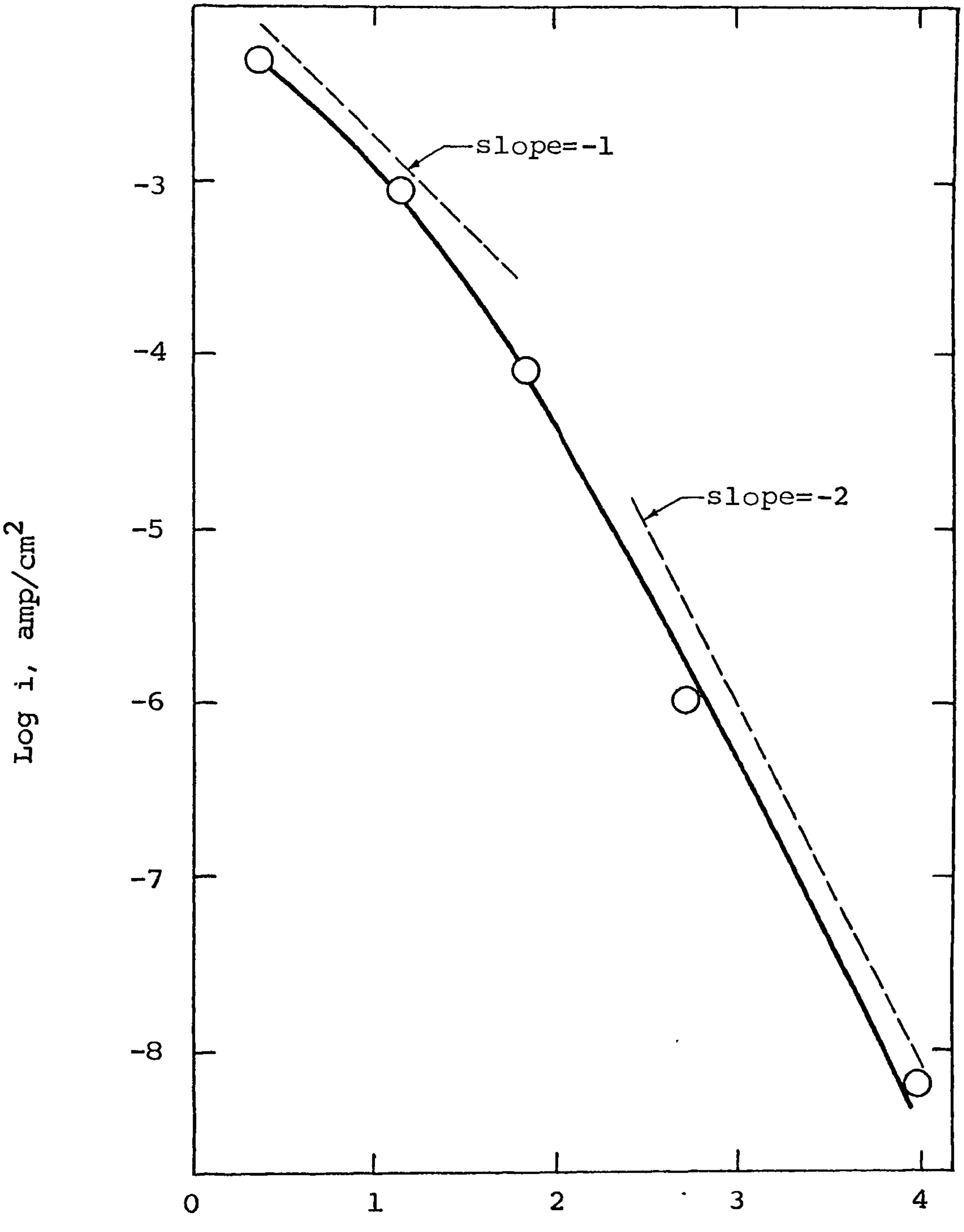

Figure 26. Effect of pH on current at constant potential (-0.45 v,SHE) and total maleic acid concentration (0.03 M) for the cathodic reduction of maleic acid on a Hg cathode.

C_{H^+} = hydrogen ion concentration, gmol/l

n = reaction order of hydrogen ion

F = Faraday's constant = 96,500 coul/g-equiv

R = gas constant

T = absolute temperature, $^{\circ}K$

V = potential, volt

With this method, the concentration of the individual maleic acid species at various pH's are needed. They have been calculated using the equilibrium relations and are tabulated in Table VII. The current densities (at constant potential) are plotted against the undissociated and singly-dissociated species concentrations as shown in Figures 27 and 28. Assuming that m in equation 4 is not a function of pH, parallel lines with slopes of unity can be drawn through each data point for the various pH's (see Figures 27 and 28) and the pH effect determined using data from these figures. Plots of current against pH at an arbitrary constant reacting species concentration are shown in Figures 29 amd 30. They are linear and have slopes of about -1 and -2, respectively. At this point, the rate expression can be represented by either

$$i = k_1 \; C_M C_{H^+} \exp(-FV/RT) \qquad (5)$$

or

$$i = k_2 \; C_{M^-} C_{H^+}^2 \exp(-FV/RT) \qquad (6)$$

TABLE VII

DEGREE OF DISSOCIATION OF MALEIC ACID AT VARIOUS pH[*]

pH	C_M/C_o	C_{M^-}/C_o	$C_{M^=}/C_o$
0.3	0.973	0.027	0.000
1.1	0.850	0.150	0.000
1.8	0.530	0.470	0.000
2.7	0.125	0.875	0.000
4.0	0.007	0.985	0.008

---

[*] Sample calculations are shown in Appendix E.

C_M = concentration of the undissociated maleic acid

C_{M^-} = concentration of the singly-dissociated maleic acid

$C_{M^=}$ = concentration of the doubly-dissociated maleic acid

C_o = total concentration of the maleic acid

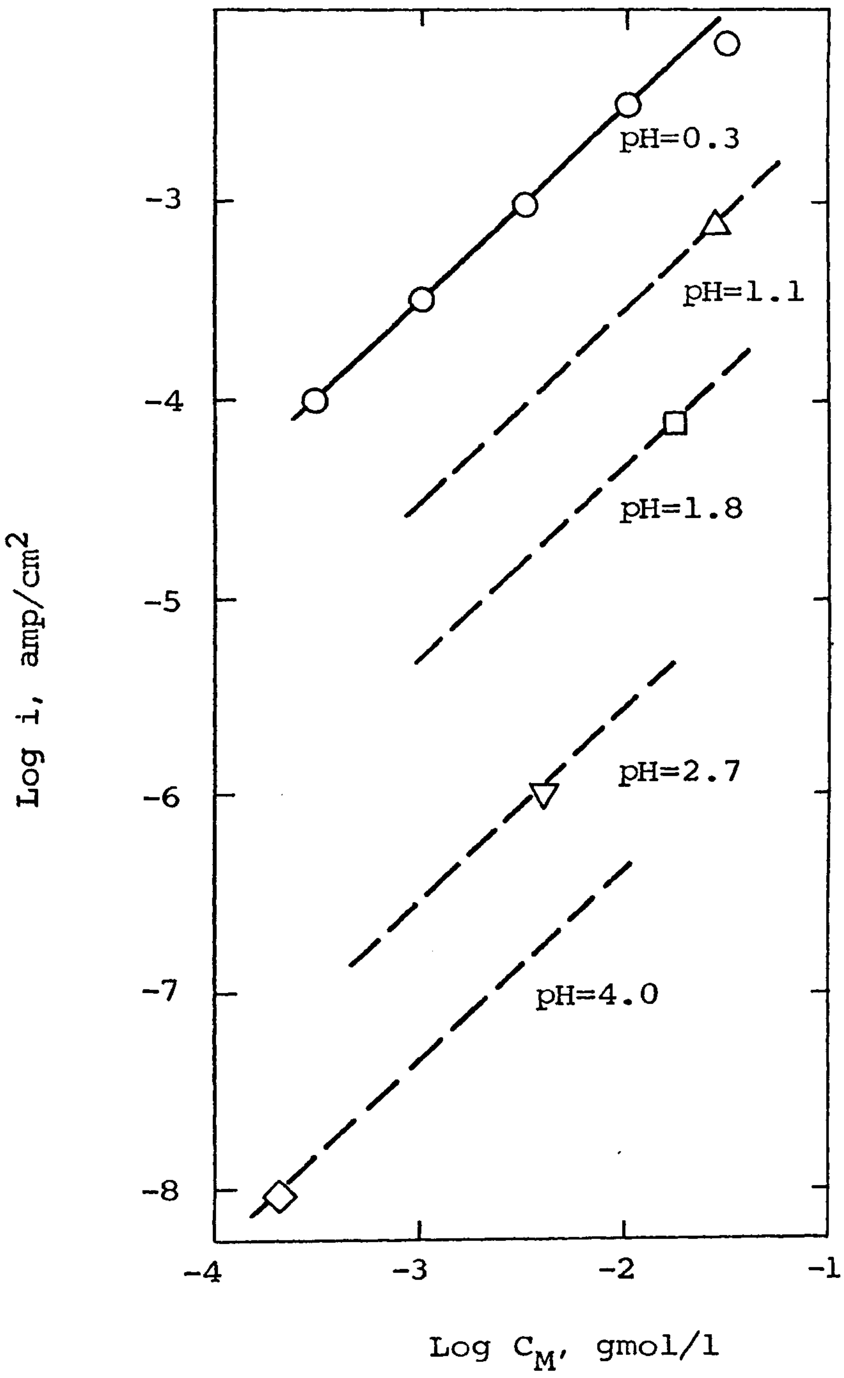

Figure 27. Plot of current against the undissociated maleic acid concentration at -0.45 v(SHE) for the cathodic reduction of maleic acid on a Hg cathode.

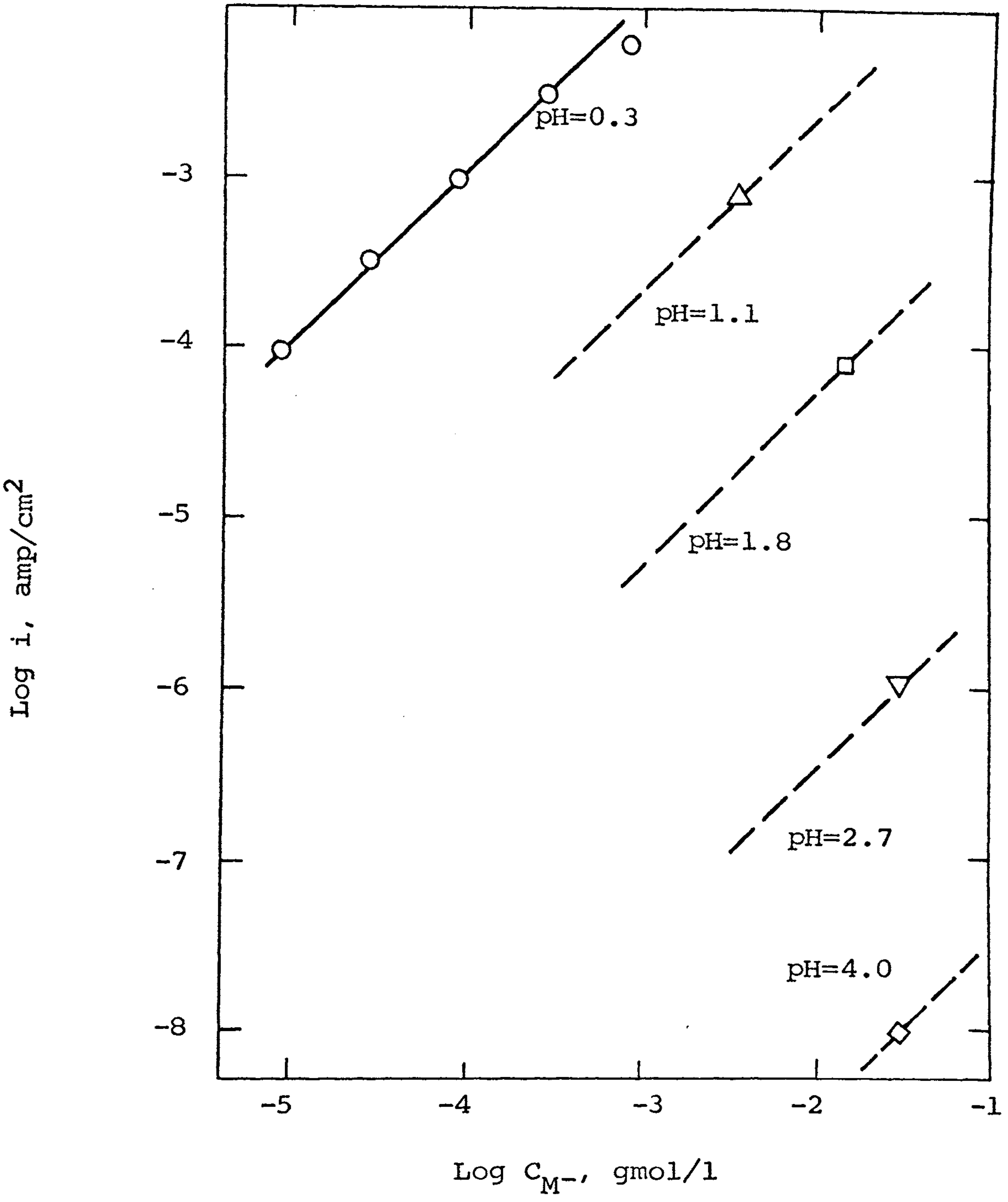

Figure 28. Plot of current against the singly-dissociated maleic acid concentration at -0.45 volts(SHE) for the cathodic reduction of maleic acid on a Hg cathode.

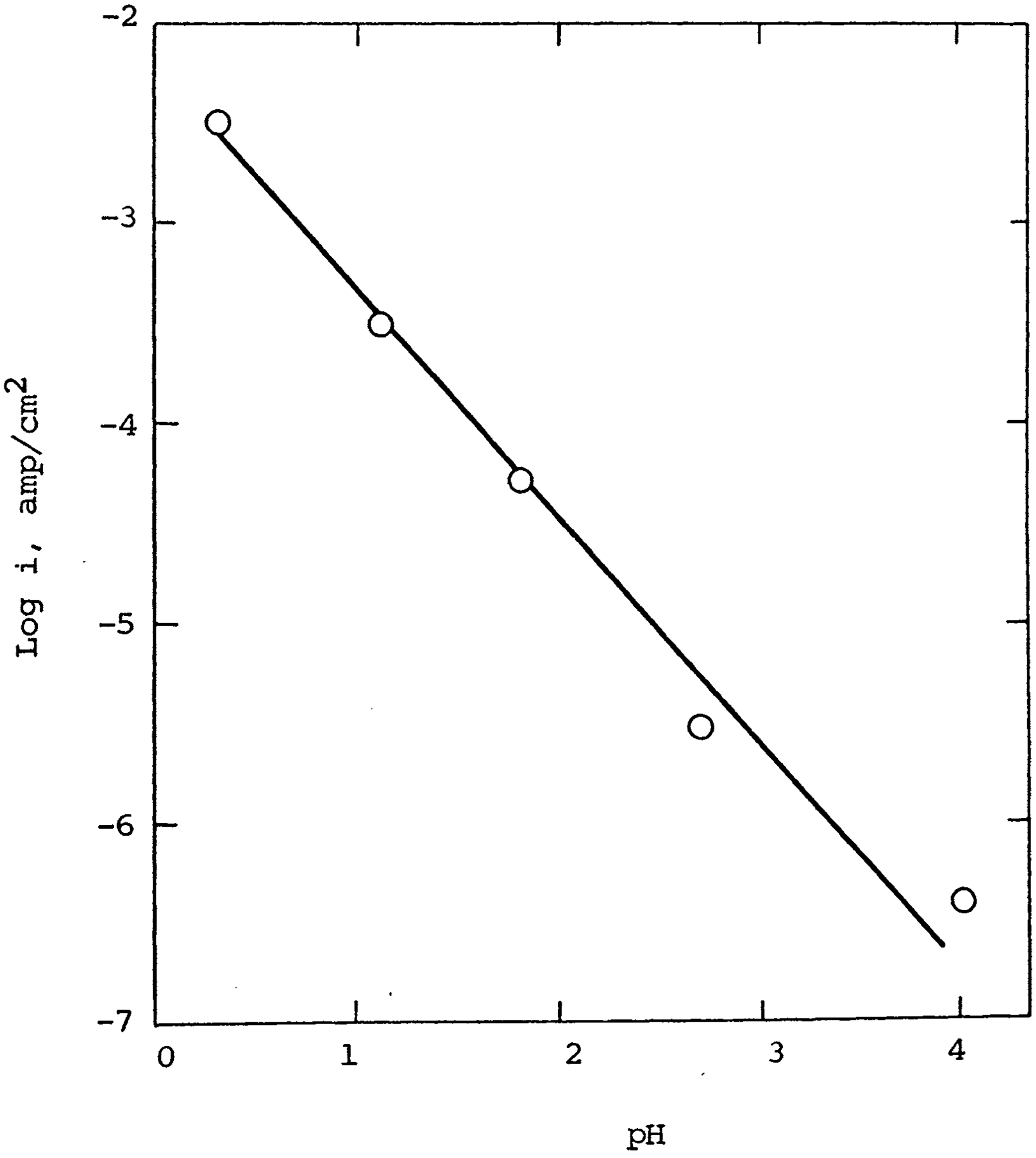

Figure 29. Effect of pH on current at -0.45 v (SHE) and C_M=0.01 M assuming the undissociated maleic acid was the reacting species for the cathodic reduction of maleic acid on a Hg cathode.

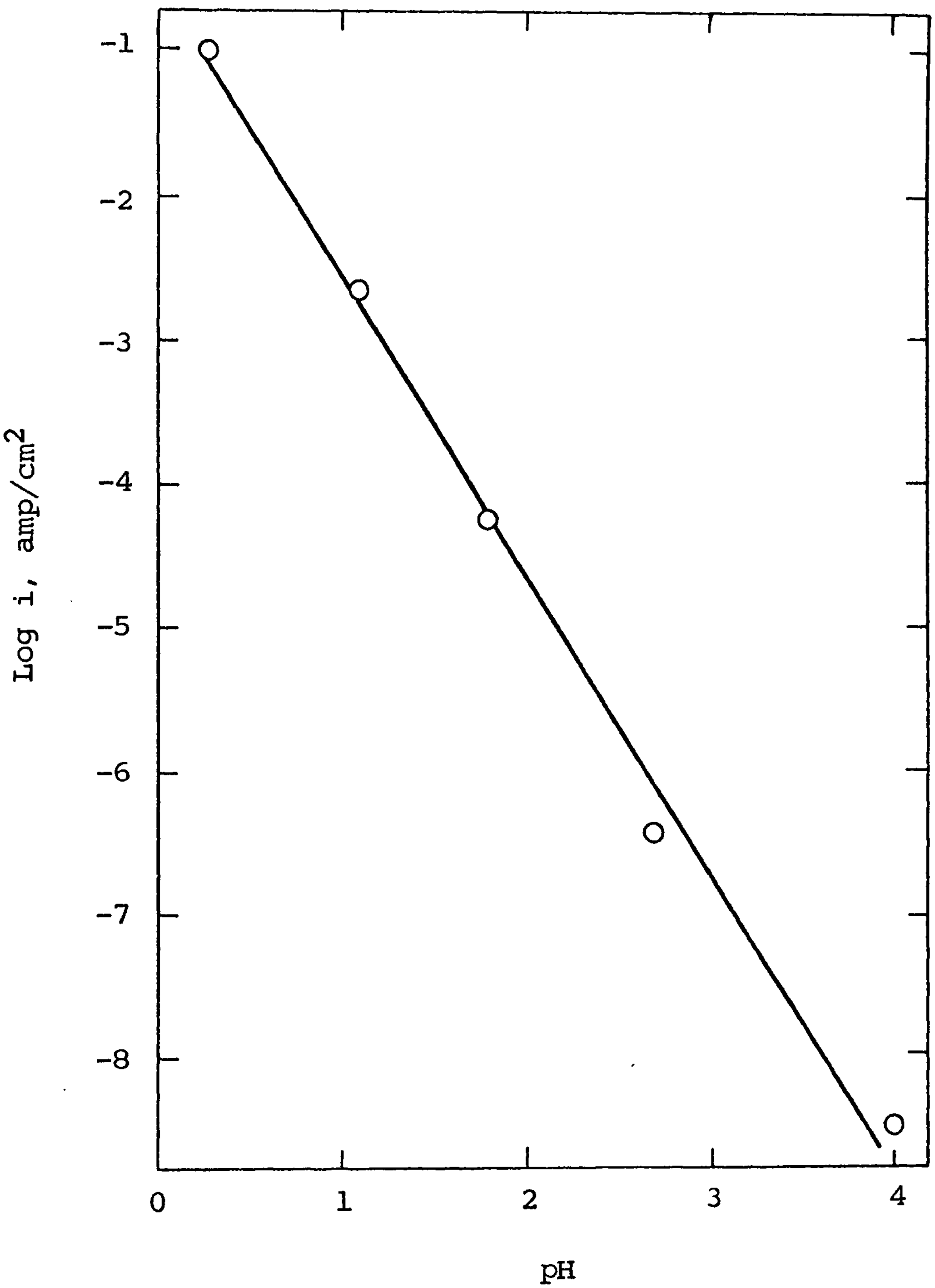

Figure 30. Effect of pH on current at -0.45 v (SHE) and C_{M^-}=0.01 M assuming the singly-dissociated maleic acid was the reacting species for the cathodic reduction of maleic acid on a Hg cathode.

These equations are actually equivalent when one considers the equilibrium between M and M^- (equation 3). Substitution of equation 3 into either of the foregoing equations will result in the other.

Further considerations indicate that the rate expression can also be represented by equation 7, which when combined with equation 3, is again equivalent to either equation 5 or 6.

$$i = (k_3 \, C_M \, C_{H^+} + k_4 \, C_{M^-} \, C^2_{H^+})\exp(-FV/RT) \qquad (7)$$

In order to select the correct expression (equation 5, 6, or 7), the reacting species must be known. It is deduced in the next section that both the undissociated and singly-dissociated acid are reduced. However, the reduction of the latter involves a combination with H^+ to form the undissociated acid before the actual reduction takes place, resulting in the observed second order reaction with respect to H^+. Strictly speaking, only the undissociated acid participates in the heterogeneous electrode reaction and the rate expression is equation 5.

The pH effects for the other cathodes were similar to those for mercury. They are shown in Figures 31 to 33.

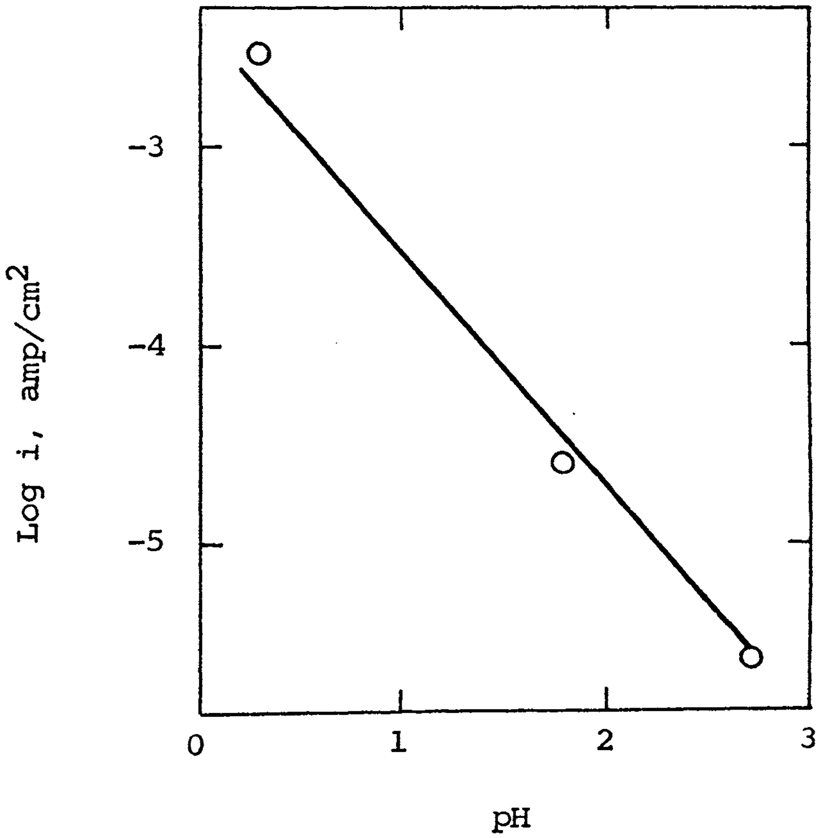

Figure 31. Effect of pH on current at -0.45 v(SHE) and C_M=0.01 M assuming the undissociated maleic acid was the reacting species for the cathodic reduction of maleic acid on a 0.5% Bi(Hg) cathode.

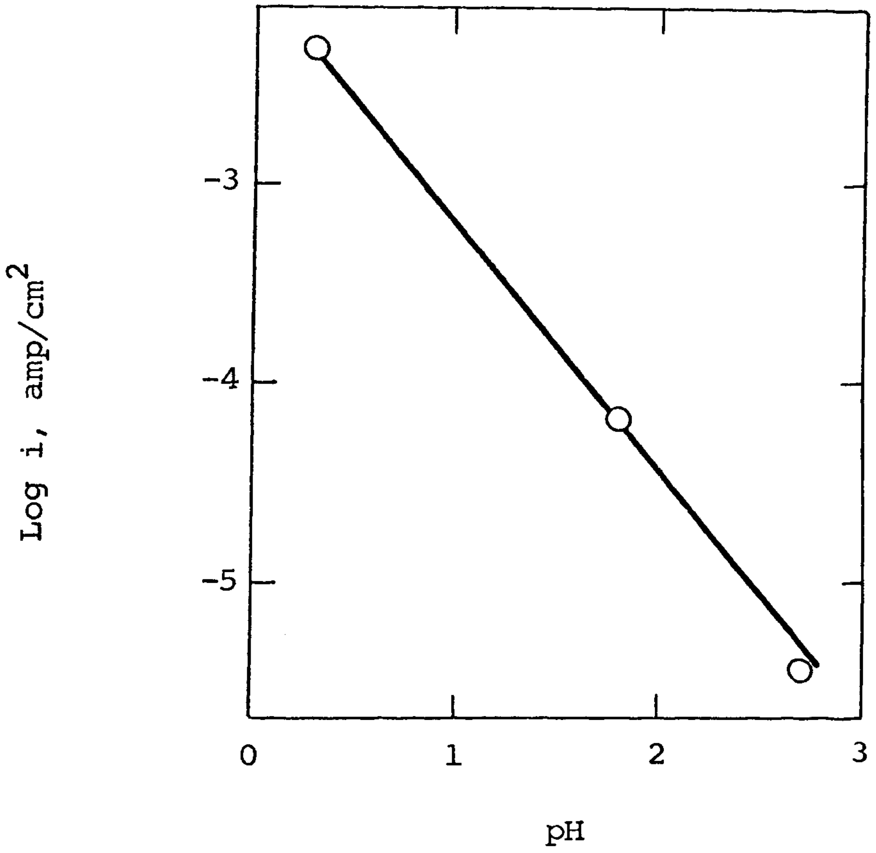

Figure 32. Effect of pH on current at -0.45 v(SHE) and C_M=0.01 M assuming the undissociated maleic acid was the reacting species for the cathodic reduction of maleic acid on a 5% Bi(Hg) cathode.

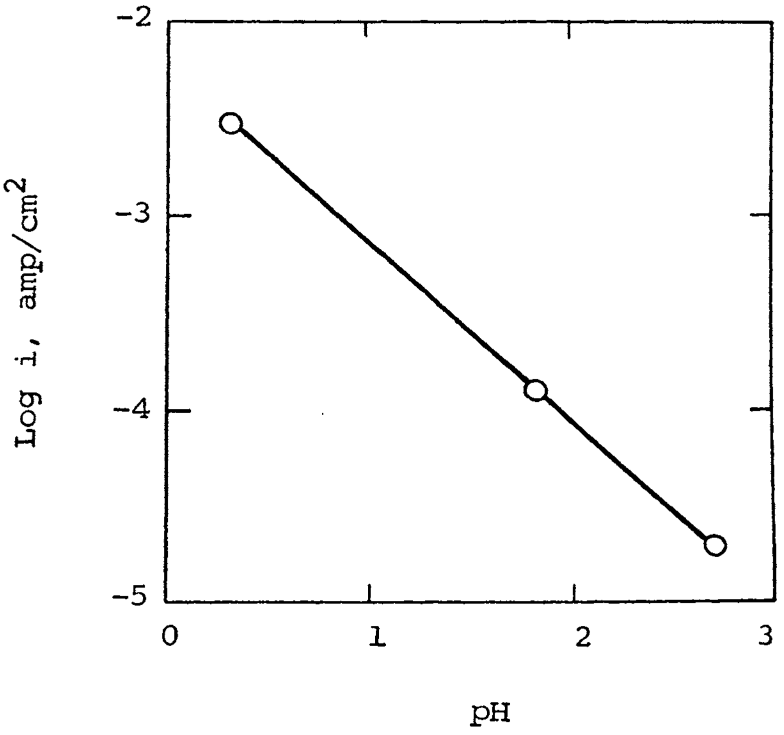

Figure 33. Effect of pH on current at -0.45 v(SHE) and C_M=0.01 M assuming the undissociated maleic acid was the reacting species for the cathodic reduction of maleic acid on a Bi cathode.

7. Reacting species.

a. Undissociated maleic acid. In 1 N H_2SO_4 (pH= 0.3), the observed limiting currents were of the same order of magnitude as those calculated with the following equation[32] assuming that the undissociated acid was the reacting species:

$$i = \frac{DzFC}{(1-t)x} \tag{8}$$

where, D = diffusion coefficient $\approx 1.5\times10^{-5}$ cm^2/sec

z = number of electrons transferred = 2

F = Faraday's constant = 96,500 coul/g-equiv

t = transport number = 0 (for uncharged species)

x = film thickness = 0.05 cm (for unstirred electrolyte)

C = bulk maleic acid concentration, gmol/l

For example, with 0.03 M maleic acid, the observed limiting current was 4 ma/cm^2 compared with a calculated value of 1.8 ma/cm^2. This indicates that the undissociated maleic acid is definitely involved in the reaction as it is the predominate species at this pH.

b. Doubly-dissociated maleic acid. In 1 N KOH ($pH \approx 13$) where the dissociation of maleic acid is practically complete, no appreciable current could be obtained until hydrogen evolved. This indicates that the doubly-dissociated acid is either not the reacting species or reacts only at potentials more negative than the h.e.r. Therefore, at $pH < 4$ (where the $M^{=}$ concentration is very low), it is reasonable to assume that $M^{=}$ is not involved in the reaction.

c. Singly-dissociated maleic acid. Figure 6 indicates that the limiting current decreases only slightly over the pH region 0.3 to 4.0. This suggests that the singly-dissociated acid is also reduced since the undissociated acid concentrations are quite low at pH's 2.7 and 4.0 (see Table VII). On the other hand, the linear Tafel region becomes shorter with increasing pH (see Figure 6) which suggests that only the undissociated acid is directly involved in the reaction. This behavior can be explained by the singly-dissociated acid not being directly reduced, but converted to the undissociated acid in the vicinity of the electrode. At this condition, M^{-} would also participate in the diffusion current and the linear Tafel region would be shorter with increasing pH since the conversion of M^{-} to M near the cathode is not likely to be complete. The conversion of M^{-} to M is believed due to a localized equilibrium in the vicinity of the cathode that is different from the bulk. The consumption of M by the reaction and the higher H^+ concentration resulting from charge transport and the negatively charged cathode will all shift the equilibrium in favor of M. The H^+ concentration increase near the cathode surface due only to its negative charges can be estimated by[19]

$$C_{H^+} = C^o_{H^+} \exp(-zF\phi_2/RT) \quad (9)$$

where, C_{H^+} = H^+ concentration near the electrode

z = valence of the H^+ = 1

ϕ_2 = potential in the plane of the closest approach to the electrode

$C^o_{H^+}$ = H^+ concentration in the bulk solution

For a solution with high concentration of supporting electrolyte (e.g., 1 N K_2SO_4), ϕ_2 is usually relatively constant and low, about -30 to -50 mv.* This gives $C_{H^+}/C^o_{H^+} \approx 4$. This coupled with the movement of H^+ to the cathode from charge transport would probably decrease the pH at the electrode by 1-2 units when that of the bulk solution is 3-4.

8. Temperature effect. The apparent activation energies ranged from 2 to 11 Kcal. As agitation of the electrolyte had no significant effect on the current, the

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* Data for 1 N NaF on Hg.[19]

lower values were not due to any diffusion limitations. Also, all the studies were made in the linear Tafel region. The variation of the apparent activation energy with potential was about 28 Kcal/volt, approximately F (23 Kcal/volt), as predicted from the Tafel slope. The true activation energy found by extrapolation to the reversible potential is in the range 35 to 40 Kcal.

B. Reaction Mechanism

1. Mechanism postulation. The reaction mechanism for the cathodic reduction of maleic acid must satisfy the following three kinetic parameters:

$$\partial V/\partial \log i = -2.3RT/F \tag{10}$$

$$\partial \log i/\partial pH = -1 \tag{11}$$

$$\partial \log i/\partial \log c_M = 1 \tag{12}$$

The high conversions to succinic acid indicate the maleic acid to be adsorbed on the cathode and to remain in the state until the final product (or its equivalent) is formed. With Langmuir type adsorption, a Tafel slope of -2.3RT/F generally fixes the rate determining step as a chemical reaction following the first electron transfer. The observed maleic acid concentration effects indicate a sufficiently low coverage of adsorbed species so that the

Langmuir isotherm is applicable. The following two reaction schemes have been found which will satisfy the above requirements.

a. The electrons are transferred from the cathode to the adsorbed maleic acid molecule (Scheme I):

$$M(sol) \rightleftharpoons M(ads) \qquad (13.1)$$

$$M(ads) + e \rightleftharpoons M^-(ads) \qquad (13.2)$$

$$M^-(ads) + H^+(sol) \xrightarrow{rds} MH(ads) \qquad (13.3)$$

$$MH(ads) \xrightarrow{H^+, e} \cdots \longrightarrow MH_2(sol) \qquad (13.4)$$

b. The electrons are transferred from the cathode to protons (Scheme II):

$$M(sol) \rightleftharpoons M(ads) \qquad (14.1)$$

$$H^+(sol) + e \rightleftharpoons H(ads) \qquad (14.2)$$

$$H(ads) + M(ads) \xrightarrow{rds} MH(ads) \qquad (14.3)$$

$$MH(ads) \xrightarrow{H^+, e} \cdots \longrightarrow MH_2(sol) \qquad (14.4)$$

A further distinction between the two schemes appears possible from a consideration of the hydrogen evolution reaction. With the same apparatus as used for the maleic acid reduction, a study of the h.e.r. was made on mercury in 1 N H_2SO_4 at 60°C. This polarization curve has also been plotted in Figure 5 to facilitate a comparison with data from the maleic acid reduction. It can be seen that the h.e.r. is much lower than the maleic acid reduction at comparable potentials. This in itself is not conclusive as maleic acid could be acting as a depolarizer for adsorbed hydrogen (discharged protons). However, as discussed in section II, the slow step of the h.e.r. on mercury is thought to be the H^+ discharge step (Tafel slope = $-2 \times 2.3RT/F \approx -130$ mv), i.e., the rate determining step is

$$H^+(sol) + e \longrightarrow H(ads) \tag{15}$$

Since the rate determining step in Scheme II would follow the hydrogen discharge step (which is even slower), this scheme cannot be correct and Scheme I appears to be the best choice. The same reasoning would also be applicable for the addition of the second hydrogen, therefore equation 13.4 might be expressed as:

$$MH(ads) + e \longrightarrow MH^-(ads)$$

$$MH^-(ads) + H^+(sol) \longrightarrow MH_2(ads)$$

$$MH_2(ads) \longrightarrow MH_2(sol)$$

The h.e.r. on Bi in 1 N H_2SO_4 was also studied at 60°C. The observed Tafel slope was about -120 mv and the exchange current density was about 10^{-9} amp/cm^2. The data have been plotted in Figure 11 and again indicate that the h.e.r. is slower than the maleic acid reduction. The observed Tafel slope suggests two possible r.d.s., either slow discharge or slow ion+atom reaction. For the former, the situation would be identical as that for mercury and Scheme I would again be the most appropriate mechanism. Mathews[24] has classified bismuth as a member of a group of metals on which the slow step for h.e.r. is the ion+atom reaction. These metals usually exhibit strong hydrogen adsorption and have appreciable hydrogen coverage, i.e., $\theta_H \rightarrow 1$. For this situation, the rate expression for Scheme II would be $i = k\ C_M$

which was not observed experimentally in the investigation.

2. Rate expression for the proposed mechanism. The rate expression for the proposed mechanism is derived in this section using the quasi-equilibrium method and assuming Langmuir-type adsorption.

Thus, from equation 13.1

$$k_1\ C_M\ (1-\theta_T) = k_{-1}\ \theta_M \tag{16}$$

For a low total coverage, i.e., $\theta_T \ll 1$

$$\theta_M = (k_1/k_{-1})\ C_M = K_1\ C_M \tag{17}$$

From equation 13.2

$$k_2\ \theta_M \exp(-\alpha FV/RT) = k_{-2}\ \theta_{M^-} \exp\left[(1-\alpha)FV/RT\right]$$

or $$\theta_{M^-} = K_2\ \theta_M \exp(-FV/RT) \tag{18}$$

The rate expression for equation 13.3 is

$$i = k_3 \ \theta_{M^-} \ C_{H^+} \tag{19}$$

Substitution of equations 17 and 18 into equation 19 gives

$$\begin{aligned} i &= k_3K_1K_2C_MC_{H^+}\exp(-FV/RT) \\ &= k \ C_M \ C_{H^+}\exp(-FV/RT) \end{aligned} \tag{20}$$

This expression is the same as equation 5 which was obtained empirically and therefore satisfies all the observed kinetic parameters.

V. CONCLUSION AND RECOMMENDATIONS

It is found that maleic acid (0.0003 to 0.3 M) in H_2SO_4-K_2SO_4-KOH electrolytes (pH 0.3-4.0) at 60°C can be reduced to succinic acid on Hg, Bi, and Bi-Hg amalgam cathodes with high (86 to 100%) current efficiencies. The reaction is first order with respect to the undissociated maleic acid and hydrogen ion concentration. The polarization curves have linear sections with Tafel slopes of $-2.3RT/F$. The reaction mechanism is proposed as being

$$M(sol) \rightleftharpoons M(ads)$$

$$M(ads) + e \rightleftharpoons M^-(ads)$$

$$M^-(ads) + H^+(sol) \xrightarrow{rds} MH(ads)$$

$$MH(ads) \xrightarrow{H^+,e} \cdots \longrightarrow MH_2(sol)$$

In order to obtain additional information on the cathodic reduction of organic compounds, it is recommended that the present studies be continued with other organic compounds, especially those similar to maleic acid, such as fumaric, acrylic, crotonic, cinnamic, and sorbic acids.

VI. 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 suppliers.

1. Bismuth. ESPI (99.9999 percent purity), Electronic Space Products, Inc., Los Angeles, Calif.

2. Maleic Acid. Superior grade (m.p. 135 to 136°C), Matheson, Coleman, and Bell, Norwood, Ohio.

3. Mercurous Sulfate. Reagent grade, Matheson, Coleman, and Bell, Norwood, Ohio.

4. Mercury. Triple distilled, Instrument grade, Bethlehem Instruments, Hellertown, Pa.

5. Nitrogen. Pre-purified, Matheson Gas Products, Joliet, Ill.

6. Potassium Hydroxide. Certified A.C.S., Fisher Scientific Company, Fairlawn, N. J.

7. Potassium Sulfate. Certified A.C.S., Fisher Scientific Company, Fairlawn, N. J.

8. Sulfuric Acid. Reagent A.C.S., Fisher Scientific Company, Fairlawn, N. J.

APPENDIX B

APPARATUS

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

1. Electrometer. Model 610B, Keithley Instruments Inc., Cleveland, Ohio.

2. Gas Chromatograph. Model 810 Research Chromatograph, F & M Scientific Corp., Avodale, Pa.

3 Milliammeter. Model 931, Weston Instruments Division, Daystrom Inc., Newark, N. J.

4. Potentiostat. Wenking 66TS1, Gerhard Bank Elektronik, Gottinger, West Germany.

5. Power Supply. Model 711A, Hewlett-Packard Company, Palo Alto, Calif.

6. Recorder. Laboratory Recorder VOM-5, Bausch & Lomb Inc., Rochester, N. Y.

APPENDIX C

DATA

The following tables include the data obtained in the studies. The listed current can be converted to current density by dividing by the surface area of the electrodes. All potential are referred to the SHE at the temperature of the experiment by means of the procedure described by Johnson, Reed, and James.[33]

TABLE VIII

CURRENT-POTENTIAL RELATIONSHIPS FOR THE CATHODIC REDUCTION OF MALEIC ACID ON A Hg CATHODE* AT 60°C IN 1 N H_2SO_4 (pH=0.3)

Maleic acid concentration					
0.0003 M		0.003 M		0.03 M	
Potential	Current	Potential	Current	Potential	Current
v, SHE	ma	v, SHE	ma	v, SHE	ma
0.515^{**}		0.512^{**}		0.502^{**}	
-0.083	0.0028	-0.083	0.0021	-0.083	0.0013
-0.183	0.0030	-0.183	0.0029	-0.163	0.0026
-0.283	0.0037	-0.263	0.0060	-0.203	0.0071
-0.323	0.0059	-0.283	0.0098	-0.223	0.013
-0.343	0.010	-0.303	0.019	-0.263	0.036
-0.363	0.021	-0.323	0.043	-0.283	0.065
-0.383	0.041	-0.343	0.098	-0.303	0.13
-0.403	0.074	-0.363	0.21	-0.323	0.28
-0.423	0.11	-0.383	0.44	-0.343	0.64
-0.463	0.19	-0.403	0.78	-0.363	1.3
-0.523	0.25	-0.443	1.6	-0.383	2.7
-0.563	0.27	-0.543	2.5	-0.403	5.0
		-0.623	2.6	-0.443	12
				-0.503	22
				-0.583	25
				-0.683	26

TABLE VIII (CONT'D)

Maleic acid concentration			
0.001 M		0.01 M	
Potential v, SHE	Current ma	Potential v, SHE	Current ma
0.505**		0.515**	
-0.083	0.0016	0.017	0.0023
-0.183	0.0016	-0.163	0.0026
-0.283	0.0037	-0.203	0.0041
-0.303	0.0074	-0.223	0.0061
-0.323	0.0016	-0.243	0.0092
-0.343	0.0036	-0.263	0.016
-0.363	0.075	-0.283	0.028
-0.383	0.15	-0.303	0.055
-0.403	0.27	-0.323	0.12
-0.443	0.56	-0.343	0.29
-0.503	0.77	-0.363	0.61
-0.583	0.84	-0.383	1.2
		-0.403	2.1
		-0.423	3.3
		-0.463	6.0
		-0.523	7.8
		-0.633	8.6
		-0.683	8.9

---

* Area = 6 cm^2.

** Rest potential.

TABLE IX

CURRENT-POTENTIAL RELATIONSHIPS FOR THE CATHODIC REDUCTION OF MALEIC ACID (0.03 M) ON A Hg CATHODE* AT 60°C

pH = 1.1		pH = 1.8	
Potential	Current	Potential	Current
v, SHE	ma	v, SHE	ma
0.524**		0.509**	
-0.183	0.0018	-0.083	0.0021
-0.223	0.0040	-0.283	0.0059
-0.263	0.011	-0.323	0.011
-0.303	0.028	-0.343	0.016
-0.323	0.045	-0.363	0.025
-0.343	0.085	-0.383	0.043
-0.363	0.18	-0.403	0.096
-0.383	0.39	-0.423	0.18
-0.403	0.84	-0.443	0.38
-0.423	1.7	-0.463	0.78
-0.443	3.2	-0.483	1.5
-0.483	8.4	-0.503	2.6
-0.583	20	-0.543	6.3
-0.683	22	-0.583	11
-0.743	23	-0.663	18
-0.783	23	-0.743	22
		-0.803	22

TABLE IX (CONT'D)

pH = 2.7		pH = 4.0	
Potential v, SHE	Current ma	Potential v, SHE	Current ma
0.495**		0.499**	
-0.183	0.0016	-0.283	0.0034
-0.383	0.0031	-0.483	0.0043
-0.443	0.0061	-0.563	0.0060
-0.483	0.018	-0.583	0.0073
-0.523	0.075	-0.603	0.010
-0.563	0.28	-0.623	0.018
-0.603	0.95	-0.643	0.031
-0.643	2.4	-0.663	0.052
-0.703	6.6	-0.683	0.096
-0.783	12	-0.703	0.18
-0.863	16	-0.723	0.28
-0.923	20	-0.743	0.46
		-0.763	0.67
		-0.803	1.3
		-0.863	2.5
		-0.943	5.5
		-1.083	11
		-1.183	12

---

* Area = 6 cm^2.

** Rest potential.

TABLE X

CURRENT-POTENTIAL RELATIONSHIPS FOR THE CATHODIC REDUCTION OF MALEIC ACID ON A 0.5% Bi(Hg) CATHODE*

AT 60°C IN 1 N H_2SO_4 (pH=0.3)

Maleic acid concentration					
0.0003 M		0.003 M		0.03 M	
Potential	Current	Potential	Current	Potential	Current
v, SHE	ma	v, SHE	ma	v, SHE	ma
0.13**		0.14**		0.13**	
-0.083	0.010	-0.083	0.0085	-0.083	0.0090
-0.223	0.011	-0.183	0.010	-0.183	0.014
-0.303	0.012	-0.243	0.012	-0.223	0.026
-0.343	0.016	-0.283	0.019	-0.243	0.035
-0.363	0.023	-0.303	0.032	-0.263	0.053
-0.383	0.035	-0.323	0.062	-0.283	0.093
-0.423	0.086	-0.343	0.13	-0.303	0.19
-0.443	0.12	-0.363	0.28	-0.323	0.39
-0.483	0.18	-0.383	0.53	-0.343	0.78
-0.533	0.22	-0.403	0.88	-0.363	1.8
-0.583	0.24	-0.423	1.3	-0.383	3.4
		-0.443	1.7	-0.403	6.1
		-0.483	2.0	-0.443	14
		-0.583	2.3	-0.503	21
		-0.683	2.3	-0.583	24

* Area = 6 cm^2.

** Rest potential.

TABLE XI

CURRENT-POTENTIAL RELATIONSHIPS FOR THE CATHODIC REDUCTION OF MALEIC ACID (0.03 M) ON A 0.5% Bi(Hg) CATHODE* AT 60°C

pH = 1.8		pH = 2.7	
Potential v, SHE	Current ma	Potential v, SHE	Current ma
0.12**		0.12**	
-0.083	0.0080	-0.183	0.0040
-0.283	0.0090	-0.283	0.0045
-0.323	0.013	-0.383	0.0055
-0.343	0.016	-0.443	0.0090
-0.363	0.020	-0.483	0.016
-0.383	0.028	-0.523	0.047
-0.403	0.049	-0.543	0.090
-0.423	0.081	-0.563	0.17
-0.443	0.16	-0.583	0.32
-0.463	0.33	-0.603	0.60
-0.483	0.63	-0.623	1.0
-0.503	1.2	-0.643	1.8
-0.523	2.2	-0.683	3.8
-0.563	5.3	-0.743	8.0
-0.603	9.9	-0.803	12
-0.683	17	-0.863	14
-0.783	20	-0.923	16
-0.883	20	-1.003	18

---

* Area = 6 cm^2.

** Rest potential.

TABLE XII

CURRENT-POTENTIAL RELATIONSHIPS FOR THE CATHODIC REDUCTION OF MALEIC ACID ON A 5% Bi(Hg) CATHODE*

AT 60°C IN 1 N H_2SO_4 (pH=0.3)

Maleic acid concentration					
0.0003 M		0.003 M		0.03 M	
Potential	Current	Potential	Current	Potential	Current
v, SHE	ma	v, SHE	ma	v, SHE	ma
0.13**		0.12**		0.13**	
-0.183	0.011	-0.083	0.020	-0.083	0.011
-0.283	0.013	-0.233	0.024	-0.183	0.023
-0.323	0.026	-0.283	0.037	-0.223	0.039
-0.343	0.044	-0.303	0.061	-0.263	0.078
-0.363	0.076	-0.323	0.12	-0.283	0.15
-0.383	0.12	-0.343	0.27	-0.303	0.32
-0.423	0.19	-0.363	0.52	-0.323	0.73
-0.483	0.23	-0.383	0.94	-0.343	1.7
-0.583	0.25	-0.403	1.5	-0.363	3.3
		-0.443	2.1	-0.383	6.6
		-0.503	2.4	-0.423	15
		-0.583	2.6	-0.483	25
				-0.583	28

---

* Area = 6 cm^2

** Rest potential.

TABLE XIII

CURRENT-POTENTIAL RELATIONSHIPS FOR THE CATHODIC REDUCTION OF MALEIC ACID (0.03 M) ON A 5% Bi(Hg) CATHODE* AT 60°C

pH = 1.8		pH = 2.7	
Potential	Current	Potential	Current
v, SHE	ma	v, SHE	ma
0.12**		0.11**	
-0.083	0.018	-0.083	0.013
-0.283	0.026	-0.283	0.014
-0.343	0.038	-0.423	0.017
-0.363	0.050	-0.483	0.028
-0.383	0.071	-0.503	0.040
-0.403	0.12	-0.523	0.060
-0.423	0.22	-0.543	0.10
-0.443	0.42	-0.563	0.18
-0.463	0.81	-0.583	0.31
-0.483	1.6	-0.603	0.53
-0.503	2.8	-0.623	0.83
-0.523	4.1	-0.663	2.1
-0.563	8.0	-0.723	5.6
-0.623	14	-0.823	11
-0.683	17	-0.923	14
-0.783	22		

* Area = 6 cm^2.

** Rest potential.

TABLE XIV

CURRENT-POTENTIAL RELATIONSHIPS FOR THE CATHODIC REDUCTION OF MALEIC ACID ON A Bi CATHODE* AT 60°C IN 1 N H_2SO_4 (pH=0.3)

Maleic acid concentration			
0.03 M		0.3 M	
Potential v,SHE	Current ma	Potential v,SHE	Current ma
0.14**		0.13**	
-0.083	0.22	-0.083	0.15
-0.183	0.22	-0.183	0.21
-0.263	0.30	-0.223	0.34
-0.283	0.35	-0.263	0.49
-0.303	0.50	-0.283	0.67
-0.323	0.79	-0.303	1.0
-0.343	1.3	-0.323	1.9
-0.363	2.1	-0.343	3.9
-0.383	3.4	-0.363	7.3
-0.403	5.0	-0.383	11
-0.443	9.0	-0.403	24
-0.503	15	-0.433	38
-0.583	19	-0.483	70
-0.683	21	-0.583	125
-0.783	25	-0.683	170
-0.883	55	-0.883	210

TABLE XIV (CONT'D)

Maleic acid concentration			
0.0003 M		0.003 M	
Potential	Current	Potential	Current
v, SHE	ma#	v, SHE	ma
0.14**		0.15**	
-0.183	0.27	-0.183	0.22
-0.283	0.27	-0.283	0.22
-0.343	0.34	-0.323	0.26
-0.383	0.50	-0.343	0.33
-0.423	0.70	-0.363	0.44
-0.483	0.83	-0.383	0.65
-0.563	0.95	-0.403	1.0
-0.643	1.6	-0.443	1.7
		-0.493	2.4
		-0.593	3.3
		-0.693	4.6
		-0.743	6.5
		-0.793	12
		-0.883	40

* Area = 3 cm^2.

\# Area = 6 cm^2.

** Rest potential.

TABLE XV

CURRENT-POTENTIAL RELATIONSHIPS FOR THE CATHODIC REDUCTION OF MALEIC ACID (0.03 M) ON A Bi CATHODE* AT 60°C

pH = 1.8		pH = 2.7	
Potential	Current	Potential	Current
v, SHE	ma	v, SHE	ma
0.13**		0.13**	
-0.083	0.11	-0.183	0.14
-0.283	0.12	-0.383	0.15
-0.343	0.15	-0.483	0.20
-0.383	0.19	-0.508	0.25
-0.403	0.27	-0.533	0.32
-0.423	0.40	-0.558	0.45
-0.443	0.66	-0.583	0.81
-0.463	1.0	-0.608	1.2
-0.483	1.8	-0.633	2.0
-0.503	2.6	-0.658	2.9
-0.523	3.7	-0.683	3.9
-0.553	5.3	-0.733	5.6
-0.623	11	-0.833	11
-0.733	21	-0.933	14
-0.833	25	-1.033	18

---

* Area = 3 cm^2.

** Rest potential.

TABLE XVI

CURRENT-POTENTIAL RELATIONSHIPS FOR THE HYDROGEN EVOLUTION REACTION ON Hg AND Bi CATHODES* AT 60°C IN 1 N H_2SO_4 (pH=0.3)

Hg		Bi	
Potential	Current	Potential	Current
v, SHE	ma	v, SHE	ma
0.53**		0.14**	
-0.083	0.0030	0.067	0.18
-0.283	0.0042	-0.047	0.18
-0.433	0.0060	-0.283	0.19
-0.533	0.011	-0.423	0.24
-0.583	0.018	-0.483	0.30
-0.633	0.035	-0.533	0.39
-0.683	0.064	-0.583	0.53
-0.733	0.12	-0.633	1.1
-0.783	0.22	-0.683	2.3
-0.833	0.53	-0.733	6.2
-0.883	1.1	-0.783	19
-0.933	2.1	-0.833	47
-0.983	4.3	-0.883	95
-1.083	17	-0.933	135
-1.183	43	-1.033	260
-1.283	78		

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* Area = 6 cm^2.

** Rest potential.

TABLE XVII

CURRENT-TEMPERATURE RELATIONSHIPS FOR THE CATHODIC REDUCTION OF MALEIC ACID (0.03 M) ON A Hg CATHODE

pH	Potential	Temperature	Current
	v, SHE	°C	ma
0.3	-0.383	70	2.78
0.3	-0.383	65	2.30
0.3	-0.383	60	1.87
0.3	-0.383	55	1.53
0.3	-0.383	50	1.25
0.3	-0.303	70	0.183
0.3	-0.303	65	0.145
0.3	-0.303	60	0.112
0.3	-0.303	55	0.086
0.3	-0.303	50	0.068
2.7	-0.533	70	0.091
2.7	-0.533	65	0.087
2.7	-0.533	60	0.084
2.7	-0.533	55	0.080
2.7	-0.533	50	0.075

TABLE XVIII

CURRENT-TEMPERATURE RELATIONSHIPS FOR THE CATHODIC REDUCTION OF MALEIC ACID (0.03 M) ON A 0.5% Bi(Hg) CATHODE

pH	Potential v,SHE	Temperature °C	Current ma
0.3	-0.383	70	2.01
0.3	-0.383	65	1.78
0.3	-0.383	60	1.55
0.3	-0.383	55	1.29
0.3	-0.383	50	1.07
0.3	-0.303	70	0.116
0.3	-0.303	65	0.096
0.3	-0.303	60	0.078
0.3	-0.303	55	0.062
0.3	-0.303	50	0.048
2.7	-0.563	70	0.190
2.7	-0.563	65	0.180
2.7	-0.563	60	0.170
2.7	-0.563	55	0.160
2.7	-0.563	50	0.145

TABLE XIX

CURRENT-TEMPERATURE RELATIONSHIPS FOR THE CATHODIC REDUCTION OF MALEIC ACID (0.03 M) ON A 5% Bi(Hg) CATHODE

pH	Potential v, SHE	Temperature °C	Current ma
0.3	-0.353	75	2.65
0.3	-0.353	70	2.45
0.3	-0.353	65	2.10
0.3	-0.353	60	1.80
0.3	-0.293	75	0.320
0.3	-0.293	70	0.265
0.3	-0.293	65	0.220
0.3	-0.293	60	0.180
2.7	-0.563	75	0.168
2.7	-0.563	70	0.163
2.7	-0.563	65	0.155
2.7	-0.563	60	0.150

TABLE XX

CURRENT-TEMPERATURE RELATIONSHIPS FOR THE CATHODIC REDUCTION OF MALEIC ACID ON A Bi CATHODE

pH	Maleic acid concentration	Potential	Temperature	Current
	gmol/l	v, SHE	°C	ma
0.3	0.3	-0.393	70	51.0
0.3	0.3	-0.393	65	44.5
0.3	0.3	-0.393	60	36.5
0.3	0.3	-0.393	55	30.0
0.3	0.3	-0.393	50	25.8
0.3	0.3	-0.333	70	9.75
0.3	0.3	-0.333	65	8.20
0.3	0.3	-0.333	60	6.50
0.3	0.3	-0.333	55	5.20
0.3	0.3	-0.333	50	4.20
2.7	0.03	-0.573	70	0.93
2.7	0.03	-0.573	65	0.89
2.7	0.03	-0.573	60	0.85
2.7	0.03	-0.573	55	0.83
2.7	0.03	-0.573	50	0.79

APPENDIX D

CHEMICAL ANALYSIS FOR SUCCINIC ACID

1. Procedure.

a. Acidify a portion of the solution containing about 40 mg of succinic acid with H_2SO_4 and treat the solution with 0.1 N $KMnO_4$ on a heated water-bath until a brown precipitate is obtained.

b. Add enough Na_2SO_3 solution to dissolve the precipitate and evaporate the solution to 10 ml.

c. Transfer the solution quantitatively into a continuous extractor* and add enough K_2SO_4 to saturate the solution.

d. Extract the solution with ether for 24 hours.

e. After extraction, add 30 ml distilled water to the ether phase and remove the ether by heating.

f. Dilute the solution to 60 ml with distilled water and adjust the pH to 6.5-7.0 with a pH meter and 0.05 N KOH.

g. Add 15.0 ml of 0.1 N $AgNO_3$ immediately to the solution and keep in the dark for two hours.

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* No. 92225, Corning catalog "Pyrex Laboratory Glassware", Corning Glass Works, Corning, N. Y.

h. Filter the solution through a fritted glass filter and wash the precipitate three times with 2 to 3 ml of 1 percent NH_4NO_3.

i. Add 10 ml 2 N HNO_3 and about 3 ml of 10 percent $Fe(NO_3)_3$ solution as an indicator to the filtrate and titrate it with 0.1 N NH_4SCN until the solution becomes a faint brown which does not disappear upon shaking.

2. Sample calculation. The analytical data are given in Table XXI. With the mercury cathode at pH 0.3, for example the electrolyte after electrolysis was diluted to 500 ml and 1/10 of it (50 ml) was taken for analysis. Since the amount of NH_4SCN used represents the excess $AgNO_3$, the amount of $AgNO_3$ precipitated as silver succinate is

$$V_1 = 15.0-(7.65)(1.125) = 6.38 \text{ ml}$$

The concentration of the succinic acid is

$$N_2 = \frac{N_1V_1}{V_2} = \frac{(0.1)(6.38)}{50} = 0.01275 \text{ N}$$

and the total amount of succinic acid is

$$W = 0.01275(118/2)(500/1,000)(1,000) = 376 \text{ mg}$$

From Table VI, the theoretical amount of succinic acid produced during the electrolysis is

$$W_t = \frac{I\ t\ A}{z\ F}$$

$$= \frac{(5.5\text{x}10^{-3})(32.13)(3,600)(118)(1,000)}{(2)(96,500)}$$

$$= 389 \text{ mg}$$

Therefore,

$$\text{Eff} = W/W_t = 376/389 = 97\%$$

TABLE XXI

ANALYTICAL DATA FOR THE FARADAIC EFFICIENCY STUDIES

Electrode	pH	V	v	$AgNO_3$ added	NH_4SCN used	Total succinic acid
		ml	ml	0.100 N	0.1125 N	mg
Hg	0.3	500	50	15.0	7.65	376
Hg	2.7	500	50	15.0	8.50	320
0.5% Bi(Hg)	0.3	500	50	15.0	7.30	400
0.5% Bi(Hg)	2.7	500	50	15.0	8.20	340
5.0% Bi(Hg)	0.3	500	50	15.0	7.10	414
5.0% Bi(Hg)	2.7	500	50	15.0	8.00	354
Bi	0.3	50	25	15.0	7.00	84
Bi	2.7	50	25	15.0	7.90	72

V = volume of electrolyte after dilution.

v = volume of electrolyte used for analysis.

APPENDIX E

SAMPLE CALCULATION OF THE MALEIC ACID DISSOCIATION AT DIFFERENT pH'S

The dissociation of maleic acid was calculated with the following three equations:

$$\frac{(H^+)(M^-)}{(M)} = K_1 = 1.4 \times 10^{-2} \qquad (1)^*$$

$$\frac{(H^+)(M^=)}{(M^-)} = K_2 = 8.6 \times 10^{-7} \qquad (2)^*$$

$$(M) + (M^-) + (M^=) = C \qquad (3)$$

where, C = total concentration of maleic acid

Expressing M^- and $M^=$ in terms of M in equations 1 and 2 and substituting into equation 3, one obtains

$$(M) = C/\left[1 + K_1/(H^+) + K_1K_2/(H^+)^2\right] \qquad (4)$$

At pH=0.3, for example, $(H^+)=0.5$

$$(M) = C/(1.0 + 2.8 \times 10^{-2} + 4.8 \times 10^{-8})$$

or $(M)/C = 0.973$

Then, from equation 1

$$(M^-)/C = 0.027$$

and, from equation 2

$$(M^=)/C = 4.6 \times 10^{-8} \approx 0.000$$

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* K_1 and K_2 are for 25°C.[30] No data at 60°C were available.

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VIII. VITA

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