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THE ANODIC OXIDATION
OF MALEIC ACID

BY

LARRY D. GILMARTIN

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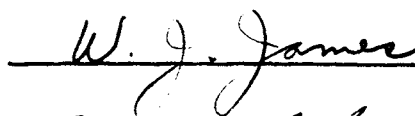
THESIS

submitted to the faculty of
THE UNIVERSITY OF MISSOURI AT ROLLA
in partial fulfillment of the requirements for the
Degree of
MASTER OF SCIENCE IN CHEMICAL ENGINEERING
Rolla, Missouri
1966

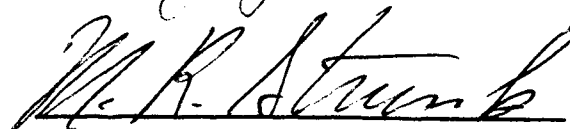
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(advisor)









THE ANODIC OXIDATION OF MALEIC ACID

Larry D. Gilmartin

ABSTRACT

The purpose of this investigation was to determine the mechanism of the anodic oxidation of maleic acid on platinized-platinum electrodes at 80°C. Current density-potential studies were conducted varying the parameters of maleic acid concentration and pH. The faradaic efficiency of the oxidation of maleic acid to yield CO₂ was determined. The effect of temperature on current density was also studied to determine the activation energy for the reaction.

The oxidation of maleic acid occurred only in acidic solutions. The faradaic efficiency was found to be approximately 97 ± 5 per cent. A linear Tafel region was found which had a slope of 145 - 170 millivolts ($\sim 2.3RT/\alpha F$). The rate decreased with increasing maleic acid concentration. There was very little, if any, effect of pH on the rate in the range 0.3 to 2.0. At pH's greater than 2.0, the rate increased rapidly. The activation energy was 33.4 kilocalories at the reversible potential.

The experimental results were interpreted with a mechanism having the following characteristics:

- (1) The first charge transfer is rate determining.

- (2) The rate is proportional to the electrode surface area free of adsorbed maleic acid molecules.
- (3) The rate determining step involves the discharge of water and/or hydroxyl ions. In strongly acidic solutions (pH = 0.3 to 2.0) the primary reaction is the discharge of water. Hydroxyl ion discharge predominates in more basic solutions (pH = 2.5 to 6.0).
- (4) Unionized maleic acid is the reacting specie.
- (5) Adsorption occurs under Langmuir conditions with four point attachment.

These characteristics are incorporated in the rate expressions:

$$i = nF(k_{(2)} a_{\text{H}_2\text{O}} + k_{(3)} a_{\text{OH}^-}) (1 - \theta_A) e^{\alpha FE/RT}$$

$$\theta_A = K(1 - \theta_A)^4 C_A$$

where,

i = current density, amps/cm²

n = number of electrons transferred in rate determining step

F = Faraday's constant

$k_{(2)}$ = rate constant for water discharge reaction

$a_{\text{H}_2\text{O}}$ = activity of water, gmols/liter

$k_{(3)}$ = rate constant for hydroxyl ion discharge reaction

- a_{OH^-} = activity of hydroxyl ions, gmols/liter
- α = 0.5
- E = potential, volts
- R = gas constant, calories/gmol/ $^{\circ}$ K
- T = temperature, $^{\circ}$ K
- θ_A = fractional coverage of adsorbed maleic acid on
the electrode
- K = equilibrium constant for the adsorption of
maleic acid
- C_A = concentration of undissociated maleic acid,
gmols/liter

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I. INTRODUCTION

Electrochemistry and its applications have come to be of considerable interest in recent years. Extensive research is being conducted in many areas.

Historically, corrosion has done much to stimulate research in electrochemistry as it occurs by an electrochemical process. Work has been carried on for many years in search of the mechanisms involved.

In a world whose population is apparently growing without limit, energy must be provided in increased amounts to meet the demands placed upon industry, communications, and government for their goods and services. Many scientists feel that a partial solution to these demands can be obtained through fuel cells which operate at higher efficiencies than present devices using the same fuels. Also, space exploration, with its inherent demand for portable, compact energy sources that produce no noxious gases or bulky wastes, has created a great impetus in fuel cell research and technology. These cells (utilizing various spontaneous oxidation-reduction systems) are limited in number at the present time. The limitation is partially due to the expense of feasible fuels and the difficulty in storing and handling them (hydrogen, oxygen, etc.). Investigations of the electrochemical properties of

more economical fuels (hydrocarbons) constitute a great amount of the work done in the various laboratories.

Considerable interest has also been generated recently by successful industrial processes in which chemicals have been synthesized electrochemically. In one process, two molecules of acrylonitrile are joined and hydrogen added to yield adiponitrile. It seems certain that many new processes involving similar techniques will be worked out in the future.

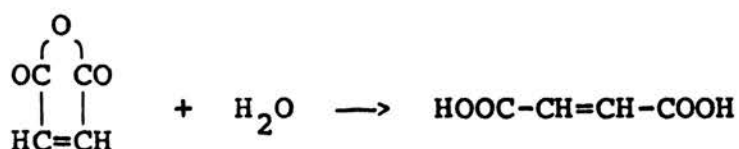
Although there is a large amount of research in electrochemistry, a large percentage of it is concerned with quite specific systems and applications. Very little work of a general nature has been reported in the literature concerning the electrochemical properties of various organic substances.

The purpose of this study was to investigate the mechanism of the oxidation of maleic acid on platinum electrodes. This, along with studies on similar compounds, will possibly give some criteria that can eventually be used to characterize electrode reactions.

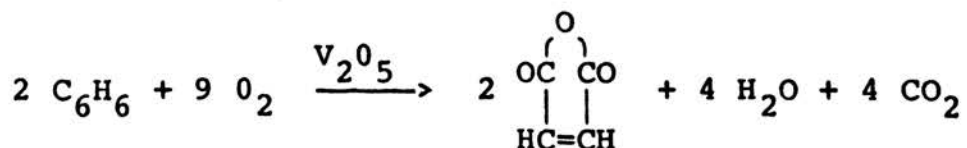
II. LITERATURE REVIEW

Maleic acid is the cis isomer of butenedioic acid. The structural formula is HOOC-CH=CH-COOH and the formula weight is 116.07. It crystallizes as a colorless, monoclinic prism with a melting point of 130.5°C.

Maleic acid is prepared commercially by absorbing cooled maleic anhydride vapors in water to give a 40 per cent solution of the acid:



The solution is decolorized, partially evaporated, and fractionally crystallized to yield small amounts of fumaric acid and essentially pure maleic acid. The maleic anhydride is produced by the vapor-phase oxidation of benzene in the presence of a vanadium oxide catalyst:



This reaction yields a vapor stream containing maleic anhydride, maleic acid, small amounts of fumaric acid, some unreacted benzene, carbon dioxide, and water. Maleic anhydride can also be obtained from the vapor-phase oxidation of numerous other substances, including toluene, xylene,

and biphenyl. More than 80 per cent of the maleic anhydride produced in the United States is made from the benzene process. Maleic acid is used mainly in the production of synthetic resins.

Maleic acid contains the conjugated maleyl grouping $-C(=O)-CH=CH-C(=O)-$ consisting of an ethylene bond in juxtaposition to two carboxyl radicals. The C=C bond in such a grouping is highly electron-deficient, but, under proper conditions, it can be induced to undergo most of the reactions common to simple olefins.⁽¹⁾

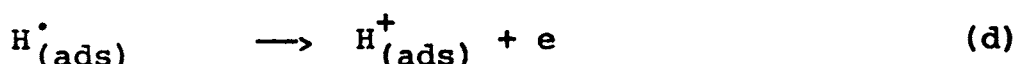
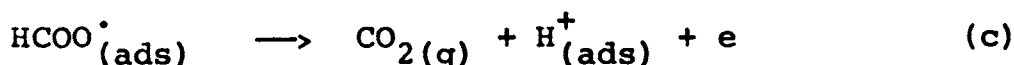
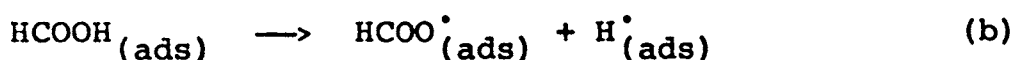
Maleic acid has been chemically oxidized in several reactions. In a mixture of $KClO_3$ and OsO_4 , mesotartaric acid is formed.⁽²⁾ Maleic acid is also oxidized to mesotartaric acid by alkaline $KMnO_4$.⁽³⁾ Solid MnO_2 oxidizes aqueous solutions of maleic acid, yielding acetylene and carbon dioxide.⁽⁴⁾

Tommila⁽⁵⁾ has studied the electrolytic oxidation of maleic acid on smooth and platinized-platinum electrodes. He used solutions of 0.25, 0.50, and 1.0 M maleic acid in 5.0 N NaOH, 2.0 N H_2SO_4 , and water. He observed that the products of the oxidation were CO_2 , $(CO_2H)_2$, traces of HCO_2H , $C_2H_4O_2$, and CO. No traces of hydrocarbon gases or alcohols were found.

No further studies have been reported in the literature on the anodic oxidation of maleic acid. However,

anodic oxidation studies on platinum electrodes have been reported on other organic compounds containing carboxyl and olefinic groups. These are of interest and will be included in the remainder of this review as both groups are contained in maleic acid.

A. Formic Acid. Breiter⁽⁶⁾ working in 1.0 N perchloric acid at 30°C found the coverage of formic acid on a bright platinum electrode to be nearly constant in the linear Tafel region. Coverages ranged from 1.0 in 1.0 N formic acid to 0.5 in 0.001 N acid. He proposed the mechanism:



In the potential range, 0.3 to 0.6 volts, it was found that equation (c) was rate controlling for concentrations, $0.001 < C_f \leq 1.0$ N. It was also found that at higher potentials (0.8 volts), equation (b) becomes the rate controlling step.

Munson⁽⁷⁾ studied the transition time of the oxidation of formic acid on a smooth platinum anode at 25°C. The pH ranged from 1.4 to 10.0. He reported that a slow pre-electrochemical conversion of the formic acid to

adsorbed hydrogen and formate best explained the experimental results.

Gottlieb⁽⁸⁾ studied the oxidation of formic acid in 1.0 N H_2SO_4 on both smooth and platinized-platinum electrodes. Tafel slopes of 100 millivolts were reported at 23°C. It was stated that hydrogen, formed by a non-electrochemical decomposition process, apparently was not a significant factor in the electrochemical behavior of the system. He also reported that platinization of the anode introduced no active catalytic sites, but only served to increase the surface area.

Fleischmann, Johnson, and Kuhn⁽⁹⁾ investigated the oxidation of 1.0 N formic acid in 5.0 N sulfuric acid on platinized-platinum electrodes at four temperatures (25, 45, 70, and 90°C). They obtained coverage and current-potential data. Coverages were reported as being greater than 0.8 in the potential region 0.0 to 0.6 volts. They also reported that the current increased with time at a constant potential when the anode was made more positive. This observation provided strong evidence for the existence of two or more reactions competing for the active platinum sites. The data taken at the lower temperatures corresponded with the mechanism proposed by Breiter. At 90°C, a two electron transfer mechanism (Tafel slope of $2.3RT/F$) was indicated. This mechanism was rejected in favor of an adsorbed intermediate concept. They felt that an explanation

possibly lay in the varying orientations in which the formic acid molecules were adsorbed on the electrode.

B. Oxalic Acid. Johnson, Wroblowa, and Bockris⁽¹⁰⁾ studied the oxidation of oxalic acid on platinized-platinum electrodes at 80°C. They used solutions of oxalic acid in H₂SO₄, Na₂SO₄, and NaOH. The linear Tafel region was in the potential range 0.5 to 0.7 volts, and had a slope of 70 millivolts (2.3RT/F). Current densities ranging from 3 x 10⁻⁵ to 10⁻³ amps/cm² were observed in the linear Tafel region. The following relations were also obtained:

$$\left| \frac{\delta \log i}{\delta \log C_{\text{ox}}} \right|_{\text{pH}, V} = 0.35, \quad \left| \frac{\delta \log i}{\delta \log H^+} \right|_{V, C_{\text{ox}}} = -0.55$$

An empirical equation for the rate was determined as:

$$i = k(C_{\text{ox}}^{0.35})(C_{\text{H}^+}^{-0.55})e^{FV/RT}$$

There was no evidence of reaction in NaOH solutions, indicating that the undissociated acid was the reactant. Both Temkin and Langmuir adsorption isotherms were used in data treatment. It was found that the Temkin isotherm best explained the experimental observations. It was concluded the organic specie supplied both electrons, and the reaction rate was determined by the rate of the second charge transfer. Faradaic efficiency of the oxidation to CO₂ was reported as ≈ 100 per cent.

Giner⁽¹¹⁾ reported that bright platinum anodes are passivated during the oxidation of oxalic acid by

a separation of oxygen from the water at the anode to form a layer of chemisorbed oxygen. Oxidation of oxalic acid ceased upon completion of the layer of oxygen.

He stated that there was evidence that oxidation occurred through an intermediate active form of oxygen, rather than by a direct yielding of electrons to the electrode.

Shams El Din⁽¹²⁾ published results agreeing in general with the findings of Giner. However, he reported evidence of oxidation on the oxide-covered electrode. The reaction under these conditions appeared to be diffusion controlled. He found the oxidation of oxalic acid to be a one electron transfer reaction involving hydroxyl radicals at high positive potentials ($E > 0.8$ volts).

C. Crotonic Acid. Cannaday⁽¹³⁾ investigated the oxidation of crotonic acid on platinized-platinum electrodes at 80°C. He studied the oxidation in solutions of H_2SO_4 , K_2SO_4 , and KOH. The faradaic efficiency for the oxidation to CO_2 was reported as ≈ 100 per cent. The slope of the linear Tafel region was determined to be 160 millivolts ($\approx 2.3RT/\alpha F$). This fixed the rate determining step as being the first charge transfer. It was reported that at constant potential, the current decreased with increasing acid concentration. For pH's greater than 2.0, a marked increase of $\left| \frac{\delta \log i}{\delta pH} \right|$ was observed. The data were treated assuming Langmuir adsorption conditions with a one-point

attachment. A mechanism was proposed assuming the oxidation of both the ionized and unionized species (appreciable currents were obtained both in acidic and basic solutions). The rate was assumed to be the sum of the rates for the two parallel reactions. In strongly acidic solutions, water discharge was the rate determining step. In basic solutions, hydroxyl ion discharge was rate determining. The empirical rate equation was determined to be:

$$i = \left| k_1 (1 + K_1 C)^{-1} + (k_2 / C_{H^+}) (1 + K_2 C^-)^{-1} \right| e^{aFV/RT}$$

D. Ethylene. Wroblowa, Piersma, and Bockris⁽¹⁴⁾ investigated the anodic oxidation of ethylene on both bright and platinized-platinum electrodes at 80°C. They reported the faradaic efficiency of the oxidation to CO₂ to be ≈ 100 per cent. This was determined in both 1.0 N H₂SO₄ and in 1.0 N NaOH. Semilog plots of potential-current data obtained at various pH's showed four distinct regions of behavior:

- (1) A potential region near the rest potential where no steady states could be obtained. The current density at constant potential decreased continually with time to negligible values.
- (2) A linear Tafel region with a slope of 140 - 160 millivolts in the pH range 0.3 to 12.5.

Current densities in this region ranged from 3×10^{-6} to 3×10^{-3} amps/cm².

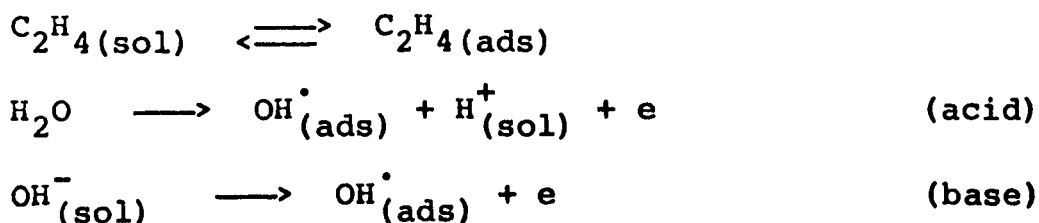
- (3) A region where the current density increased slowly with potential until a limiting value was reached.
- (4) A potential region above 0.9 volts where the current density rapidly decreased to negligible values.

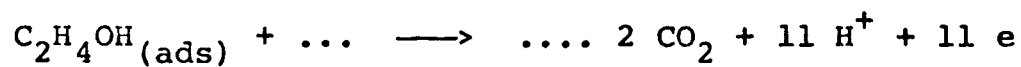
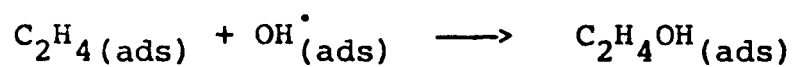
It was observed that the current density decreased approximately logarithmically with increasing partial pressure of ethylene.

The following relationships were determined from the data:

$$\left| \frac{\delta \log i}{\delta \text{pH}} \right|_{V,P} = 0.45, \quad \left| \frac{\delta i}{\delta P} \right|_{V,\text{pH}} < 0$$

Ethylene surface coverage was estimated to be 0.5 ± 0.2 and independent of potential in the range 0.1 to 0.8 volts. The Tafel slopes corresponded to $2.3RT/\alpha F$. This indicated the first electron transfer to be rate determining. Water discharge was concluded to be the rate determining step. The following mechanism was presented:





It was further reported that at potentials higher than those of the linear Tafel region, the reaction was diffusion controlled. In some cases evidence of the formation of passivating oxide layers was also observed.

III. EXPERIMENTAL

The experimental section is presented in five parts: (1) materials, (2) apparatus, (3) method of procedure, (4) data and results, and (5) sample calculations. The different phases of the experimentation involved the effect of maleic acid concentration and pH on the oxidation rate, faradaic efficiency of oxidation to CO₂, and the effect of temperature on the reaction rate.

A. Materials. All chemicals and reagents were Fisher "Certified" with the exception of maleic acid which was Matheson "Superior Grade". A list of these materials is given in Appendix A. Distilled water was used to make all solutions.

B. Apparatus. A list of apparatus is included in Appendix B. A further elaboration on some items is given below.

1. The Cells. The pyrex glass cell used for all studies with the exception of the faradaic efficiency determination is shown in Figure 1. The anodic and cathodic compartments (360 milliliter capacity) were separated by a glass frit (Pyrex Fine), 1.25 inches in diameter. The cell used for the faradaic efficiency determination is shown in Figure 2. In this cell, the anodic and cathodic compartments were separated by a

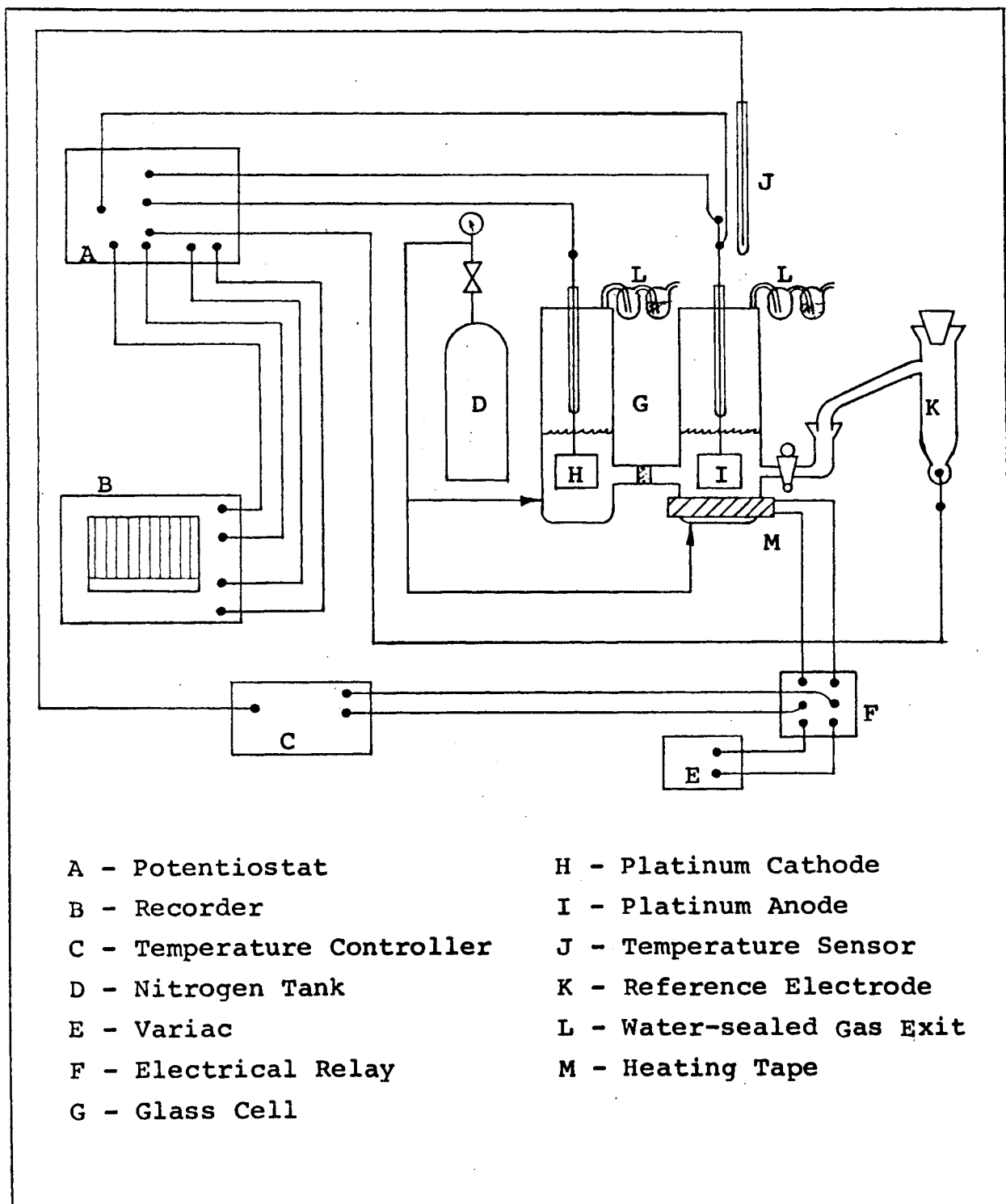


Figure 1. Diagram of the apparatus used for the current-potential studies.

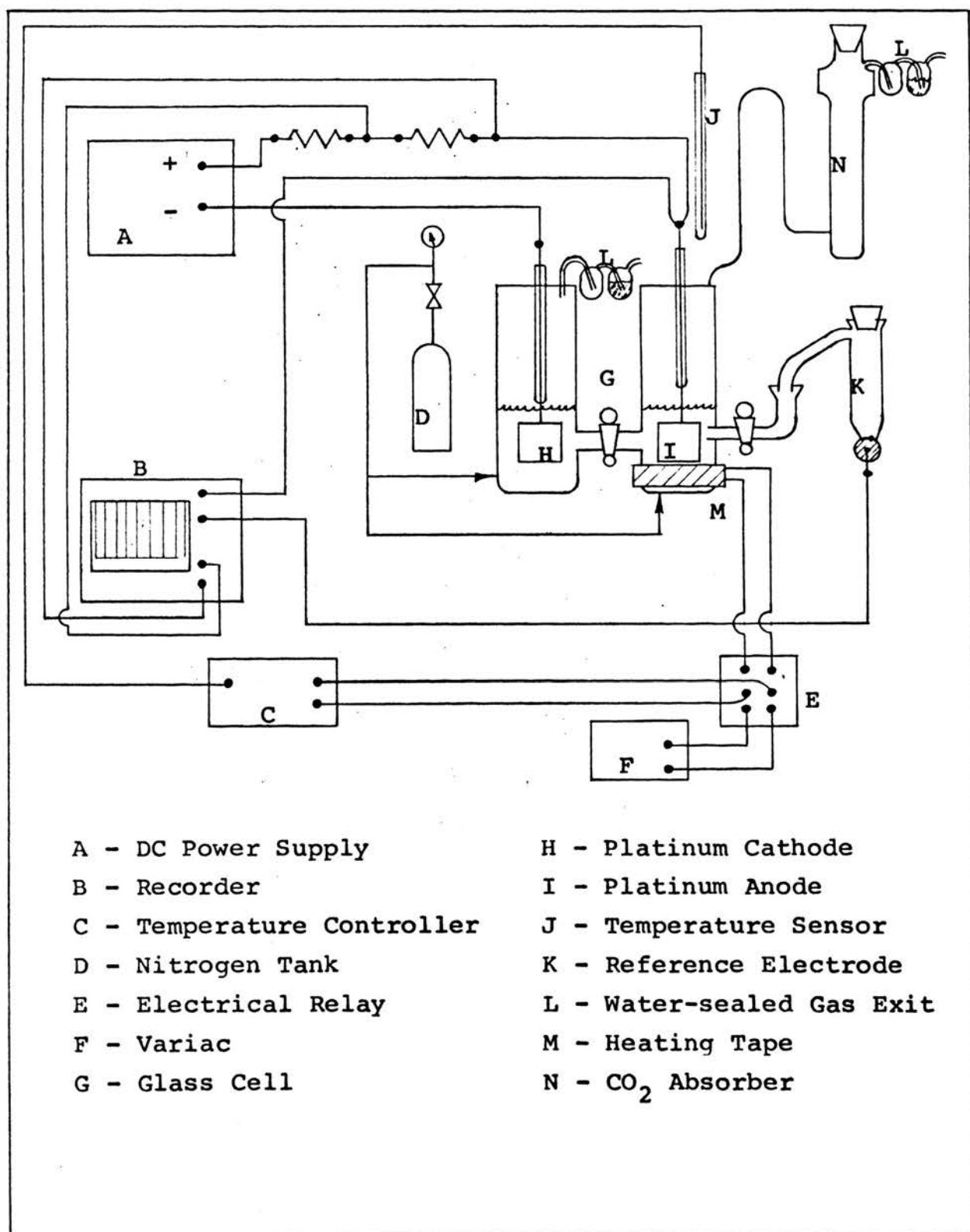


Figure 2. Diagram of the apparatus used for the faradaic efficiency study.

water-sealed stopcock which was closed during operation. A reference electrode was connected to the anodic compartment through a water-sealed stopcock and Luggin capillary. This stopcock remained closed. The reference electrodes were mercurous sulfate with 1.0 N H_2SO_4 electrolyte (0.651 volts at 80°C) and calomel with 1.0 N KCl electrolyte (0.268 volts at 80°C). The calomel electrode was used as the reference for basic solutions, faradaic efficiency determination, and activation energy studies. The mercurous sulfate electrode was used as the reference in the remainder of the studies. Both anodic and cathodic compartments contained inlets for the nitrogen purge. The outlets were water-sealed. The anodic compartment was thermostated at $80 \pm 0.5^\circ\text{C}$. Heat was supplied by a heating tape wrapped around the compartment. The heating and cooling cycles were made the same by adjusting the applied voltage to the tape with a variable transformer.

2. The Electrodes. The electrodes were made of 52 mesh platinum wire gauze folded on platinum wire frames for support. The platinum lead wires were sealed in four millimeter glass tubes. The electrodes were platinized using a platinum chloride solution to which a trace of lead acetate had been added. The anode in all potentiostatic experiments had a geometric surface area of 42.6 square centimeters.

3. Electronic Equipment. A potentiostat was

used to maintain a constant potential on the anode. The potential difference between the anode and reference electrode, and the current flowing between the anode and cathode, were transmitted by the potentiostat to a dual-channel potentiometric recorder. A diagram of the assembled equipment for potentiostatic experiments is also shown in Figure 1. Power for constant current (galvanostatic) experiments was supplied by a regulated power supply. The current was measured from the potential drop across a calibrated resistance in the working circuit. It and the potential difference between the anode and reference electrode were again recorded on the dual-channel recorder. A diagram of the apparatus for galvanostatic operation is shown in Figure 2.

4. Carbon Dioxide Absorber. The absorber was a long glass chamber containing barium hydroxide solution. It had an inlet in the bottom for the exit gases from the anodic compartment of the cell. A magnetic stirrer was used to break up the bubbles as they entered the absorber.

C. Method of Procedure. The anode was activated immediately before each experiment. It was placed in a solution of dilute H_2SO_4 (1.0 N) along with a small strip of platinum which served as a counter-electrode. The electrodes were approximately 2.5 inches apart. A power supply was connected to the electrodes through a DPDT

switch which was used to reverse the polarity of the current. A current of 4.2 amps was used to activate the 42.6 cm² electrode. The anode was alternately made cathodic (hydrogen evolution) and anodic (oxygen evolution) for pulses of five seconds during a two minute period. The pulsing was stopped on a cathodic pulse and hydrogen was evolved on the anode for two minutes. It was immediately removed, rinsed thoroughly with distilled water, and transferred to the cell. The cell was charged with enough solution to completely cover the electrodes (~ 450 milliliters). An activated anode was placed in the cell and nitrogen purging and heating initiated.

1. Potentiostatic Experiments. To reduce the ohmic overpotential, the anode was adjusted so that its bottom edge just contacted the Luggin capillary. Potential measurements were started when the nitrogen purge and heating commenced. The potential was allowed to come to steady state with no current flowing (rest potential). It was usually obtained within 1.5 hours after starting and was about +0.29 volts (NHS) in 1.0 N H₂SO₄. The rest potential decreased from this value when the pH was increased. After the rest potential had been obtained, the potential on the anode was increased approximately 100 millivolts and held constant by means of the potentiostat. When the current had come to a steady state, the potential

was increased by 50 millivolts. (Usually the current became steady, less than a ten per cent change per hour, within 45 minutes.) This procedure was continued until a limiting value of the current was reached. The current and potential were recorded simultaneously.

2. Galvanostatic Experiments. The rest potential was obtained in the same manner as described above. The stopcock between compartments was closed and the current adjusted to a desired value by varying the voltage applied with the power supply. Current fluctuations in the cell due to resistance changes were prevented by placing a large resistance (55,000 ohms) in series with the cell.

3. Carbon Dioxide Determination. A measured amount of saturated $\text{Ba}(\text{OH})_2$ solution was charged into the absorber. A 50 milliliter sample was withdrawn from the absorber and titrated with hydrochloric acid. After the exit gases from the anodic compartment of the cell had passed through the absorber for a predetermined time, another 50 milliliter sample was taken from the absorber and titrated. All vessels were flushed with nitrogen and closed so that no air contacted the $\text{Ba}(\text{OH})_2$ solution during the absorption or analysis. Using the above information and the total volume of the absorbate, the number of moles of CO_2 absorbed, i.e., produced by the reaction, was determined. Using the CO_2 produced, the

constant current flow, and the elapsed time, the faradaic efficiency for CO_2 production was calculated. The faradaic efficiency determination was made at a potential in the upper portion of the linear Tafel region.

D. Data and Results. Tables of the current-potential data are included in Appendix C. Appendix C also includes data taken during current-temperature (activation energy) studies.

It was noted during the potentiostatic studies that the current decreased continually with time.

1. Concentration Effect. Tafel plots (potential versus log current density) are shown in Figures 3 to 7. Different concentrations of maleic acid were investigated in solutions of constant pH and sulfate concentration. The sulfate concentration was held constant at 1.0 N using the necessary quantities of H_2SO_4 and K_2SO_4 to give the desired pH. Six concentrations of maleic acid (0.003, 0.01, 0.03, 0.10, 0.30, and 1.0 M) were investigated at a pH of 0.3. Five concentrations (0.003, 0.01, 0.03, 0.10, and 0.30 M) were used for a pH of 2.0. The ionization of maleic acid was such that at a concentration of 1.0 M, it alone gave a pH less than 2.0. For this same reason, it was only possible to use two concentrations of maleic acid (0.003 and 0.01 M) to make solutions of pH = 4.0. Solutions of higher concentrations of maleic acid (0.03,

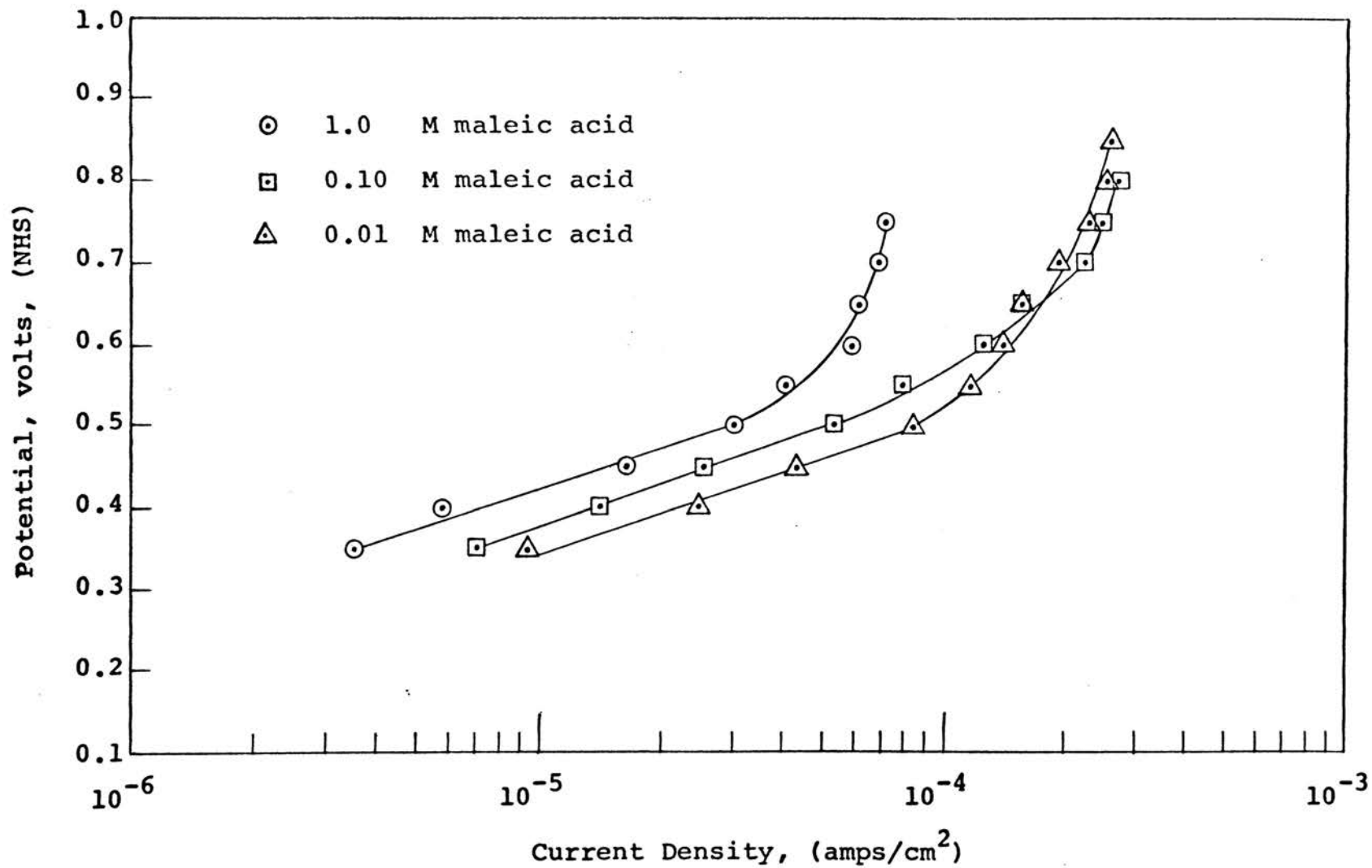


Figure 3. Tafel plot for the anodic oxidation of maleic acid in 1.0 N H_2SO_4 (pH = 0.3) on platinized-platinum electrodes at 80°C.

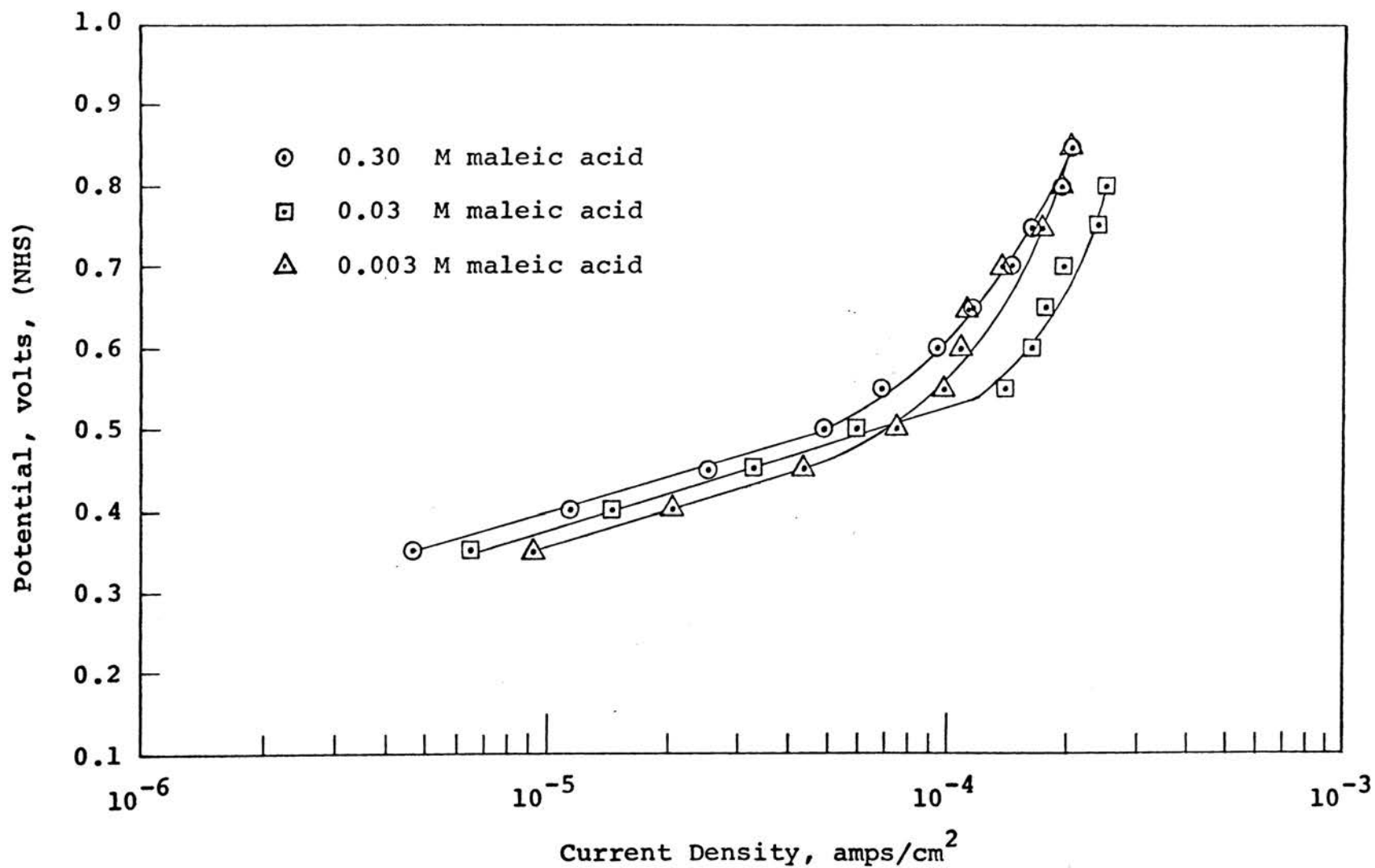


Figure 4. Tafel plot for the anodic oxidation of maleic acid in 1.0 N H_2SO_4 (pH = 0.3) on platinized-platinum electrodes at 80°C.

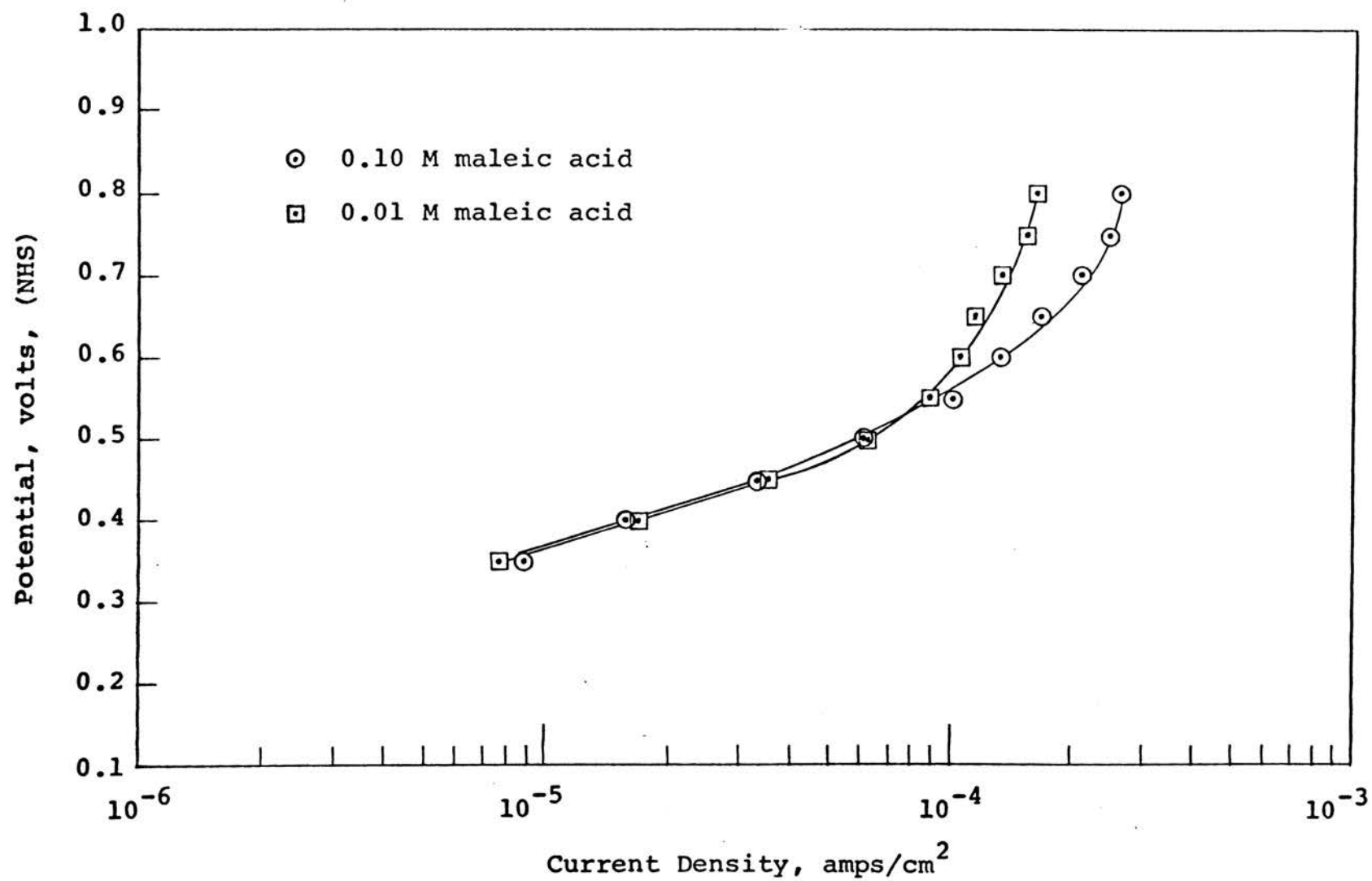


Figure 5. Tafel plot for the anodic oxidation of maleic acid in H_2SO_4 - K_2SO_4 (pH = 2.0) on platinized-platinum electrodes at 80°C.

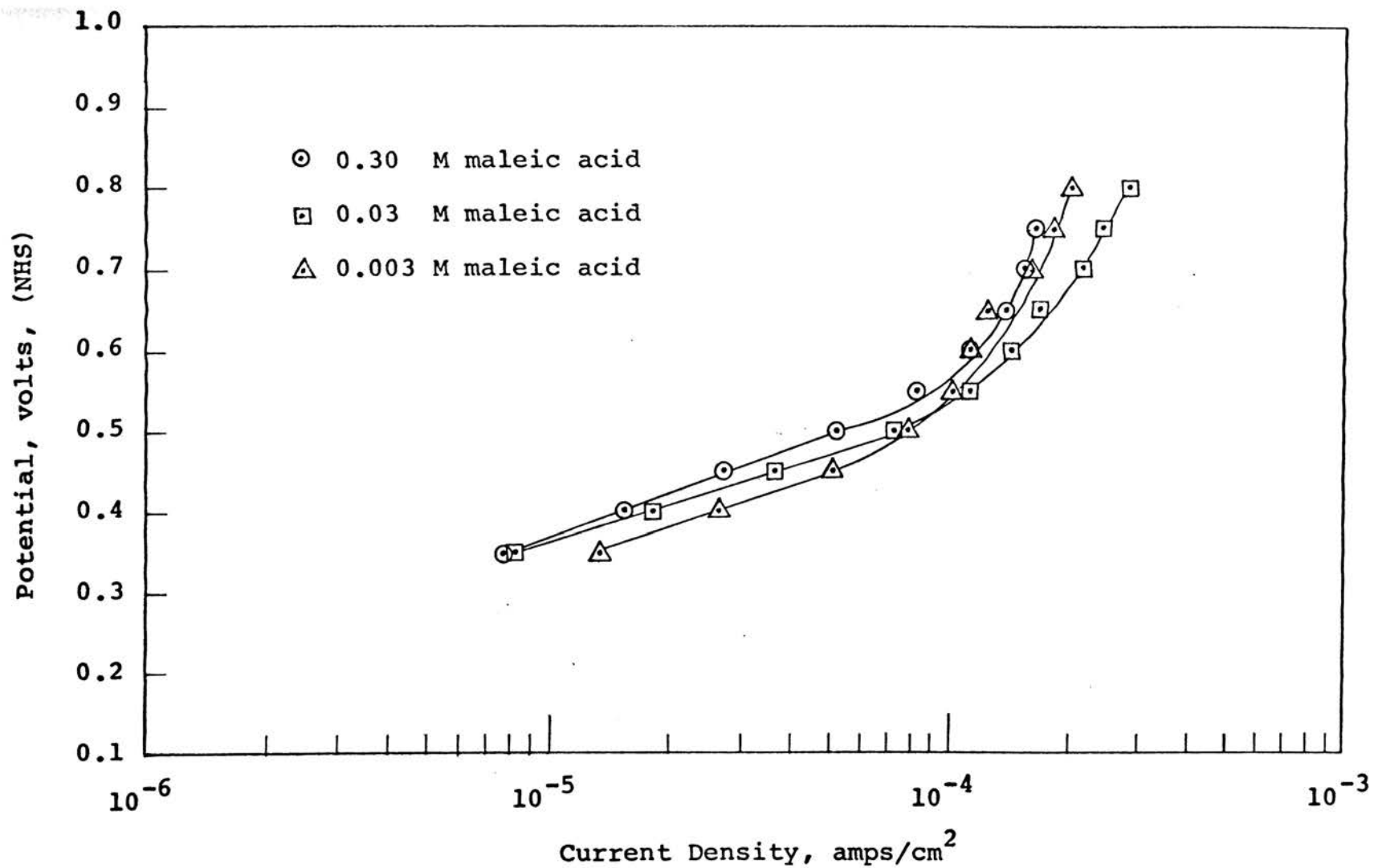


Figure 6. Tafel plot for the anodic oxidation of maleic acid in H_2SO_4 - K_2SO_4 (pH = 2.0) on platinized-platinum electrodes at 80°C.

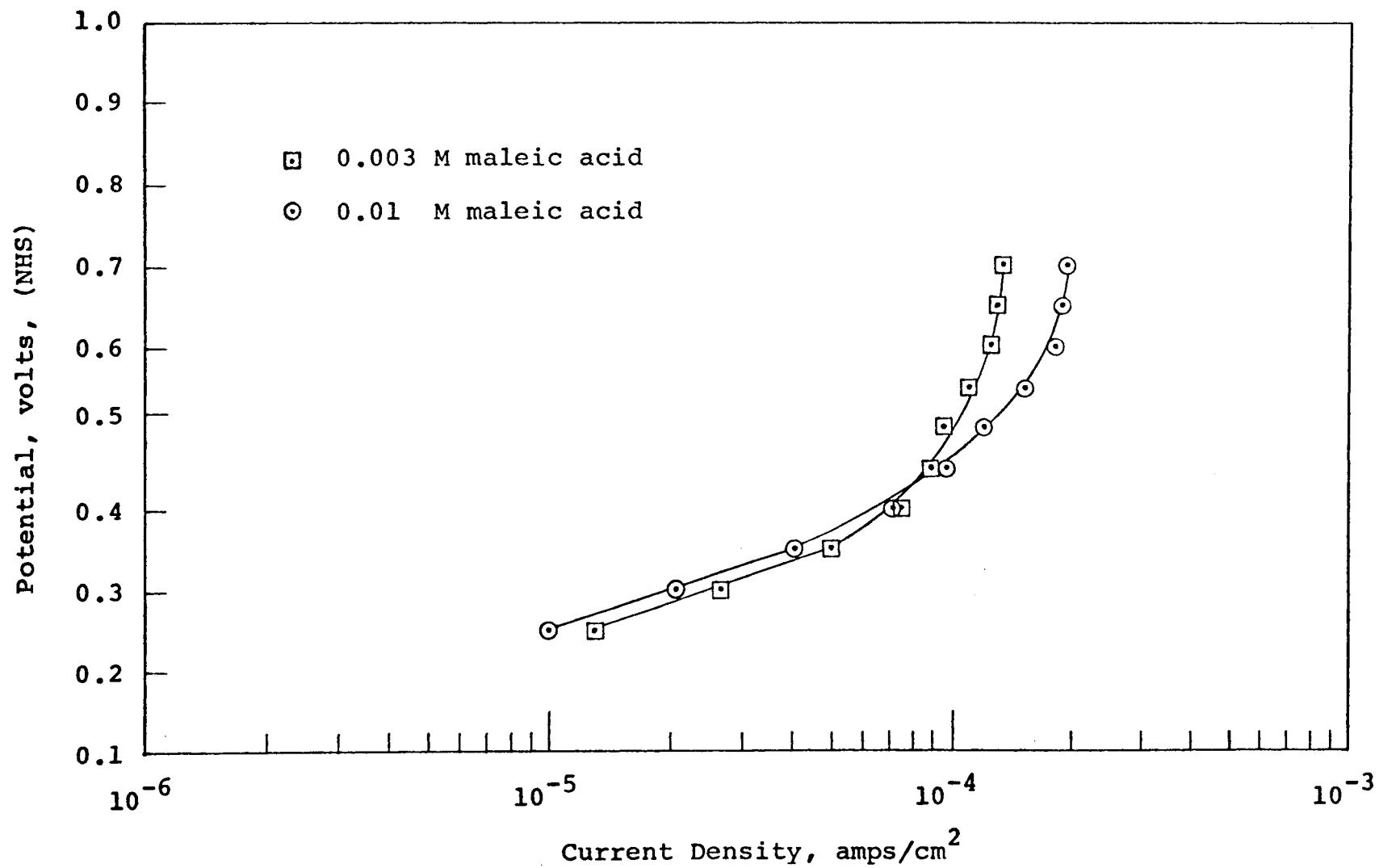


Figure 7. Tafel plot for the anodic oxidation of maleic acid in H_2SO_4 - K_2SO_4 (pH = 4.0) on platinized-platinum electrodes at 80°C.

0.10, 0.30, and 1.0 M) were made with 1.0 N K_2SO_4 solution. The pH of these solutions ranged from just less than 4.0 to approximately 2.0.

The oxidation of maleic acid in basic solutions yielded currents significantly less than in acidic solutions. In 1.0 N KOH, current densities of $\sim 10^{-6}$ amps/cm² were observed in the region corresponding to the linear Tafel region in acidic solution studies. In a solution where the ratio of singly ionized maleic acid to unionized maleic acid was calculated as being 1×10^4 , diffusion-limited current densities of 5×10^{-5} amps/cm² were obtained.

2. Temperature Effect. The dependence of current on temperature for 0.10 M maleic acid in 1.0 N H_2SO_4 is shown in Figure 8.

E. Sample Calculations. All potentials are referred to the normal hydrogen electrode ($E_H = 0.0$) at 80°C.

1. Anode Potential. The anode potential was calculated using the expression:

$$E = E_r + E_m$$

where,

E = anode potential, volts

E_r = potential of reference electrode, volts

E_m = measured potential difference between the reference electrode and anode, volts

The value of E_r used was 0.651 volts for the mercurous

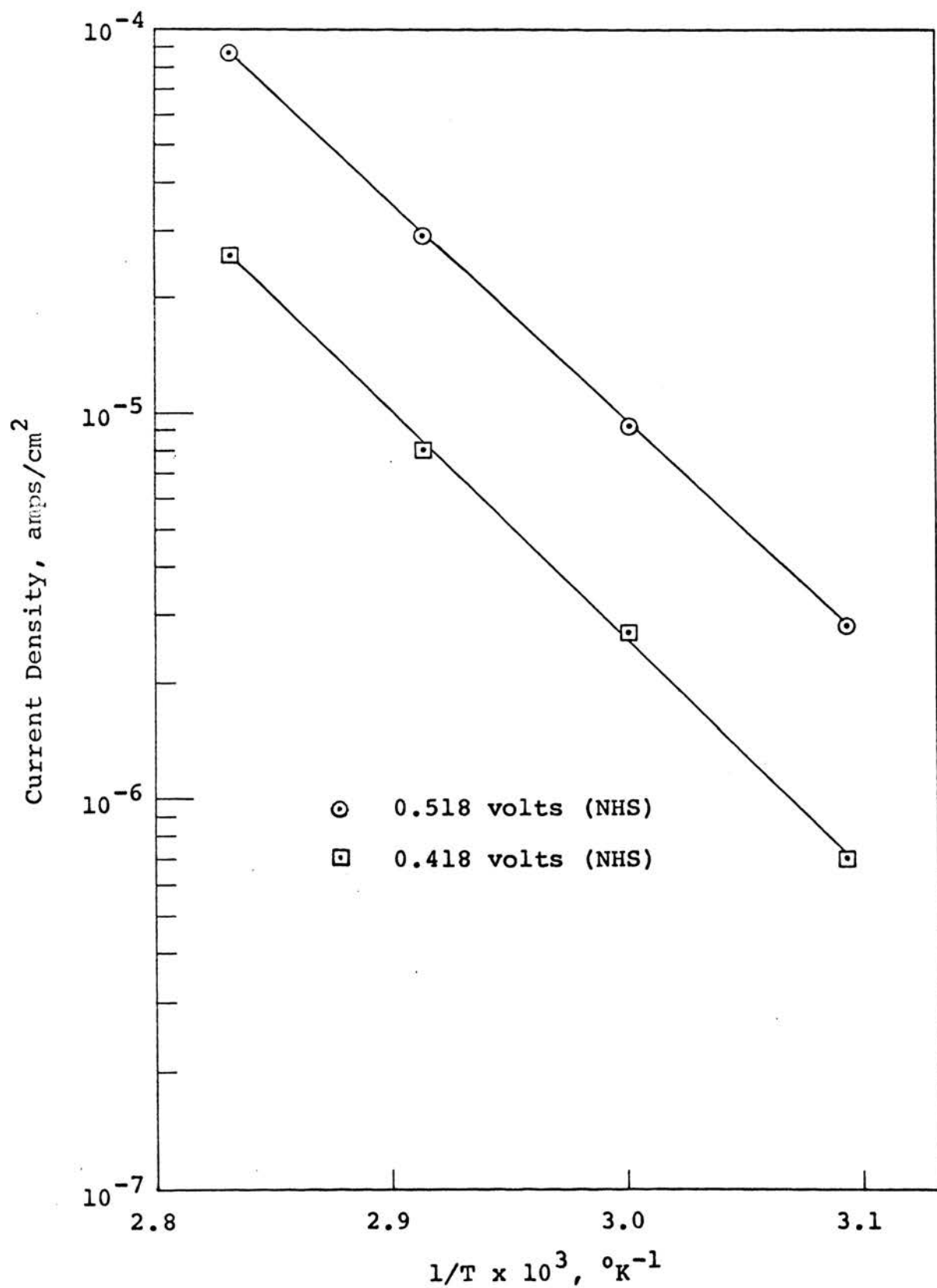


Figure 8. Arrhenius plots for the anodic oxidation of 0.10 M maleic acid in 1.0 N H₂SO₄ (pH = 0.3) on platinized-platinum.

sulfate electrode (1.0 N H_2SO_4) and 0.268 volts for the calomel electrode (1.0 N KCl). Substituting numerical values, using data from Table 1:

$$E = 0.651 + (-0.100) = 0.551 \text{ volts}$$

2. pH of the Solution. The concentrations of K_2SO_4 and H_2SO_4 for a required pH and given maleic acid concentration were calculated using the expression:

$$2A = H + 0.5H/(K_s + H) - K_m M/(K_m + H)$$

where,

A = required concentration of H_2SO_4 , gmols/liter

H = desired hydrogen ion concentration,
gmols/liter

K_s = second ionization constant of H_2SO_4 at 80°C
(first ionization assumed complete)
 $= 2.36 \times 10^{-3}$ (15)*

K_m = first ionization constant of maleic acid at
 80°C (second ionization was found to be
negligible in the pH ranges studied)
 $= 7.6 \times 10^{-3}$ (16)*

M = concentration of maleic acid, gmols/liter

*The values of the ionization constants were obtained by plotting the cited data as $\log K$ versus $1/T$ and extrapolating to 80°C .

The above expression was developed for a constant sulfate concentration of 1.0 equivalent per liter. Thus the concentration of K_2SO_4 could be calculated from:

$$P = 0.5 - A$$

where,

$$P = \text{concentration of } K_2SO_4, \text{ gmols/liter}$$

Substituting numerical values for the case where the desired pH was 2.0 and the maleic acid concentration was 0.10 M:

$$2A = 1 \times 10^{-2} + (0.005)/(1.236 \times 10^{-2}) \\ - 7.6 \times 10^{-5}/(1.76 \times 10^{-2})$$

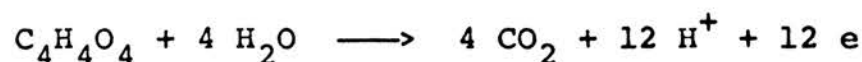
$$= 0.372 \text{ gmols/liter}$$

$$A = 0.186 \text{ gmols/liter}$$

$$P = 0.5 - 0.186$$

$$= 0.314 \text{ gmols/liter}$$

3. Faradaic Efficiencies. The anode reaction for the complete oxidation of maleic acid is:



The theoretical amount of CO_2 formed for a given passage of charge can be calculated using Faraday's law:

$$C_t = 4it/12F$$

where,

$$C_t = CO_2 \text{ theoretically formed for complete} \\ \text{oxidation, gmols}$$

- i = current, amps
 t = time, seconds
 F = Faraday's constant
 = 96,500 coulombs/equivalent

The amount of CO_2 actually formed was calculated by the expression:

$$C_a = 10^{-5} DNV$$

where,

- C_a = CO_2 actually formed, gmols
 D = difference in amount of HCl used to titrate
 50 milliliter aliquots of $\text{Ba}(\text{OH})_2$ from the
 absorber before and after absorption,
 milliliters
 N = normality of HCl, equivalents/liter
 V = volume of $\text{Ba}(\text{OH})_2$ in the absorber during
 absorption, milliliters

The faradaic efficiency is defined as the actual amount of CO_2 formed during the oxidation divided by the theoretical amount formed for complete oxidation. Substituting numerical values for the oxidation of 0.10 M maleic acid in 1.0 N H_2SO_4 (performed for 50 hours 13 minutes at a current of 4.0 milliamperes), where the titration difference was 6.00 milliliters of 0.2718 N HCl:

$$\begin{aligned}
 C_t &= (4)(181,020)(4.0 \times 10^{-3}) / (12)(96,500) \\
 &= 2.50 \times 10^{-3} \text{ gmols}
 \end{aligned}$$

$$C_a = (10^{-5}) (6.00) (0.2718) (149)$$

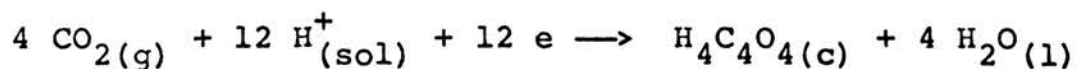
$$= 2.43 \times 10^{-3} \text{ gmols}$$

$$\text{faradaic efficiency} = C_a/C_t = 2.43/2.50$$

$$= 0.97$$

4. Reversible Potential. The reversible electrode potential is that which exists across the metal-solution interface at equilibrium conditions, i.e., no net current. This reversible potential should theoretically correspond to the rest potential. It has been found however, that the reversible and rest potential differ widely for most hydrocarbon oxidation reactions, probably due to the smallness of the exchange current normally found for them. (When the exchange current is small, various impurities in the solution will control the rest potential rather than the desired reaction.) The value of the reversible potential for this reaction is of interest because it is necessary to evaluate both the exchange current and the true activation energy. Its calculation is shown below.

The reversible potential desired is for the following reaction:



It was calculated as follows:

$$E_{298}^{\circ} = - \Delta F^{\circ}/nF$$

where,

E_{298}° = standard electrode potential at 298°K,
volts

ΔF° = standard free energy change of the above
reaction, calories

n = number of electrons transferred

F = Faraday's constant
= 23,060 calories/equivalent

ΔF_{298}° for use in the above equation was calculated using standard free energies of formation and found to be 880 calories. To calculate the standard potential at 353°K, it was necessary to obtain the temperature coefficient for the reaction. Due to the limited thermodynamic data available and the smallness of the correction, the temperature coefficient was evaluated at 25°C and assumed to remain constant over the range 25 to 80°C. It was calculated from:

$$\left| \frac{\delta E}{\delta T} \right|_p = \frac{\Delta S}{nF}$$

where,

ΔS = entropy change for the reaction
= - 286.7 calories/°K

$\left| \frac{\delta E}{\delta T} \right|_p$ = temperature coefficient
= - 1.036 x 10⁻³ volts/K°

Thus, the standard potential at 353°K was calculated using the expression:

$$E_{353}^{\circ} = E_{298}^{\circ} + 55 \left| \frac{\delta E}{\delta T} \right|_p$$

The reversible potential at the experimental condition was calculated using the Nernst equation:

$$E_{353} = E_{353}^{\circ} + \frac{RT}{nF} \log \frac{(a_{CD})^4 (a_{H^+})^{12}}{(a_{MA}) (a_W)^4}$$

where,

E_{353} = reversible electrode potential, volts

a_{CD} = activity of CO_2

a_{H^+} = activity of hydrogen ions

a_W = activity of water, = 1.0

a_{MA} = activity of maleic acid

At the concentrations studied, the activity of maleic acid (a neutral molecule) could be approximated by its concentration. The activity of CO_2 was assumed to be the concentration of dissolved CO_2 in solution as calculated in the latter part of this section. Substituting numerical values for a pH = 0.3 and maleic acid concentration = 0.1 M:

$$E_{298}^{\circ} = (-880)/(12)(23,060) = -0.003 \text{ volts}$$

$$\begin{aligned} E_{353}^{\circ} &= -0.003 + 55(-1.036 \times 10^{-3}) \\ &= -0.060 \text{ volts} \end{aligned}$$

$$\begin{aligned}
E_{353} &= -0.060 + \frac{(0.07)(4)}{12} \log a_{\text{CD}} + (0.07) \log a_{\text{H}^+} \\
&\quad - \frac{0.07}{12} \log a_{\text{MA}} \\
&= -0.060 + \frac{(0.07)(4)(-4.39)}{12} + (0.07)(-0.30) \\
&\quad - \frac{(0.07)(-1.0)}{12} \\
&= -0.060 - 0.102 - 0.021 + 0.006 \\
&= -0.177 \text{ volts}
\end{aligned}$$

The concentration of dissolved CO_2 at the electrode was assumed to be controlled by diffusion of CO_2 away from the electrode and was estimated by the expression: ⁽¹⁴⁾

$$i = \frac{zFD}{\delta}(C_E - C_B)$$

where,

$$\begin{aligned}
i &= \text{current density} \\
&= 2.35 \times 10^{-5} \text{ amps/cm}^2 \\
z &= \text{electrons transferred/mole } \text{CO}_2 \\
&= 3 \\
F &= \text{Faraday's constant} \\
&= 96,500 \text{ coulombs/equivalent} \\
D &= \text{diffusivity of } \text{CO}_2 \\
&= 2 \times 10^{-5} \text{ cm}^2/\text{sec} \\
\delta &= \text{thickness of diffusion layer} \\
&= 0.01 \text{ cm} \\
C_E &= \text{concentration of } \text{CO}_2 \text{ at electrode,} \\
&\quad \text{gmols/cm}^3
\end{aligned}$$

C_B = concentration of CO_2 in the bulk solution
= 0.0 gmols/cm³ (as solution was continuously flushed with nitrogen)

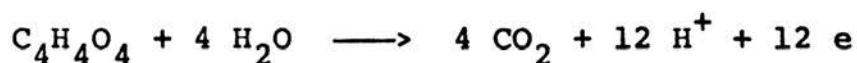
Therefore,

$$\begin{aligned}C_E &= (2.35 \times 10^{-7}) / (3) (96,500) (2 \times 10^{-5}) \\&= 4.07 \times 10^{-8} \text{ gmols/cm}^3 \\&= 4.07 \times 10^{-5} \text{ gmols/liter}\end{aligned}$$

IV. DISCUSSION

In this section, the results of the phases of experimentation are analyzed. The analysis is made with the purpose of determining a reaction mechanism. Where applicable, the results are compared with those from other hydrocarbon oxidation studies reported in the literature.

A. Faradaic Efficiency. The reaction was found to yield CO_2 with an efficiency of 97 ± 5 per cent. Thus, the overall reaction in acidic solution can be expressed as:



The observed efficiency of oxidation permits the assumption that essentially no side reactions were occurring. No efficiency studies were made in basic solutions as current-potential data for $\text{pH} > 7.0$ indicated that maleic acid was not being oxidized.

B. Exchange Current Densities. Reversible potentials at 353°K were estimated for maleic acid concentrations (0.003 to 1.0 M, $\text{pH} = 0.3$) as being -0.168 to -0.183 volts, respectively. An example of this estimation has been presented elsewhere (see page 30). Extrapolation of the linear section of the Tafel plots to their respective reversible potentials gives exchange current densities

of approximately 10^{-8} amps/cm². This exchange current density is approximately that reported for the oxidation in 1.0 N H₂SO₄, of ethylene⁽¹⁴⁾ and crotonic acid.⁽¹³⁾

C. Current-Potential Relationships. Points on the Tafel curves in the experimental section could be reproduced within 10 per cent. There were three distinguishable regions at potentials greater than the rest potential:

- (1) A linear Tafel region, where after 45 minutes at constant potential, there was little (< 10 per cent/hour) or no change in current density with time. This region was of greatest interest as it pertained only to the oxidation reaction.
- (2) A region where the potential-log current density plot was non-linear. This may be explained by ohmic overpotentials which would be expected at increased currents. Others have shown that in some instances oxide coverage of the electrode becomes extensive at these potentials, thus causing the electrode to be further polarized.⁽¹⁴⁾
- (3) At potentials greater than 0.8 volts (pH = 0.3), the current density decreased continually with time until it reached a negligible value. It was assumed that in

this region, the electrode had been covered by an oxide layer which prevented the adsorption of the organic molecules.⁽¹⁷⁾

In this study, the linear Tafel regions commenced at potentials near (100 millivolts above) the rest potential. In this respect they differed from those obtained in other oxidation studies.^(13,14)

Experimental slopes obtained in this study ranged from 145 to 170 millivolts. At 80°C, with α assumed as 0.5, this would correspond most nearly to a theoretical slope of $2.3RT/\alpha F$ (140 millivolts). A combination of variance in α and experimental measurements could easily account for this difference between the theoretical and observed slopes. A slope of 140 millivolts indicates the first charge transfer to be rate determining. Theoretical Tafel slopes for other possible rate determining steps are less than 140 millivolts.

D. Effect of Maleic Acid Concentration. Figures 9 and 10 are plots of current density versus maleic acid concentration for two potentials in the linear Tafel region. It may be seen that the current density increased as the maleic acid concentration was decreased. This effect has been noted by others conducting similar anodic oxidation studies.^(10,13,14,18) This indicates that maleic acid is not a direct participant in the rate

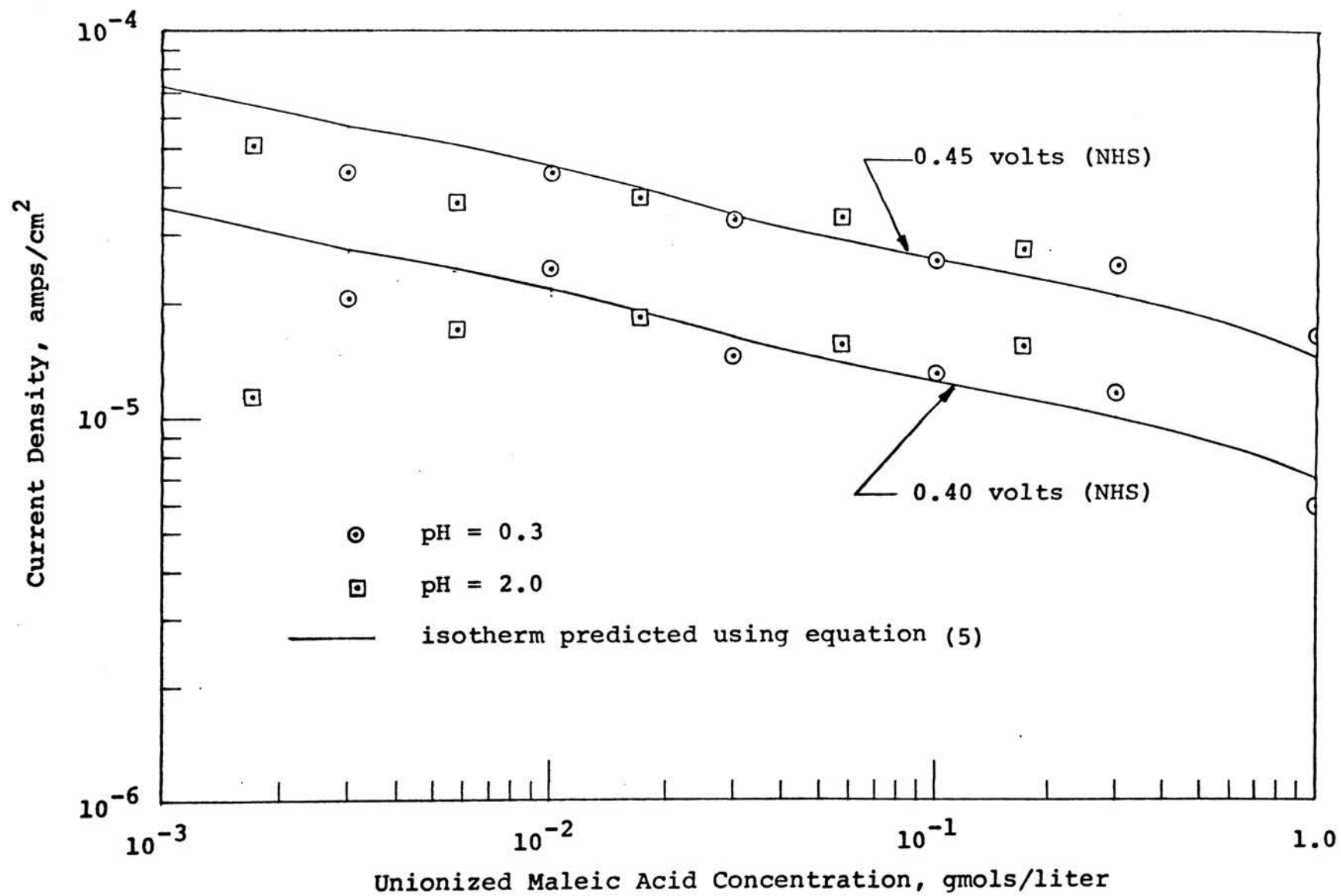


Figure 9. Effect of concentration on the anodic oxidation of maleic acid on platinized-platinum electrodes at 80°C.

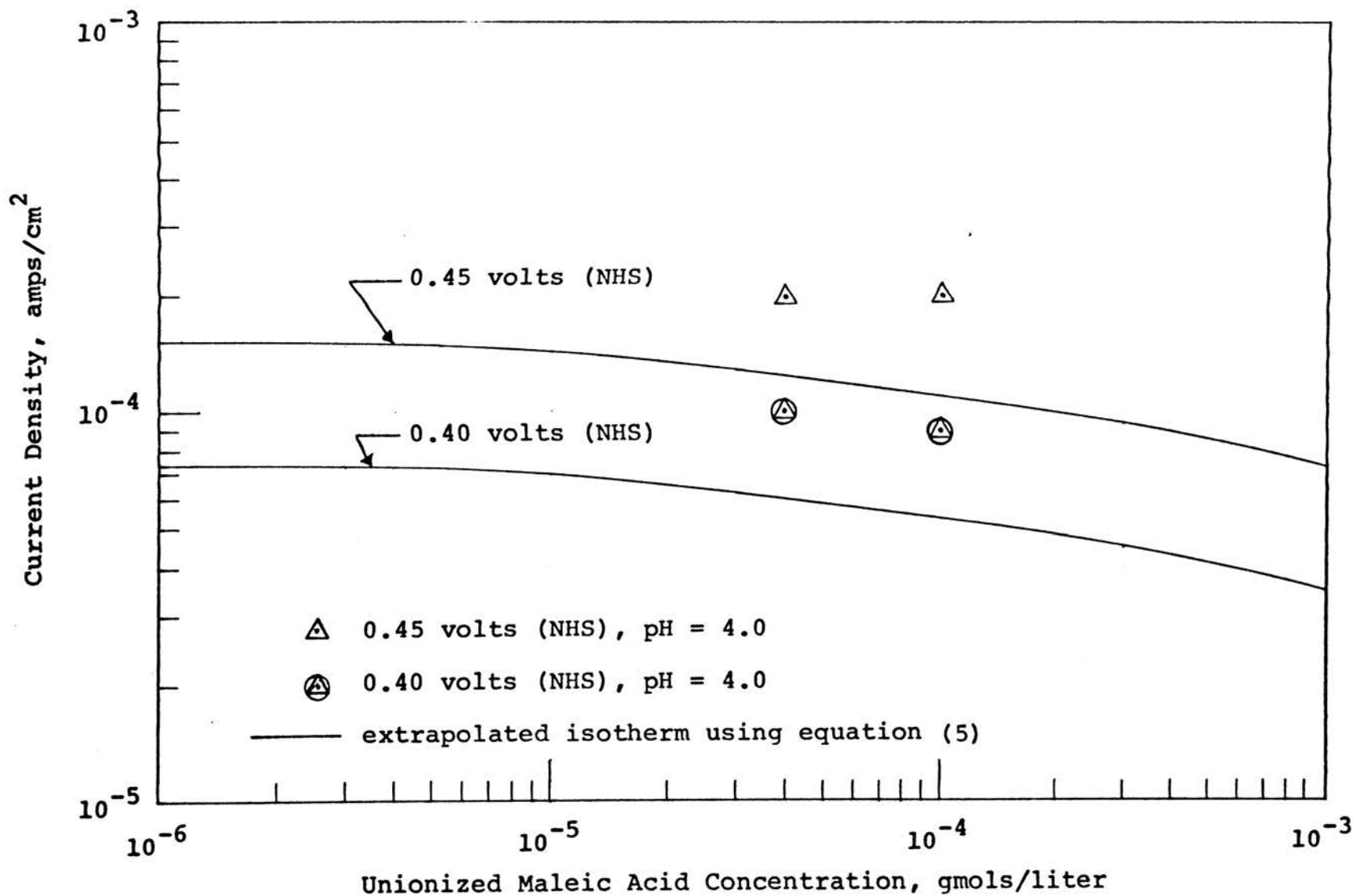


Figure 10. Effect of concentration on the anodic oxidation of maleic acid on platinized-platinum electrodes at 80°C.

determining step and that the reaction rate is dependent on the amount of electrode surface free of adsorbed maleic acid or other intermediates derived from it.

E. Effect of pH. Figure 11 shows the experimental data for the effect of pH on current density in the pH region, 0.3 to 4.0. The pH at the electrode for an electrolyte pH of 4.0 was calculated using a relationship presented in the previously cited work.⁽¹⁹⁾ In the pH range 0.3 to 2.0, it can be seen that there was no apparent effect of pH on the oxidation. This has also been observed in other studies.⁽¹⁸⁾

F. Activation Energy. Figure 8 is a plot of log current density versus $1/T$ for two potentials in the linear Tafel region. The maleic acid concentration was 0.1 M and the H_2SO_4 concentration was 1.0 N (pH = 0.3). The slopes of $-5650^\circ K$ (0.518 volts) and $-5890^\circ K$ (0.418 volts) yield activation energies of 25.8 and 26.9 kilocalories, respectively, from the Arrhenius relation. The change in activation energy per volt was calculated to be - 11 kilocalories/volt. Thus, the activation energy at the reversible potential (- 0.177 volt) was evaluated as 33.4 kilocalories.

G. The Reaction Mechanism. In order to be meaningful, a reaction mechanism must account for the experimental observations. In this case, an acceptable mechanism must

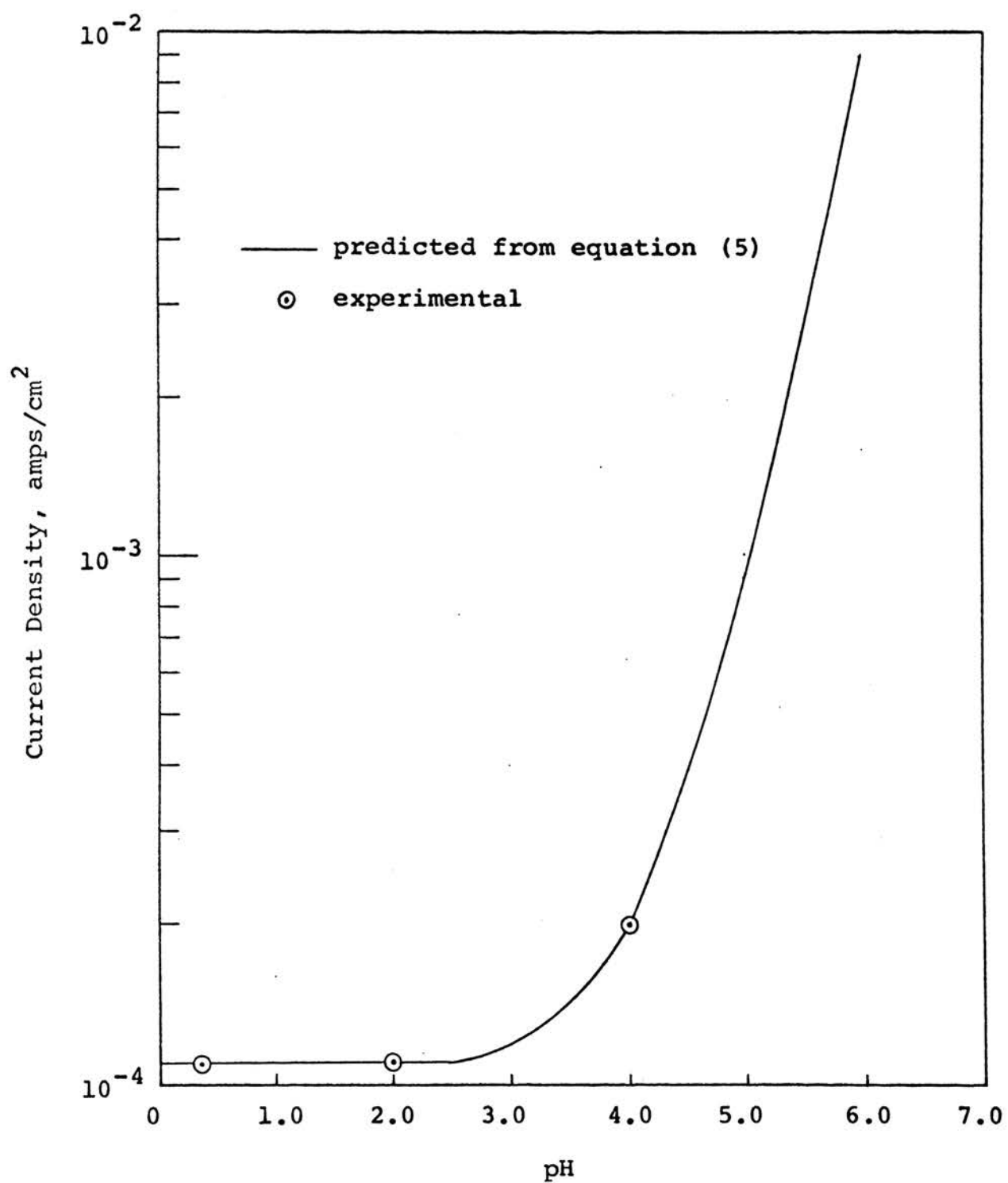
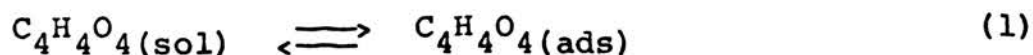


Figure 11. Effect of pH on the anodic oxidation of maleic acid on platinized-platinum electrodes at 80°C.

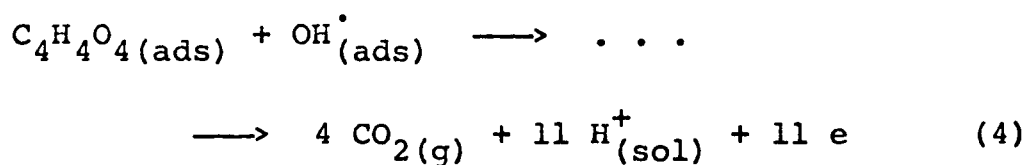
account for the previously discussed Tafel slope, negative concentration effect, pH effect, and incorporate unionized maleic acid as the reactive species.

The final qualification stems from the previously discussed observation of diffusion-limited current densities $\sim 5 \times 10^{-5}$ amps/cm² in solutions containing singly ionized maleic acid and maleic acid in the ratio of 1×10^4 . Assuming the ionized maleic acid to be the reacting specie, the predicted diffusion-limited current density would be $\approx 1.3 \times 10^{-1}$ amps/cm². (Note that the diffusion current density is approximately that which would be expected for unionized maleic acid.) In 1.0 N KOH solutions, where the doubly ionized specie would predominate, negligible current densities were obtained. Thus, unionized maleic acid was determined to be the specie oxidized.

Previous investigators, observing kinetic parameters similar to those of this study, have proposed an oxidation mechanism involving the discharge of water or OH⁻ ions as rate determining steps.^(13,18) Accordingly, for maleic acid:



r.d.s.



Assuming equations (2) or (3) to be rate determining, an expression for the current density has been developed:⁽¹⁸⁾

$$i = nF(k_{(2)} a_{\text{H}_2\text{O}} + k_{(3)} a_{\text{OH}^-}) (1 - \theta_A) e^{\alpha EF/RT} \quad (5)$$

where,

i = current density, amps/cm²

n = number of electrons transferred in r.d.s.
= 1.0

F = Faraday's constant

$k_{(2)}$ = rate constant for equation (2)

$a_{\text{H}_2\text{O}}$ = activity of water, = 55.5 gmols/liter

$k_{(3)}$ = rate constant for equation (3)

a_{OH^-} = activity of hydroxyl ions, gmols/liter

θ_A = fractional coverage of adsorbed maleic acid
on the electrode

α = 0.5

If water (or OH⁻) discharge is rate determining, then the maleic acid adsorption can be assumed to be at equilibrium, thus:

$$K C_A (1 - \theta_A)^S = \theta_A \quad (6)$$

where,

K = equilibrium constant for the adsorption reaction (1)

C_A = concentration of maleic acid, gmols/liter

s = the number of sites occupied by one adsorbed maleic acid molecule

Assuming various values for K and s , θ_A was evaluated at different maleic acid concentrations. From equation (5) at constant potential:

$$i = k'(1 - \theta_A) \quad (7)$$

For a 1.0 M maleic acid solution, k' was evaluated using values of i and E taken from the Tafel plot for this concentration. Values of i were taken directly from the Tafel plot rather than using the experimental data. This was done because the correlation described below is particularly sensitive to the starting values and at the selected potentials, 0.40 and 0.45 volts, there seemed to be considerable scatter in the data. Using the value for k' and coverages calculated from equation (6), values of i at various concentrations for a given K and s were predicted. It was found that the predicted values of i best matched the experimental data for $K = 10^4$ and $s = 4$. These predicted i 's are shown in Figures 9 and 10.

It can be seen from Figure 10 that the current densities for $\text{pH} = 4.0$ do not lie on the isotherm

corresponding to pH's 0.3 and 2.0. This is explained by the proposed mechanism (equation (5)) as in this pH region it has been previously observed⁽¹⁸⁾ that the discharge of OH⁻ ions begins to contribute to the current density, i.e., $k_{(3)} a_{\text{OH}^-}$ becomes significant compared to $k_{(2)} a_{\text{H}_2\text{O}}$. The experimental data indicated that K was constant in the pH range 0.3 to 2.0. As coverage is relatively insensitive to slight variations in K's of this magnitude, the further assumption that K is constant up to a pH of 4.0 should not introduce appreciable error. Thus, evaluation of the constants $k_{(2)}$ and $k_{(3)}$ was accomplished by evaluating the term $i/(1 - \theta_A)$ which was constant for $K = 10^4$. Neglecting the value of $k_{(3)} a_{\text{OH}^-}$ at pH = 0.3 the relationship:

$$i/(1 - \theta_A) = nF(k_{(2)} a_{\text{H}_2\text{O}}) e^{\alpha EF/RT}$$

$$1.528 \times 10^{-4} = 96,500(k_{(2)}) (55.5) (1,630)$$

$$\text{yields } k_{(2)} = 1.75 \times 10^{-14}.$$

At a pH of 4.0, $C_A = 1 \times 10^{-4}$ gmols/liter,

$i = 2 \times 10^{-4}$ amps/cm², and $1 - \theta_A = 0.72$:

$$i/(1 - \theta_A) = nF(k_{(2)} a_{\text{H}_2\text{O}} + k_{(3)} a_{\text{OH}^-}) e^{\alpha EF/RT}$$

$$2.78 \times 10^{-4} = 96,500 | (1.75 \times 10^{-14}) (55.5) \\ + k_{(3)} (2.51 \times 10^{-9}) | (1,630) \\ k_{(3)} = 3.18 \times 10^{-4}.$$

It can be seen that in strongly acidic solutions, $k_{(2)}$ will control the magnitude of the current density, while in more basic solutions (pH = 4.0 to 6.0), $k_{(3)}$ will be the controlling factor. At a pH greater than 7.0 it would appear that the current would be increased significantly. However, since the unionized acid is the reacting species, the current actually decreases to negligible values. Thus, the developed relationship is applicable only at pH's < 7.0.

The foregoing development assumed Langmuir's isotherm to be applicable. Langmuir's isotherm is applicable only for constant heats of adsorption, i.e., no lateral or a constant lateral interaction of adsorbed species and a constant activity of adsorption sites. Generally speaking, all adsorbed species meet this criteria when the coverage of the specie is either < 0.2 or > 0.8. For $K = 10,000$, the coverage of maleic acid on the electrode was determined to be > 0.8 for the majority of the acidic solutions. Thus, the assumption of a Langmuir isotherm is reasonably valid.

V. RECOMMENDATIONS

In the interest of further pursuit of this study, the following recommendations are made:

- (1) Since the reaction rate increases with temperature, studies in strongly basic solutions should be made at temperatures greater than 80°C.
- (2) Studies carried out on longer chain unsaturated acids or substituted maleic acid compounds should yield information on the contributions of the various constituent groups to the oxidation mechanism.

VI. SUMMARY AND CONCLUSIONS

The following were studied to determine the mechanism for the oxidation of maleic acid on platinized-platinum electrodes at 80 °C:

- (1) current density-potential relationships at 80 °C, with maleic acid concentration and pH as variables,
- (2) faradaic efficiency at a current density and potential in the linear Tafel range, and
- (3) effect of temperature on current density.

The current density-potential relationships were established using steady state data taken at potentials greater than the rest potential. It was found that the linear Tafel regions had slopes of 145 - 170 millivolts. These approximate the theoretical Tafel slope of $2.3RT/\alpha F$ (140 millivolts). No evidence of oxidation was observed in solutions whose pH's were greater than 7.0. Solutions where the singly ionized acid specie was predominant gave diffusion-limited current densities that were much less than those expected if the singly ionized specie were being oxidized. As concentration of maleic acid was increased, the current density decreased.

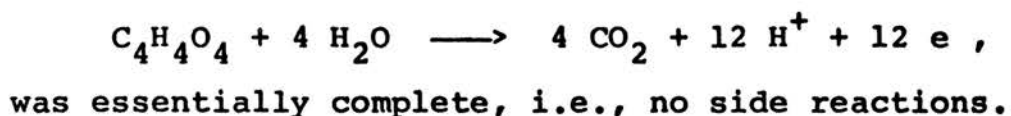
The faradaic efficiency of oxidation to CO_2 , determined by measuring the amount of CO_2 produced, was found to be

97 ± 5 per cent. This efficiency was for a 0.10 M maleic acid solution whose pH was 0.3.

The temperature-current density studies, 50 - 80°C, yielded an activation energy of 33.4 kilocalories for the reaction at the reversible potential.

From the foregoing observations, it was concluded:

- (1) The first charge transfer was rate determining.
- (2) Undissociated maleic acid was the reacting specie.
- (3) The reaction,



- (4) The reaction rate was proportional to the electrode surface area free of adsorbed maleic acid molecules.
- (5) The discharge of water (pH = 0.3 to 2.0) or the discharge of hydroxyl ions (pH = 2.5 to 6.0) was the specie involved in the rate determining step.

With the above information, a mechanism assuming Langmuir type adsorption with a four-point attachment of the maleic acid molecule was found to adequately correlate the data. The rate expression for this mechanism is:

$$i = nF(k_{(2)} a_{\text{H}_2\text{O}} + k_{(3)} a_{\text{OH}^-}) (1 - \theta_A) e^{\alpha_{\text{FE}}/RT}$$

where,

- i = current density, amps/cm^2
 n = number of electrons transferred in rate determining step
 = 1.0
 F = Faraday's constant
 $k_{(2)}$ = rate constant for water discharge reaction
 = 1.75×10^{-14}
 $a_{\text{H}_2\text{O}}$ = activity of water, gmols/liter
 $k_{(3)}$ = rate constant for hydroxyl ion discharge
 = 3.18×10^{-4}
 a_{OH^-} = activity of hydroxyl ions, gmols/liter
 α = 0.5
 E = potential, volts
 R = gas constant, = 1.987 calories/gmol/ $^\circ\text{K}$
 T = temperature
 θ_A = fractional coverage of adsorbed maleic acid on the electrode
 = $K(1 - \theta_A)^4 C_A$
 K = equilibrium constant for the adsorption of maleic acid
 C_A = concentration of undissociated maleic acid, gmols/liter

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VIII. VITA

Larry Delbert Gilmartin was born March 11, 1943, in Iantha, Missouri. He attended public schools in Liberal, Missouri, and graduated from Liberal High School in May, 1960.

He enrolled in the Missouri School of Mines and Metallurgy, Rolla, Missouri, in September, 1960, and received the Bachelor of Science degree in Chemical Engineering in August, 1964.

He entered the Graduate School of the University of Missouri at Rolla in September, 1964. He received a National Science Foundation Traineeship for the academic year 1964-65, and was appointed as Graduate Assistant for the academic year 1965-66.

APPENDIX A

MATERIALS

The following is a list of the materials and reagents used in this investigation. A detailed analysis of the reagents may be obtained from the chemical catalogue of the respective supplier.

1. Acid, Hydrochloric. Reagent grade, Fisher Scientific Company, Fairlawn, N. J.
2. Acid, Sulfuric. Reagent grade, Fisher Scientific Company, Fairlawn, N. J.
3. Acid, Maleic. Superior grade, Matheson, Coleman & Bell, Chicago, Illinois. A typical analysis of this material follows: (20)

Assay	99.5 per cent
Melting Point	135-136° C.
Fumaric Acid	0.5 per cent
Maleic Anhydride	none
4. Mercurous Chloride. Reagent grade, Fisher Scientific Company, Fairlawn, N. J. (used in reference electrode).
5. Mercurous Sulfate. Reagent grade, Fisher Scientific Company, Fairlawn, N. J. used in reference electrode).
6. Potassium Chloride. Reagent grade, Fisher Scientific Company, Fairlawn, N. J. (used in reference electrode).

7. Potassium Hydroxide. Reagent grade, Fisher Scientific Company, Fairlawn, N. J.

8. Potassium Sulfate. Reagent grade, Fisher Scientific Company, Fairlawn, N. J.

9. Nitrogen. Pre-Purified, Matheson, Coleman & Bell, Chicago, Illinois.

APPENDIX B

APPARATUS

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

1. Glass Cell. Designed by Dr. J. W. Johnson, University of Missouri at Rolla, built by Mr. R. Wren, University of Missouri at Columbia.
2. Magnetic Stirrer. Magnestir model 1250, Lab-line Instruments, Inc., Melrose Park, Illinois.
3. Potentiostat. Anotrol, Model 4100, Anotrol Division of Continental Oil Company, Ponca City, Oklahoma.
4. Power Supply. C-500 v, 0-100 ma, Model 711A, Hewlett-Packard Company, Palo Alto, California.
5. Power Supply. 0-500 v, 0-10 amp, Gates Electronics Company, New York, New York.
6. Recorder. Moseley Autograph, Model 7100A strip chart recorder, F. L. Moseley Company, 433 North Fair Oaks Avenue, Pasadena, California.
7. Temperature Controller. YSI Thermistemp Model 71, Yellow Springs Instrument Company, Yellow Springs, Ohio.
8. Carbon Dioxide Absorber. Designed by Dr. J. W. Johnson, University of Missouri at Rolla, built by Mr. R. Wren, University of Missouri at Columbia.

APPENDIX C

DATA

The following tables include the time dependency of the current-potential measurements. The potential listed is that actually measured. The electrode potential can be calculated as shown in the sample calculations. The reported current can be converted to current density by dividing by the geometric surface area of the electrode. The dash marks (-) indicate that the current had reached a steady value at the previous entry and further readings were not taken. The point at which a limiting current was obtained is indicated by the word "limit" in the tables.

TABLE I
CURRENT-POTENTIAL RELATIONSHIPS FOR MALEIC ACID
OXIDATION IN 1.0 N H₂SO₄ (pH = 0.3) AT 80°C
ON PLATINIZED-PLATINUM ELECTRODES**

Time min	Potential* volts	Maleic acid concentration		
		1.00 M Current ma	0.30 M Current ma	0.10 M Current ma
0	-0.300	0.500	0.500	0.410
15	-0.300	0.200	0.250	0.365
30	-0.300	0.200	0.200	0.330
45	-0.300	0.150	-	0.310
60	-0.300	-	-	0.300
0	-0.250	1.000	0.700	1.000
15	-0.250	0.400	0.600	0.750
30	-0.250	0.300	0.500	0.630
45	-0.250	0.250	0.490	0.610
60	-0.250	-	-	0.600
0	-0.200	1.000	1.300	1.750
15	-0.200	0.850	1.250	1.250
30	-0.200	0.750	1.150	1.150
45	-0.200	0.700	1.075	1.100
60	-0.200	-	-	1.080
0	-0.150	1.680	3.100	2.500
15	-0.150	1.550	2.550	2.400
30	-0.150	1.400	2.400	2.355
45	-0.150	1.300	2.200	2.250
60	-0.150	1.280	2.090	-
0	-0.100	3.500	5.000	5.000
15	-0.100	2.450	3.650	4.350
30	-0.100	2.100	3.350	4.050
45	-0.100	1.850	3.000	3.520
60	-0.100	1.750	2.920	3.330

*Versus mercurous sulfate reference electrode

**Geometric surface area of electrode = 42.6 cm²

TABLE I (continued)

Time min	Potential* volts	Maleic acid concentration		
		1.00 M Current ma	0.30 M Current ma	0.10 M Current ma
0	-0.050	3.800	5.450	6.550
15	-0.050	2.800	4.350	5.550
30	-0.050	2.650	4.120	5.350
45	-0.050	2.500	4.030	5.280
60	-0.050	-	-	-
0	0.000	3.500	7.100	8.500
15	0.000	2.750	5.350	7.350
30	0.000	2.700	5.080	6.850
45	0.000	2.600	5.150	6.700
60	0.000	-	4.950	6.600
0	0.050	4.100	7.650	15.100
15	0.050	3.250	6.400	11.250
30	0.050	3.050	6.200	10.750
45	0.050	2.950	6.175	9.750
60	0.050	2.900	-	9.400
0	0.100	4.300	8.400	12.900
15	0.100	3.300	7.450	10.650
30	0.100	3.100	7.250	10.550
45	0.100	3.020	7.150	10.400
60	0.100	-	7.100	-
0	0.150	6.250	9.750	18.200
15	0.150	limit	8.700	13.700
30	0.150		8.350	12.150
45	0.150		8.225	11.700
60	0.150		-	11.400
0	0.200		10.150	19.350
15	0.200		limit	limit

*Versus mercurous sulfate reference electrode

TABLE II
 CURRENT-POTENTIAL RELATIONSHIPS FOR MALEIC ACID
 OXIDATION IN 1.0 N H₂SO₄ (pH = 0.3) AT 80°C
 ON PLATINIZED-PLATINUM ELECTRODES**

Time min	Potential* volts	Maleic acid concentration		
		0.30 M Current ma	0.03 M Current ma	0.01 M Current ma
0	-0.300	0.350	0.550	0.550
15	-0.300	0.300	0.280	0.450
30	-0.300	0.200	0.275	0.400
45	-0.300	-	-	-
0	-0.250	0.750	0.850	1.550
15	-0.250	0.650	0.750	1.325
30	-0.250	0.550	0.655	1.250
45	-0.250	0.490	0.625	1.110
60	-0.250	0.475	-	1.050
0	-0.200	1.500	2.100	2.250
15	-0.200	1.300	1.650	1.950
30	-0.200	1.100	1.450	1.850
45	-0.200	0.970	1.400	1.825
60	-0.200	0.925	-	-
0	-0.150	2.600	3.300	5.000
15	-0.150	2.250	2.800	3.750
30	-0.150	2.150	2.600	3.625
45	-0.150	2.050	2.550	3.550
60	-0.150	2.000	2.530	3.525
0	-0.100	4.500	8.550	6.750
15	-0.100	3.700	6.750	5.350
30	-0.100	3.420	6.350	5.050
45	-0.100	3.230	6.150	4.980
60	-0.100	-	5.975	-

*Versus mercurous sulfate reference electrode

**Geometric surface area of electrode = 42.6 cm²

TABLE II (continued)

Time min	Potential* volts	Maleic acid concentration		
		0.30 M Current ma	0.03 M Current ma	0.01 M Current ma
0	-0.050	6.450	10.100	7.250
15	-0.050	4.850	7.350	6.200
30	-0.050	4.250	6.950	6.100
45	-0.050	4.000	6.930	6.000
60	-0.050	3.800	-	5.900
0	0.000	6.350	8.500	7.750
15	0.000	5.100	7.800	6.850
30	0.000	4.750	7.655	6.700
45	0.000	4.700	7.550	6.600
60	0.000	4.650	-	-
0	0.050	6.850	8.950	8.780
15	0.050	5.450	8.450	8.100
30	0.050	5.300	8.350	-
45	0.050	5.200	8.300	-
60	0.050	5.150	-	-
0	0.100	7.550	11.600	11.150
15	0.100	6.250	10.250	9.950
30	0.100	5.750	10.200	9.850
45	0.100	5.600	-	9.700
60	0.100	-	-	-
0	0.150	7.500	12.250	11.850
15	0.150	6.225	11.350	11.200
30	0.150	5.750	10.500	10.950
45	0.150	5.600	10.250	10.740
60	0.150	limit	10.200	10.700
0	0.200		12.900	13.000
15	0.200		11.450	11.700
30	0.200		limit	11.250
45	0.200			11.000
60	0.200			10.950
0	0.250			11.500
15	0.250			limit

*Versus mercurous sulfate reference electrode

TABLE III
 CURRENT-POTENTIAL RELATIONSHIPS FOR MALEIC ACID
 OXIDATION IN 1.0 N H₂SO₄ (pH = 0.3) AT 80°C
 ON PLATINIZED-PLATINUM ELECTRODES**

Time min	Potential* volts	Maleic acid concentration
		$\frac{0.003 \text{ M}}{\text{Current}}$ ma
0	-0.300	0.725
15	-0.300	0.550
30	-0.300	0.450
45	-0.300	0.400
60	-0.300	-
0	-0.250	1.250
15	-0.250	1.050
30	-0.250	0.950
45	-0.250	0.875
60	-0.250	-
0	-0.200	2.500
15	-0.200	2.150
30	-0.200	1.850
45	-0.200	-
60	-0.200	-
0	-0.150	4.100
15	-0.150	3.550
30	-0.150	3.400
45	-0.150	3.330
60	-0.150	3.200
0	-0.100	5.750
15	-0.100	4.550
30	-0.100	4.300
45	-0.100	4.200
60	-0.100	-

*Versus mercurous sulfate reference electrode

**Geometric surface area of electrode = 42.6 cm²

TABLE III (continued)

Time min	Potential* volts	Maleic acid concentration
		0.003 M Current ma
0	-0.050	6.700
15	-0.050	5.100
30	-0.050	4.700
45	-0.050	4.650
60	-0.050	-
0	0.000	5.750
15	0.000	5.050
30	0.000	4.950
45	0.000	4.880
60	0.000	4.850
0	0.050	6.250
15	0.050	5.750
30	0.050	5.875
45	0.050	-
60	0.050	-
0	0.100	7.500
15	0.100	7.250
30	0.100	7.275
45	0.100	-
60	0.100	-
0	0.150	9.050
15	0.150	8.550
30	0.150	8.300
45	0.150	8.250
60	0.150	-
0	0.200	10.000
15	0.200	9.250
30	0.200	8.800
45	0.200	8.650
60	0.200	-
0	0.250	10.500
15	0.250	limit

*Versus mercurous sulfate reference electrode

TABLE IV
 CURRENT-POTENTIAL RELATIONSHIPS FOR MALEIC ACID
 OXIDATION IN $K_2SO_4 - H_2SO_4$ (pH = 2.0) AT $80^\circ C$
 ON PLATINIZED-PLATINUM ELECTRODES**

Time min	Potential* volts	Maleic acid concentration		
		0.30 M Current ma	0.10 M Current ma	0.03 M Current ma
0	-0.300	0.550	0.850	0.750
15	-0.300	0.450	0.550	0.500
30	-0.300	0.400	0.400	0.400
45	-0.300	0.350	0.375	0.350
60	-0.300	0.325	-	-
0	-0.250	0.900	1.150	1.200
15	-0.250	0.755	0.800	0.925
30	-0.250	0.700	0.700	0.800
45	-0.250	0.650	0.675	0.775
60	-0.250	-	-	-
0	-0.200	1.550	1.850	2.050
15	-0.200	1.350	1.625	1.800
30	-0.200	1.250	1.500	1.650
45	-0.200	1.200	1.450	1.600
60	-0.200	1.175	1.425	1.575
0	-0.150	2.600	3.350	3.760
15	-0.150	2.370	2.750	3.300
30	-0.150	2.250	2.650	3.250
45	-0.150	2.225	2.625	3.150
60	-0.150	-	-	-
0	-0.100	4.100	5.250	5.800
15	-0.100	3.770	4.550	5.100
30	-0.100	3.600	4.350	4.850
45	-0.100	3.550	4.300	4.825
60	-0.100	-	-	-

*Versus mercurous sulfate reference electrode
 **Geometric surface area of electrode = 42.6 cm^2

TABLE IV (continued)

Time min	Potential* volts	Maleic acid concentration		
		0.30 M Current ma	0.10 M Current ma	0.03 M Current ma
0	-0.050	5.700	6.900	7.250
15	-0.050	5.050	5.800	6.350
30	-0.050	4.900	5.750	6.200
45	-0.050	4.850	5.700	6.100
60	-0.050	4.825	5.650	-
0	0.000	6.750	8.750	8.300
15	0.000	6.250	7.450	7.500
30	0.000	6.050	7.300	7.350
45	0.000	6.000	7.255	7.250
60	0.000	5.950	7.150	-
0	0.050	8.350	10.000	10.800
15	0.050	7.050	8.950	9.400
30	0.050	6.900	-	9.325
45	0.050	6.775	-	-
60	0.050	-	-	-
0	0.100	9.250	11.500	11.900
15	0.100	7.725	10.700	11.100
30	0.100	7.350	10.500	10.750
45	0.100	7.225	-	10.550
60	0.100	7.175	-	10.450
0	0.150	8.900	13.200	13.650
15	0.150	7.650	11.750	12.500
30	0.150	limit	11.250	12.250
45	0.150	-	11.200	12.150
60	0.150	-	11.150	-
0	0.200	-	13.800	14.600
15	0.200	-	limit	12.700
30	0.200	-	-	limit

*Versus mercurous sulfate reference electrode

TABLE V
 CURRENT-POTENTIAL RELATIONSHIPS FOR MALEIC ACID
 OXIDATION IN $K_2SO_4 - H_2SO_4$ (pH = 2.0) AT $80^\circ C$
 ON PLATINIZED-PLATINUM ELECTRODES**

Time min	Potential* volts	Maleic acid concentration	
		0.01 M Current ma	0.003 M Current ma
0	-0.300	0.350	0.850
15	-0.300	0.325	0.655
30	-0.300	-	0.575
45	-0.300	-	-
0	-0.250	0.950	1.650
15	-0.250	0.775	1.300
30	-0.250	0.750	1.210
45	-0.250	0.725	1.125
60	-0.250	-	-
0	-0.200	1.900	2.700
15	-0.200	1.680	2.400
30	-0.200	1.625	2.300
45	-0.200	1.550	2.210
60	-0.200	1.525	2.175
0	-0.150	3.250	4.250
15	-0.150	2.875	3.700
30	-0.150	2.700	3.450
45	-0.150	2.650	3.380
60	-0.150	-	-
0	-0.100	5.100	5.350
15	-0.100	4.150	4.700
30	-0.100	3.875	4.525
45	-0.100	3.800	4.350
60	-0.100	-	4.325

*Versus mercurous sulfate reference electrode

**Geometric surface area of electrode = 42.6 cm^2

TABLE V (continued)

Time min	Potential* volts	Maleic acid concentration	
		0.01 M Current ma	0.003 M Current ma
0	-0.050	5.650	6.250
15	-0.050	4.750	5.350
30	-0.050	4.625	4.950
45	-0.050	4.500	4.830
60	-0.050	-	-
0	0.000	5.800	6.200
15	0.000	5.150	5.550
30	0.000	5.000	5.500
45	0.000	4.950	5.430
60	0.000	-	-
0	0.050	6.650	7.000
15	0.050	5.750	6.700
30	0.050	5.700	6.750
45	0.050	-	6.850
60	0.050	-	-
0	0.100	7.450	8.750
15	0.100	6.950	8.250
30	0.100	6.650	8.150
45	0.100	6.600	7.955
60	0.100	6.580	7.825
0	0.150	8.250	10.450
15	0.150	7.550	9.350
30	0.150	7.225	9.050
45	0.150	7.050	8.750
60	0.150	6.900	8.650
0	0.200	9.150	11.150
15	0.200	7.500	9.550
30	0.200	limit	9.150
45	0.200		limit

*Versus mercurous sulfate reference electrode

TABLE VI
 CURRENT-POTENTIAL RELATIONSHIPS FOR MALEIC ACID
 OXIDATION IN $K_2SO_4 - H_2SO_4$ (pH = 4.0) AT $80^\circ C$
 ON PLATINIZED-PLATINUM ELECTRODES**

Time min	Potential* volts	Maleic acid concentration	
		0.01 M Current ma	0.003 M Current ma
0	-0.400	0.950	1.200
15	-0.400	0.550	0.725
30	-0.400	0.500	0.550
45	-0.400	0.450	-
60	-0.400	0.425	-
0	-0.350	1.350	1.450
15	-0.350	1.225	1.250
30	-0.350	1.000	1.200
45	-0.350	0.900	1.150
60	-0.350	-	1.125
0	-0.300	2.220	2.650
15	-0.300	1.900	2.300
30	-0.300	1.810	2.150
45	-0.300	1.750	2.125
60	-0.300	-	-
0	-0.250	3.700	4.250
15	-0.250	3.200	3.350
30	-0.250	3.050	3.250
45	-0.250	-	3.200
60	-0.250	-	-
0	-0.200	5.150	5.150
15	-0.200	4.250	3.850
30	-0.200	4.125	3.750
45	-0.200	-	-

*Versus mercurous sulfate reference electrode

**Geometric surface area of electrode = 42.6 cm^2

TABLE VI (continued)

Time min	Potential* volts	Maleic acid concentration	
		0.01 M Current ma	0.003 M Current ma
0	-0.150	6.350	5.500
15	-0.150	5.250	4.300
30	-0.150	5.150	4.200
45	-0.150	5.100	4.100
60	-0.150	-	4.050
0	-0.100	7.350	5.700
15	-0.100	6.450	4.700
30	-0.100	-	-
0	-0.050	8.800	6.150
15	-0.050	7.850	5.500
30	-0.050	7.750	5.375
45	-0.050	-	-
0	0.000	10.450	6.800
15	0.000	8.730	5.850
30	0.000	8.250	5.650
45	0.000	8.150	5.550
60	0.000	8.050	5.500
0	0.050	10.850	7.650
15	0.050	9.400	6.350
30	0.050	8.650	5.800
45	0.050	8.350	5.750
60	0.050	8.250	5.650
0	0.100	11.500	7.775
15	0.100	limit	6.250
30	0.100		5.850
45	0.100		limit

*Versus mercurous sulfate reference electrode

TABLE VII
 CURRENT-POTENTIAL RELATIONSHIPS FOR MALEIC ACID
 OXIDATION ON PLATINIZED-PLATINUM ELECTRODES**
 RATIO: IONIZED ACID/UNIONIZED ACID = 1×10^4
 AT 80°C

Time min	Potential* volts	Current ma
0	-0.100	4.500
15	-0.100	2.200
30	-0.100	1.650
45	-0.100	1.550
60	-0.100	-
0	-0.050	3.000
15	-0.050	2.150
30	-0.050	1.950
45	-0.050	1.900
60	-0.050	-
0	0.000	3.150
15	0.000	2.450
30	0.000	2.300
45	0.000	2.250
60	0.000	-
0	0.050	3.900
15	0.050	2.650
30	0.050	2.500
45	0.050	2.430
60	0.050	limit

*Versus calomel reference electrode

**Geometric surface area of electrode = 42.6 cm^2

TABLE VIII
 CURRENT-POTENTIAL RELATIONSHIPS FOR MALEIC ACID
 OXIDATION IN 1.0 N KOH AT 80°C
 ON PLATINIZED-PLATINUM ELECTRODES**

Time min	Potential* volts	Maleic acid concentration
		$\frac{0.10 \text{ M}}{\text{Current}}$ ma
0	-0.600	0.275
15	-0.600	0.100
30	-0.600	0.080
45	-0.600	-
0	-0.550	0.275
15	-0.550	0.175
30	-0.550	0.150
45	-0.550	0.138
60	-0.550	-
0	-0.500	0.385
15	-0.500	0.275
30	-0.500	0.250
45	-0.500	0.245
60	-0.500	-
0	-0.450	0.670
15	-0.450	0.470
30	-0.450	0.425
45	-0.450	0.400
60	-0.450	-

*Versus calomel reference electrode

**Geometric surface area of electrode = 42.6 cm²

TABLE VIII (continued)

Time min	Potential* volts	Maleic acid concentration
		<u>0.10 M</u> Current ma
0	-0.400	0.880
15	-0.400	0.645
30	-0.400	0.565
45	-0.400	0.530
60	-0.400	-
0	-0.350	0.750
15	-0.350	0.625
30	-0.350	0.585
45	-0.350	-
0	-0.300	0.785
15	-0.300	0.610
30	-0.300	limit

*Versus calomel reference electrode

TABLE IX
 CURRENT-TEMPERATURE RELATIONSHIPS
 FOR OXIDATION OF MALEIC ACID*
 ON PLATINIZED-PLATINUM ELECTRODES***

Potential** volts	Temperature °C	Current ma
0.250	80	3.700
0.250	70	1.250
0.250	60	0.400
0.250	50	0.120
0.150	80	1.100
0.150	70	0.345
0.150	60	0.115
0.150	50	0.030

*0.10 M maleic acid in 1.0 N H₂SO₄

**Versus calomel reference electrode

***Geometric surface area of electrode = 42.6 cm²