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Electrochemical Oxidation of Formic Acid

by
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CAMBRIDGE 39, MASSACHUSETTS

SCIENTIFIC REPORT NO. 5

CONTRACT NO. Nonr 1841(78)
Authorization No. ARPA Order No. 214-62
M.I.T. Project DSR 8848



401 932

January 1963

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ABSTRACT
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This report is identical to a thesis submitted to the Department of Chemical Engineering, Massachusetts Institute of Technology, January, 1963, in partial fulfillment of the requirements for the degree Doctor of Science.

This investigation was undertaken to obtain a better understanding of the mechanism of the electrochemical oxidation of formic acid on a plain platinum electrode. Attention was focused on the unusual voltage behavior observed in formic acid solutions, namely the minimum open circuit potential observed after an oxide was caused to form on the platinum electrode and the rise in potential at open circuit after this minimum potential had developed. Experiments were carried out to determine the effect of pretreatment on subsequent electrode performance and to gain insight into the nature of the galvanostatic voltage oscillations observed with formic acid solutions.

The effect of electrode pretreatment on chronopotentiometry and current-potential double layer capacitance relationships was determined. Minimum open circuit potentials were obtained as a function of pH in the presence of nitrogen, carbon monoxide, and carbon dioxide. Capacitance-potential curves were obtained at constant potential in H_2SO_4 as a function of formic acid concentration. In the same system capacitance-potential relationships were studied during galvanostatic voltage oscillations.

It was concluded that the minimum open circuit potential observed with formic acid on platinum in neutral and acid media is due to the presence of hydrogen on the electrode. The rise of potential at open circuit was found to be caused by the adsorption of an unknown, uncharged organic species on the platinum electrode. Both the hydrogen and the uncharged organic species were formed from the chemical decomposition of formic acid.

Since the adsorbed organic species was more difficult to oxidize than formic acid and it forms rather slowly, the electrode performance is highly dependent on previous electrode pretreatment. There were strong indications that this unknown species was carbon monoxide.

The adsorbed species seems to be the cause of the voltage oscillations. Platinum oxide may also play an important role.

ACKNOWLEDGEMENT

The author wishes to express his sincere appreciation to Professor Charles N. Satterfield under whose supervision this investigation was performed. Thanks are also due to Professor Satterfield and Professor Herman P. Meissner for their efforts in obtaining financial support for this study. The work reported in this document was made possible through support extended the Massachusetts Institute of Technology, School of Engineering, by the Department of the Navy, Office of Naval Research, under Contract Nonr. 1841(78) authorized by Advanced Research Projects Agency Order No. 214-62.

Special appreciation is expressed to Professor David K. Roe for many helpful discussions and his interest in the project.

Appreciation is also expressed to J. H. Porter and A. R. Reti for helpful suggestions; to X. L. Simon for his assistance during the summer of 1962; and to J. P. Bell for his assistance in the fall of 1962.

The author wishes to extend his deepest appreciation to his parents for their help and interest and to his wife, Susan, for her devotion, encouragement, and unfailing confidence.

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I. SUMMARY

A. Introduction

In recent years much interest and study has been centered on the mechanism of the electrochemical oxidation of simple oxygenated organic compounds on noble metals. The reason for this revival of activity in the field of electrochemical oxidation of these materials can be traced to the rapidly growing interest in the fuel cell as an energy conversion device. The fuel cell has long been known to be a medium for converting chemical energy directly to electrical energy. However, it is only recently that practical applications of fuel cells have seemed feasible.

One of the more interesting types of fuel cells being considered is the low temperature fuel cell fed with a water-soluble organic fuel. This has the advantage of operation at atmospheric pressure and low temperature using fuels which are relatively inexpensive. A principal bottleneck in the development of all fuel cells lies in the current outputs per unit area of electrode surface achievable at practicable potentials. This problem is especially severe with unreactive fuels such as saturated hydrocarbons. However, partially oxygenated compounds such as the lower molecular weight alcohols are much more reactive.

Heath, et al,²⁷ have conducted a survey of partially oxygenated organic compounds which are soluble in water and react electrochemically to carbon dioxide and water. They have found that methanol is the best fuel for a low temperature cell based on the criterion of maximum kilowatt hours per unit cost or kilowatt hours per pound.

The electrochemical oxidation of methanol in a practical cell would have to take place in acid or neutral solution in order to prevent the formation of carbonate. In acid and neutral solution, methanol exhibits some unusual electrochemical phenomena. In particular, when an oxide has been caused to form on a platinum electrode and then the circuit has been broken while the

electrode is in the presence of methanol, the methanol reduces the platinum oxide. After this oxide reduction takes place, the open circuit potential drops to a minimum value and then slowly rises.^{43 50} (See Figure 1). Furthermore, when a constant current is applied to a platinum electrode in an acid solution of methanol, voltage oscillations are observed.^{43 50}

These same phenomena are also observed in the electrochemical oxidation of formic acid,^{40 41} which has been shown to be an intermediate in the electrochemical oxidation of methanol.⁹ Since formic acid is known to be electrochemically oxidized only to carbon dioxide^{27 40 41} and hydronium ions whereas methanol is oxidized through at least two intermediates, formaldehyde and formic acid,⁹ a study of these phenomena should be more straightforward when undertaken in conjunction with an investigation of formic acid.

Muller^{39 40 41} carried out extensive studies of the electrochemical oxidation of formic acid in the 1920's. According to his theories, the minimum potential shown in Figure 1 would be attributed to the presence of hydrogen on the platinum electrode. On the other hand, Muller's experiments led him to believe that formic acid would not decompose to hydrogen on smooth metals to any reasonable extent. The reasons for the potential rise from the minimum potential at open circuit have never been studied to any extent.

Muller⁴¹ explained the galvanostatic voltage oscillations by postulating the following two step reaction. First, formate ion was assumed to be electrochemically oxidized to an adsorbed formate radical. The formate radical then accumulated on the surface. Finally a potential was attained at which the formate radical was thought to decompose very rapidly to an adsorbed hydrogen atom and carbon dioxide. The adsorbed hydrogen was easily oxidized and the process started over again.

Recent investigators^{10 18 26 27} of methanol, formaldehyde, and formic acid have focused on other problems rather than finding an explanation for this unusual behavior.

The present investigation was undertaken in order to obtain a better understanding of the mechanism of the electrochemical oxidation of formic acid on plain platinum. In particular, it was desired to gain more insight into the unusual voltage behavior exhibited by formic acid.

Initially, it was planned to study the mechanism of the electrochemical oxidation of formic acid on a plain platinum electrode by chronopotentiometry. However, when it was found that the nature of the pretreatment of the electrode caused unexpected and important effects, major attention was shifted towards determining the effect of electrode pretreatment on the nature of the species present on the electrode surface by examining the double layer capacitance of the electrode.

Observations of the minimum potential at open circuit were examined as a function of pH, electrode pretreatment and the presence of certain gases.

B. Apparatus

1. Chronopotentiometry

Chronopotentiometric experiments were carried out in a glass cell on a plain platinum foil electrode. The current was generated by three 12 volt storage batteries and controlled by a Clarostat 240-C decade resistor. The current was read on a Weston 911 ammeter. The potential-time behavior was measured on a Sargeant MR recorder vs. a Beckman saturated calomel reference electrode. The reference electrode was kept in a separate beaker and was connected to the glass cell by a capillary bridge.

2. Double Layer Capacitance Apparatus

Double layer capacitance measurements were carried out by analyzing the voltage response of the plain platinum electrode to an a.c. square wave current. The square wave current was generated by a Hewlett-Packard 202A function generator. The voltage response was read out on a Tektronix 502 double beam oscilloscope. A Tektronix C-12 camera with Polaroid back could

be mounted on the oscilloscope to take pictures of rapidly changing traces.

These measurements were carried out while the electrode was held at a fixed potential or while a constant current was passed through the electrode. The potential was held constant through the use of a 6 volt storage battery connected to an 11 ohm resistor used as a voltage divider. The maintenance of a constant potential was verified by measuring the potential of the platinum electrode against a calomel reference electrode by the use of the Sargeant MR recorder.

C. Experimental Procedure

1. Materials

The platinum for electrode manufacture was obtained from Englehard Industries and was 99.8 per cent pure. When an electrode was not in use it was kept in a covered beaker of distilled water. Before using the electrode it was cleaned by subsequent rinses in benzene, acetone, distilled water, sulfuric acid, and a final rinse in distilled water.

Glassware was cleaned in chromic acid and thoroughly rinsed. The formic acid used was A.R. grade obtained from Baker. The sodium formate was reagent grade obtained from Merck. No further purification of chemicals was undertaken except where noted.

2. Chronopotentiometry

One of the electrochemical techniques which can provide insight into the nature of electrode processes is chronopotentiometry. This is the study of the voltage-time behavior of an electrode placed in a dilute solution of a reactant and held at constant current. The reactant is supplied to the electrode by diffusion only. Before a typical run the electrode was cleaned by a brief oxidation. Then nitrogen was bubbled through the solution for a set amount of time. During the nitrogen bubbling the platinum oxide formed

in the pre-oxidation was generally reduced by the formic acid in solution as evidenced by the fact that the electrode potential did not remain in the region of II in Figure 1. However, when very low formic acid concentrations were present, this reduction took too long. In this case, a small cathodic current was passed through the platinum test electrode. Great care was taken to ensure that no hydrogen was formed at the electrode during this process by turning off the cathodic current well above the potential at which hydrogen is discharged.

After the nitrogen was turned off, the electrode was left at open circuit for a fixed amount of time. Then the current was applied and the potential-time curve followed by the voltage recorder.

3. Minimum Open Circuit Potential

Two different pretreatments were given to the platinum electrode before minimum open circuit potentials were taken. In one the electrode was subjected to an anodic current pulse of 10 to 80 ma/cm² lasting less than one second. The voltage at the end of the pulse seemed to have no effect on the minimum open circuit potential subsequently observed. The other electrode pretreatment consisted of holding the potential of the electrode constant at over 1.5 v. vs. a hydrogen electrode in the same solution for one minute. At this potential all organic species should be oxidized. In both cases the potential-time behavior of the electrode was followed by use of the Sargeant MR voltage recorder. The minimum potential at open circuit was investigated in the presence of nitrogen, carbon monoxide, and carbon dioxide.

4. Double Layer Capacitance Measurements

Double layer capacitance measurements were taken at constant current or at constant voltage. Constant current capacitance measurements were used to determine the effect of electrode pretreatment and to observe the change of capacitance on the platinum electrode during the galvanostatic voltage oscillations. When studying the effect of electrode pretreatment, the constant

current was turned on either after the electrode had been left in solution for thirty minutes at open circuit or the constant current was turned on immediately after the minimum open circuit potential was reached.

Constant voltage capacitance measurements were taken in the presence of nitrogen bubbling. The electrode had been pretreated by holding the potential at over 1.5 v. vs. a hydrogen electrode in the same solution for sixty seconds. Then the circuit was broken and the minimum open circuit potential allowed to develop. Immediately following this, the potential of the test electrode was set at the desired level and held there for twenty minutes before the final capacitance was recorded.

D. Results and Discussion

1. Chronopotentiometry

Since other investigators^{8 39} had found that the electrochemical oxidation of formic acid proceeded most easily in neutral solutions, chronopotentiometric experiments were performed on plain platinum with a solution composed of 2.50×10^{-2} M HCOOH and 1.33M NaH_2PO_4 at 26°C. The transition time at a given current density under these conditions was found to be a function of electrode pretreatment.

For a given current density the square root of the transition time is directly proportional to the amount of material reacted at the electrode before the concentration of the reactant at the electrode-solution interface drops to zero. Surprisingly, the transition time was found to increase when the time between runs was decreased. In an acid solution, composed of 0.226M NaNO_3 , 3.52×10^{-2} H_2SO_4 , and 1.78×10^{-2} NaCOOH , the effect was even more apparent than in neutral solution. In the acid solution, the transition time varied from 21 seconds when the electrode was allowed to remain undisturbed in the solution at open circuit for two minutes, to 161 seconds when only three seconds were taken between runs. The data at each pretreatment condition were fairly reproducible, having a range of less than 8 seconds.

If the transition time were seen to increase with increasing time between experiments, the explanation would be that adsorption of a reactive species

was taking place. In order to account for the opposite behavior, three possibilities were considered: (1) Dissolved oxygen, present in the solution, could be reacting with the formic acid near the electrode at open circuit; (2) An impurity present in the solution was being adsorbed on the electrode and "blocking" a part of the electrode. It had been observed by Gierst and Juliard²⁰ that transition times decrease markedly when a strongly adsorbable substance is present in solution. This effect is observed with very low concentrations of gelatin. This was accounted for by assuming that the adsorption of gelatin on the electrode decreases the effective area of the electrode; (3) The "blocking agent" could be formed from the chemical decomposition of formic acid itself.

In order to determine whether the phenomena of decreasing transition time was due to impurities in the system, a highly purified solution was prepared. A liter of solution of 1.33M NaH_2PO_4 was pre-electrolyzed for twenty-four hours at over 25 ma. and then boiled to remove dissolved hydrogen and oxygen. Part of this solution was added to 20 ml. of a 0.25M NaCOOH solution made from recrystallized sodium formate and distilled deionized water to make total volume of 250 ml. To avoid possible chloride contamination, a glass electrode was used for a reference electrode, the potential difference being read on a Beckman Zeromatic pH Meter.

The same phenomena were observed in this system as had been observed previously. When the electrode was left in solution for only two minutes the transition time ranged between 25.9 and 26.4 seconds in five runs, for a current density of 4.00 ma/cm². This yields an $(i.\tau^{1/2}/C^\circ)$ product of 520. A reactant undergoing a two electron process with a diffusivity of 10^{-5} cm²/sec would yield an $(i.\tau^{1/2}/C^\circ)$ product of 540 ma. sec.^{1/2} l./m. However, when the electrode was left in solution for sixteen minutes, the transition time decreased to 14.8 seconds. Thus, the decrease in the transition time could not be caused by an impurity.

When air was bubbled through the solution the same effects were noted as when nitrogen was being bubbled. There was no important change in transition time due to the presence of air. The transition times observed when

air was present were almost identical with those observed when nitrogen was present for the same pretreatment.

2. Minimum Open Circuit Potential

There was other evidence that some species could be forming on the electrode surface while the electrode was sitting in the formic acid. For example, the open circuit potential was rising after the minimum open circuit potential was attained. This minimum potential being developed immediately after the reduction of platinum oxides formed during the previous run (see Figure 1).

Before attempting to decide what could be causing the rise in open circuit potential, it was felt that the cause of the minimum potential itself should be determined.

This investigation was carried out by pretreating the electrode in either of two different ways and then breaking the circuit and following the voltage behavior on the Sargeant MR recorder. The purpose of the pretreatment was to "clean off" the adsorbed species. One technique was to pass a anodic current pulse of 10 to 80 ma./cm.² for a duration of less than one second. The other was to hold the potential of the electrode constant at a level at least +1.5 v vs. a hydrogen electrode in the same solution for 60 seconds.

A number of solutions, 1M in formic acid but at various pH values ranging from a pH of 11.32 to 5M H₂SO₄, were investigated. When nitrogen or carbon dioxide was bubbled past the electrode to stir the solution, the average minimum open circuit potential obtained in neutral solutions by the current pulse technique was less than 50 mv. above the hydrogen potential. However, in acid solutions the minimum open circuit potential obtained by the current pulse technique became much higher than the hydrogen potential, the average value in 5M H₂SO₄ and 1M HCOOH being +.27 v. vs. a hydrogen electrode.

When minimum potentials were examined by the constant potential pre-treatment technique, however, the average values observed in acid solution were much closer to the hydrogen potential. In 1M H_2SO_4 and 1M HCOOH an average minimum open circuit potential of +.010 v. vs. a hydrogen electrode was obtained.

It was noted that the potential rose more rapidly at open circuit after the minimum potential as the solutions became more acid. An explanation for the failure of the current pulse technique in acid solution is that the pre-treatment just did not clean off the electrode. The species being adsorbed on the electrode and causing the potential to rise is postulated to form faster in acid solution. It is assumed then that the current pulse can remove only a certain fraction of the adsorbed species. When the species does not form rapidly, as in the neutral solutions, the current pulse technique is apparently adequate for cleaning the electrode.

The postulate of a more rapid formation of the adsorbed species in acid solution plus the presumption that the adsorbed species is formed from the chemical decomposition of formic acid indicates that the species might be carbon monoxide. Carbon monoxide is a well known product of formic acid decomposition and the reaction has been shown to be acid catalyzed.⁴⁹ Furthermore, Havel, et al,²⁶ have demonstrated that carbon monoxide is not easily oxidized electrochemically at room temperature on a platinized carbon electrode.

When carbon monoxide was bubbled through the solution, minimum open circuit potentials obtained by the current pulse technique were close to the hydrogen potential. However, the rise of the potential at open circuit after the minimum potential was vastly accelerated and the open circuit potential rose to much higher steady state values when carbon monoxide was present. This was especially noticeable in neutral solutions where the potential rose very slowly when nitrogen or carbon dioxide was being bubbled through the solution.

3. Double Layer Capacitance

If an adsorbed species were being formed on the platinum electrode in the dilute formic acid solutions used in chronopotentiometry and this species were formed from the formic acid, then the effect of this species should be even greater in more concentrated formic acid solutions. Thus the current-potential relationships observed under conditions where diffusion is not an important consideration should be a strong function of the electrode pretreatment. Greater polarization should be observed as the plain platinum electrode is left in the solution for longer times after the minimum open circuit potential.

Also, if the adsorbed species is an uncharged organic substance, as would be the case for carbon monoxide, the double layer capacitance should be affected. The longer the time the electrode is left in solution after the minimum potential is attained, the lower the double layer capacitance should be at a given potential.

In order to check this theory a solution of 1M HCOOH and 1.33M Na₂HPO₄ was prepared and both double layer capacitance and voltage measurements were taken at constant current as a function of electrode pretreatment. Two pretreatments were chosen. In one, the electrode was left in solution at open circuit for thirty minutes after a minimum potential and the current was raised in steps. Readings of capacitance and voltage were taken one half minute after a new current was established. Then the current was changed. In the other the current was set immediately after the minimum open circuit potential and voltages and double layer capacitances were taken fifteen seconds after the current was set. A minimum potential was established before each run.

The results of this experiment confirmed the theory. At +0.030 v. vs. SCE the short open circuit treatment carried over fifty times as much current. The amount of current is a direct measure of the reactivity of the electrode and the drop with increased time between experiments indicates that the electrode is being deactivated. The double layer capacity was 26 $\mu\text{f}/\text{cm}^2$ as

compared to $15 \mu\text{f}/\text{cm}^2$ when the electrode was left in solution for thirty minutes. The adsorption of an uncharged species on the electrode pushes the charged ions further into the solution. This causes a greater amount of charge separation, and hence lowers the double layer capacitance. Similar data were obtained at other potentials.

Double layer capacitance measurements were also obtained at constant voltage in sulfuric acid solutions with no formic acid, $1.56 \times 10^{-3}\text{M HCOOH}$, $1.56 \times 10^{-1}\text{M HCOOH}$, and 1.56M HCOOH . The data resembled capacitance-voltage curves obtained in a similar manner from amyl alcohol in the presence of perchloric acid on a platinum wire by Breiter,⁴⁵ and he concluded that adsorption was occurring in his studies also.

Using the same apparatus, the external circuitry was modified to pass a constant current. Then galvanostatic voltage oscillations were induced at the highest formic acid concentration. No reasonably steady oscillations could be obtained at lower formic acid concentrations.

When the double layer capacitance was measured during the oscillations, it was seen that the capacitance values were lower than those obtained at the same potential during the constant voltage experiments. Furthermore, the peak potential of the oscillations in this experiment was the same as that at which the platinum surface was covered with oxide in the presence of formic acid in the constant voltage experiments. Thus, it was felt that the platinum oxide as well as the adsorbed species played an important role in these voltage oscillations.

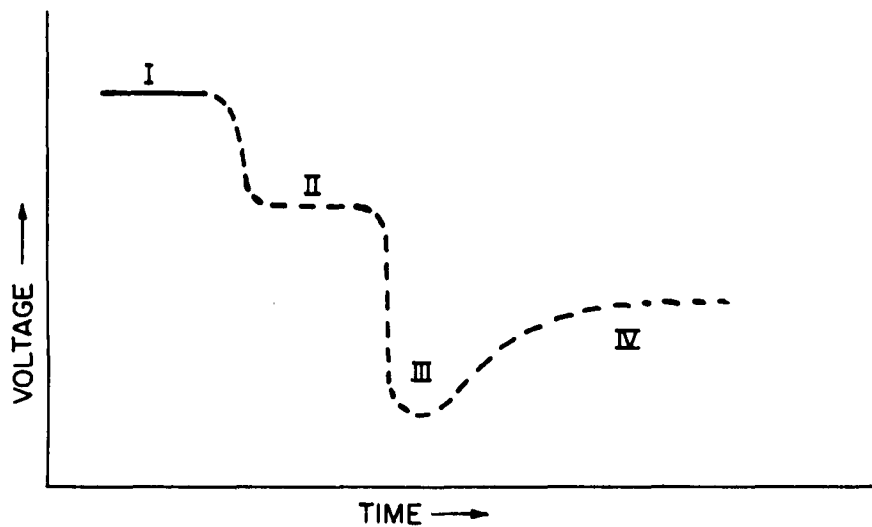
E. Conclusions

1. The minimum open circuit potential observed with formic acid on platinum in neutral and acid media is due to the presence of hydrogen on the electrode.
2. The rise of the potential at open circuit after the minimum potential is caused by the adsorption of an unknown, uncharged organic species on the platinum electrode.

3. Both the hydrogen and the uncharged organic species are formed from the chemical decomposition of formic acid.

4. The organic adsorbed species is more difficult to oxidize than formic acid. There are strong indications that this unknown species is carbon monoxide.

5. The adsorbed species seems to be the cause of the voltage oscillations. Platinum oxide may also play an important role.



- I CURRENT ON, OXIDE FORMED
- II CURRENT OFF, OXIDE REGION
- III MINIMUM OPEN CIRCUIT POTENTIAL
- IV RISE OF POTENTIAL AT OPEN CIRCUIT

Fig. 1 Voltage Behavior after Oxide Formation When Current is Cut Off at a Plain Platinum Electrode in Formic Acid.

II. INTRODUCTION

A. The Fuel Cell as an Energy Conversion Device

Recently, considerable interest and effort has been devoted towards the development of various types of fuel cells. The fuel cell is a device for converting chemical energy to electrical energy by electrochemical means. It operates as a battery where the fuel and oxidant are continuously supplied while reaction products and electricity are continuously withdrawn.

The principal advantage of the fuel cell as opposed to non-electrochemical energy conversion devices is that there is no theoretical limit to the conversion efficiency. Theoretically, 100% of the available free energy of a reaction can be transferred to usable electrical energy; whereas due to the high temperature limitations on existing construction materials and the Carnot Cycle restriction, the best present day steam plants operate at about 40% efficiency.

The major limitation of the fuel cell is the low power output per unit electrode area. Because of the low voltages encountered in fuel cells, it is necessary to operate at current densities of at least 0.1 amperes per square centimeter in order to achieve reasonable power outputs per unit size and weight. When no net current is being drawn from a fuel cell and no side reactions occur at either electrode, the cell voltage is determined by the free energy of the reaction, ΔG :

$$n F E = - \Delta G \quad (1)$$

where n is the number of electrons transferred; F is Faraday's number, expressing the coulombs per equivalent; and E is the voltage. However, as the amount of current drawn from the cell is increased, the cell voltage decreases until a current is reached where the cell voltage is zero and no higher current can be drawn. This phenomena of decreasing voltage with increased current drain is called polarization.

There are three mechanisms which cause the over voltage to decrease with increased current drain. One is simply due to the cell resistance. This iR drop can be minimized by proper cell design. Another, called concentration polarization, is caused by insufficient rate of transport of fuel or oxidant from the bulk phase to the electrode surface where reaction is taking place. Since the potential at each electrode is a function of the concentration of the species reacting at the surface, this will cause a change in the cell potential (see equation (20)). The third reason for voltage loss with increased current is the rate of the intrinsic electrochemical reactions themselves, and this is termed activation polarization.

The current density is a direct measure of the sum of the rates of all electrochemical reactions occurring on an electrode. For the simple case where only one electrochemical reaction proceeds at an electrode, the current density is a measure of that rate. As the current density is increased, the reaction rate must increase proportionately. For an irreversible reaction this increase of rate can be attained only with the aid of some part of the available potential. The study of the phenomena of activation polarization is called electrochemical kinetics and will be discussed further. It is important to realize that the easier an electrochemical reaction can proceed, the less the voltage drop due to activation polarization.

Historically, the fuel cell has not been a new concept. As early as 1801, Davy reported on a zinc, oxygen fuel cell¹⁵ and the following year¹⁶ he discussed a carbon, oxygen cell operating in nitric acid. However, to the present time, a practical economical fuel cell which can compete commercially with other forms of energy conversion has not been developed.

The reasons for this are quite straightforward. The inexpensive fuels used in Carnot Cycle power plants such as coal, coke, oil, or even purified hydrocarbons are not sufficiently reactive electrochemically at ambient temperatures. In order to enhance the reactivity of these substances much higher temperatures must be used. But this means that heat must be expended

to raise the temperature of the fuel and oxidant (air), some heat losses must occur, and the free energy change for the reaction will be lower than that at ambient temperature. These and other considerations cast doubt that the fuel cell will ever replace a steam plant as a central power station.¹⁴ For some operations, such as space or certain military applications the fuel cell seems to be quite competitive with other energy sources, as evidenced by the recent announcement that the Apollo spacecraft will be using a fuel cell system for auxiliary power.

1. The Methanol Fuel Cell

One important area of investigation is the development of a low temperature fuel cell using a water soluble organic fuel and an air oxidant. Such a cell should have a number of advantages including high energy per pound, simplicity of operation, ease of removal of reaction products, reasonable cost of fuel, high efficiency and high reliability.

A survey of soluble oxygenated hydrocarbon fuels was made recently by Heath, et al.²⁷ These authors examined low molecular weight alcohols, acids, aldehydes, ketones, glycols, and glycerols. Cost per kilowatt hour was calculated assuming a 70% voltage efficiency and complete conversion of fuel to CO_2 and H_2O when electrochemically oxidized with air on platinum black in sulfuric acid. Those fuels which Heath, et al, found to be oxidized completely to CO_2 and H_2O are tabulated in Table I with cost per kilowatt hour and kilowatt hours per pound. From Table I it is quite clear that methyl alcohol is the most inexpensive oxygenated hydrocarbon and has the highest energy per pound among the reactive fuels. Furthermore, in a different investigation, Gentile, et al,¹⁸ concluded that methanol was more easily oxidized than any of the other four fuels in Table I.

2. The Electrochemical Oxidation of Methanol and Formic Acid

In the electrochemical oxidation of methanol at constant current in acid or neutral solution unusual phenomena have been observed. At low current

TABLE I
Soluble Carbonaceous Fuels for Fuel Cells²⁷

Fuel	kWh/lb	d/kWh
Methyl Alcohol	1.94	2.32
Formaldehyde	1.52	7.12
Ethylene Glycol	1.68	8.03
Glycerin	1.55	15.3
Formic Acid	0.55	31.1

densities with a platinized platinum electrode the potential of the platinized platinum with respect to a reference electrode rises slightly due to irreversibilities in the reaction. When the current is increased, the potential is found to oscillate.^{43 50} At higher current densities the potential rises to the electrode oxide potential.

If the current is turned off at this point, the potential drops to a definite level, indicating the existence of platinum oxide. After the oxide is completely reduced by the methanol the potential drops again to a low value and then slowly rises.^{43 50}

The same phenomena have been observed in the constant current oxidation of formic acid,^{40 41} which is an intermediate in the oxidation of methanol. Methanol is electrochemically oxidized through two intermediates, formaldehyde and formic acid,⁹ where as formic acid goes directly and solely to carbon dioxide in the potential region below the potential at which metal oxides are formed on the electrode.^{27 40 41} Thus, fewer complications would be expected in the electrochemical oxidation of formic acid than would occur in the electrochemical oxidation of methanol. Because of this, the study of phenomena of the minimum potential after oxide reduction, the rise of potential after this minimum at open circuit, and the galvanostatic voltage oscillations were chosen to be investigated here in the system of formic acid rather than methanol.

B. Fundamental Relationships

1. The Reversible Cell: Electrochemical Equilibrium

a. Voltage

The voltage behavior of a reversible cell has been described by Nernst in terms of the activities of the reactants and products of a reaction.⁴² However, because at least some of these species are ions in an electrochemical reaction, it would be advantageous to examine this relationship critically.

The concept of an electrode potential is not a simple matter. An electrode potential implies the existence of a potential difference between the metal of the electrode and the solution with which it is in equilibrium. In classical electrostatics, all that is needed to determine a potential at a given point is to measure the work required to bring a test charge from infinity to that point. But what can be used as a test charge in this case? A metal consists of a close-packed ionic lattice which provides macro-orbitals for the accommodation of electrons in quantized energy bands. Energy equal to the work function is liberated when a free electron is dropped into the highest energy level. An electron dropped into an aqueous solution would perform a reduction, since it is the most powerful reducing agent. Similar considerations arise from considering other charged particles as test charges. They are all atomic constituents or chemical reagents and whenever a real charged particle is brought close to matter of any kind, powerful non-coulombic forces are encountered.²⁹ Guggenheim summarizes these principles as follows, "The electric potential difference between two points in different media can never be measured, and has not yet been defined in terms of physical realities. It is, therefore, a conception which has no physical significance."

What, then, is meant by an electrode potential? It is a universal criterion of equilibrium within a system that the chemical potential, μ_i , of any component i shall have a uniform value in all parts of the system. The definition of chemical potential

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_j} \quad (2)$$

does not seem to be directly applicable to an ionic species, since it is impossible to add a single kind of ion to any system because in natural systems no departure from electroneutrality is possible. This does not invalidate the definition because dG is a perfect differential,

$$dG = \left(\frac{\partial G}{\partial n_1} \right)_{T,P,n_j} dn_1 + \left(\frac{\partial G}{\partial n_j} \right)_{T,P,n_1} dn_j \quad (3)$$

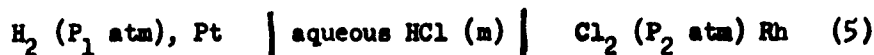
but it does mean that the chemical potential of a single ion cannot be separated. Thus, the chemical potential of sodium chloride ions in aqueous solution is unambiguously the sum of the chemical potentials of sodium and chloride ions.²⁹

In spite of these restrictions, it has been deemed convenient to define an electrochemical potential, $\bar{\mu}_i^a$

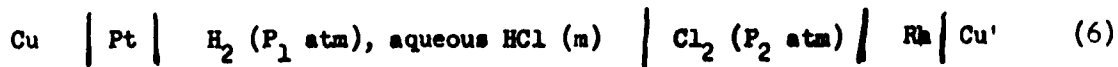
$$\bar{\mu}_i^a = \mu_i^a + Z_i F \psi^a \quad (4)$$

where $\bar{\mu}_i^a$ is the electrochemical potential of the charged component i in phase α , μ_i^a its chemical potential and $Z_i F$ its charge per mole with appropriate sign, F the value of the Faraday, and ψ^a is the inner electrical potential of the phase α . None of the three terms in this equation is separately determinable. In particular, the potential ψ^a is not determinable, and neither is the difference between the internal electrical potentials of two phases which is called the Galvani potential.⁶

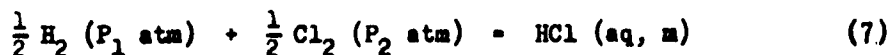
Let us then consider a galvanic cell which derives the electrical energy which it can provide from a chemical reaction, which is usually represented as,



but, as will be seen, should be represented as



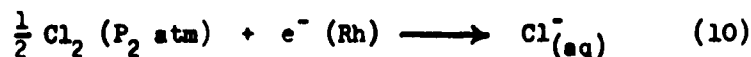
The net reaction for this cell is



At open circuit, the system is in equilibrium and no net reaction occurs. If the reaction is carried out reversibly, the maximum electrical work is obtained and it must be equal to the loss in free energy due to the reaction. The voltage across the cell is the intensity factor of the maximum electrical work, and the capacity factor is nF coulombs, where n is the number of faradays which are transferred per mole. Thus,

$$n F E = - \Delta G \quad (8)$$

Within the cell, the following reactions take place



The changes in electrochemical potentials accompanying these reactions are

$$\bar{\mu}_{H^+}^{(soln.)} + \bar{\mu}_{e^-}^{(Pt)} - \frac{1}{2} \mu_{H_2}^{(gas)} \quad (13)$$

$$- \frac{1}{2} \mu_{Cl_2}^{(gas)} - \bar{\mu}_{e^-}^{(Rh)} + \bar{\mu}_{Cl^-}^{(soln)} \quad (14)$$

$$\bar{\mu}_{e^-}^{(Cu)} - \bar{\mu}_{e^-}^{(Pt)} \quad (15)$$

$$\bar{\mu}_{e^-}^{(Rh)} - \bar{\mu}_{e^-}^{(Cu')} \quad (16)$$

Adding reactions (13) to (16) and setting the total equal to zero, since both the free energy loss and the work obtained are included, we obtain

$$\bar{\mu}_{H^+}^{(soln.)} + \bar{\mu}_{Cl^-}^{(soln)} - \frac{1}{2} \mu_{H_2}^{(gas)} - \frac{1}{2} \mu_{Cl_2}^{(gas)} + \bar{\mu}_{e^-}^{(Cu)} - \bar{\mu}_{e^-}^{(Cu')} = 0 \quad (17)$$

b. Current

The concept of current passing through an electrode has no real meaning in a reversible cell. Current is a measure of the net rate of reaction and, since the reversible cell is at equilibrium, the net reaction proceeds at an infinitesimal rate at most.

2. The Irreversible Cell: Electrochemical Kinetics

The first attempt to quantitatively describe the relation between current and voltage on a theoretical basis was made by Tafel in 1905.⁵¹ Tafel, studying the evolution of hydrogen formed from the discharge of hydronium ions, thought that the observed current-voltage relationships on metal electrodes could be explained by assuming that the rate of the recombination of hydrogen atoms was the rate limiting step in the process. If an electrode surface is sparsely covered with atomic hydrogen, the rate of the reaction



is given by kh^2 where k is the rate constant and h is the number of atoms per unit area of electrode surface. Since the rate of the reverse process will be negligible if appreciable current is flowing,

$$i = kh^2 \quad (23)$$

If one assumes that the activity of the hydrogen atoms is proportional to the concentration, then

$$E = E_e + \frac{RT}{F} \ln \frac{h}{h_e} \quad (24)$$

where h_e is the number of hydrogen atoms per unit area of electrode at equilibrium. The difference in voltage from the reversible voltage, E_e , is then

$$\eta = E - E_e = \frac{RT}{F} \ln \frac{h}{h_e} \quad (25)$$

If we now eliminate the electrochemical potential by the use of equation (4) and noting that,

$$\mu_e^{(Cu)} = \mu_e^{(Cu')} \quad (18)$$

we obtain

$$(\mu_H^{(soln)} + \mu_{Cl}^{(soln)}) - \frac{1}{2} \mu_{H_2}^{(gas)} - \frac{1}{2} \mu_{Cl_2}^{(gas)} = F (\psi^{(Cu)} - \psi^{(Cu')}) \quad (19)$$

or

$$\Delta G_{\text{reaction}} = n F E \quad (8)$$

Upon substituting activities for chemical potentials and setting $n F E^\circ = \Delta G^\circ$ where ΔG° has its usual significance, we obtain the more familiar form,

$$E = E^\circ + \frac{RT}{2F} \ln \frac{P_{H_2} P_{Cl}}{a_H + a_{Cl^-}} \quad (20)$$

E° values are commonly tabulated for half cell reactions and comprehensive compilations have been prepared by Latimer³³ and Conway.¹³ This is allowable only because of the universal convention of setting

$$2M_H + M_{H_2} - 2EF = 0 \quad (21)$$

When an electrochemical cell is established, the measured potential is often not that calculated by equation (20). This may be due to a number of circumstances. The current density drawn by the voltage measuring device may be high enough so that one of the electrodes is not at equilibrium, but is polarized. The problem in this case becomes one of electrochemical kinetics. Another possibility is that side reactions may be taking place, in which case the proper cell reactions have not been written. Furthermore, other potential-determining species may exist in solution as impurities.

and upon substituting (21)

$$i. = k \eta_e^2 \exp \left[\frac{2F}{RT} \eta \right] \quad (26)$$

$$= \frac{RT}{2F} \ln (i.) - \frac{RT}{2F} \ln (I^*) \quad (27)$$

where I^* is the value of the current at equilibrium in the cathodic or anodic direction and is called the exchange current.

Thus, a plot of overpotential, η , versus the log of the current density, $i.$, should be a straight line and should yield a slope of $\frac{RT}{2F}$. Although a plot of overvoltage against log $i.$ generally has been found to be a straight line for the hydrogen evolution reaction, the slope is seldom $\frac{RT}{2F}$. In order to explain this discrepancy, the theory of absolute reaction has been invoked.²¹ 45
The linear plot of log $i.$ versus overvoltage is commonly called "a Tafel line".

To demonstrate the application of absolute reaction rates to electrochemical reactions, consider the case of an electrode composed of metal, M, and of unit area in contact with a solution having M^+ cations. The situation can be pictured as in Figure 2 for slow ionization.⁴⁵

The distribution of energy among the reacting particles is governed by Maxwell's distribution law, which shows that the number of particles, ρ , with free energy in excess of a value ΔG^* is related to the total number of particles, ρ_t , by

$$\rho = \rho_t \exp \left[-\frac{\Delta G^*}{RT} \right] \quad (28)$$

Referring to Figure 2, if it is assumed that all particles exceeding a free energy of ΔG_1^* and reaching the activated state complete their reaction path, then the rate of ionization, $\bar{V}_1$, is

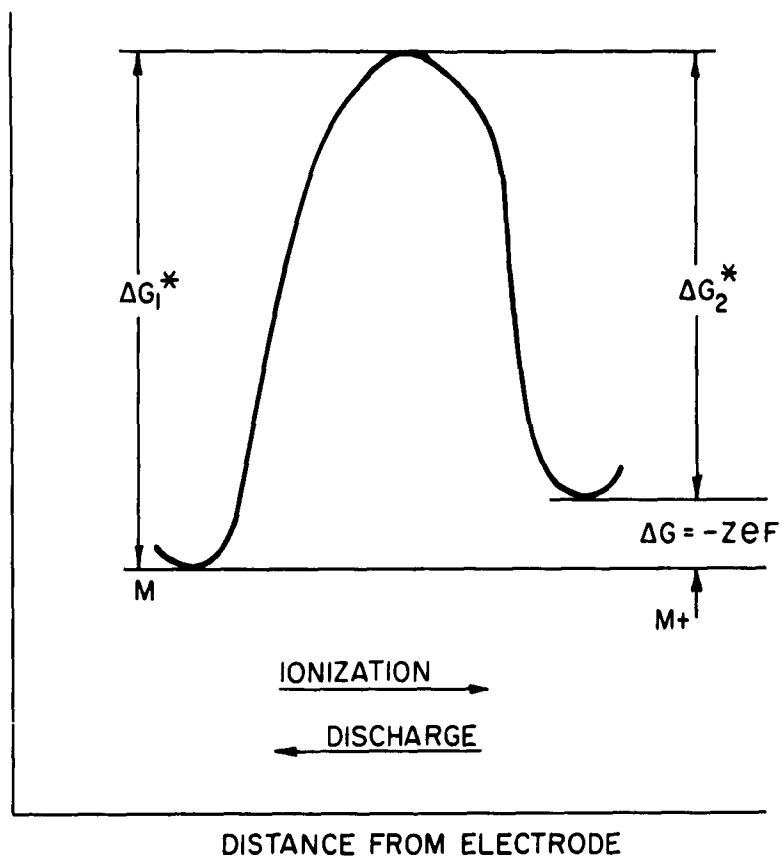


Fig. 2 Energy Barrier for Irreversible Electrode Process.

$$\bar{V}_1 = K_1 \exp - \frac{\Delta G_1^*}{RT} \quad (29)$$

where K_1 is a constant depending on the nature of the M-M bond. Similarly, the rate of the reverse reaction is

$$\bar{V}_2 = a_M^t K_2 \exp - \frac{\Delta G_2^*}{RT} \quad (30)$$

In order that a net reaction take place at the electrode, the energy barrier for the reaction must be lowered, or the energy barrier for the reverse reaction must be increased. Since a net reaction in either direction implies a departure from equilibrium, the voltage changes from its equilibrium value by an amount η . The effect of the overpotential is shown in Figure 3 to be two-fold; part of the overpotential decreases the forward reaction rate energy barrier from ΔG_1^* to $(\Delta G_1^* - (1 - \alpha) \eta F)$ and the remainder increases the reverse reaction rate energy barrier from ΔG_2^* to $(\Delta G_2^* + (\alpha) Z \eta F)$. Thus, the forward reaction rate is increased and the reverse rate decreased.

The terms V_1 and V_2 at equilibrium conditions are equal and correspond to the exchange current density, I_0 . The net current density, i , is:

$$i = V_1 - V_2 = I_0 \left\{ \exp \left[\frac{(1-\alpha) Z \eta F}{RT} \right] - \exp \left[\frac{-\alpha Z \eta F}{RT} \right] \right\} \quad (31)$$

Note that since $\eta = E - E^*$, when the reverse reaction is negligible, equation (28) reduces to

$$E = E^* + \frac{RT}{(1-\alpha) ZF} \ln i = \frac{RT}{(1-\alpha) ZF} \ln I_0 \quad (32)$$

Equation (32) is quite similar to the Tafel equation (27) with the exception that the number "2" is replaced by the product " $(1-\alpha) Z$ ". The term " Z " is quite clearly the number of electrons that are transferred before one act of the rate limiting step can take place. The term " α ", on the other hand, represents the fraction of the overpotential which reduces the energy barrier for the forward reaction. It is often pointed out that $\alpha = \frac{1}{2}$ represents a symmetrical energy barrier. Calculated energy curves for the system

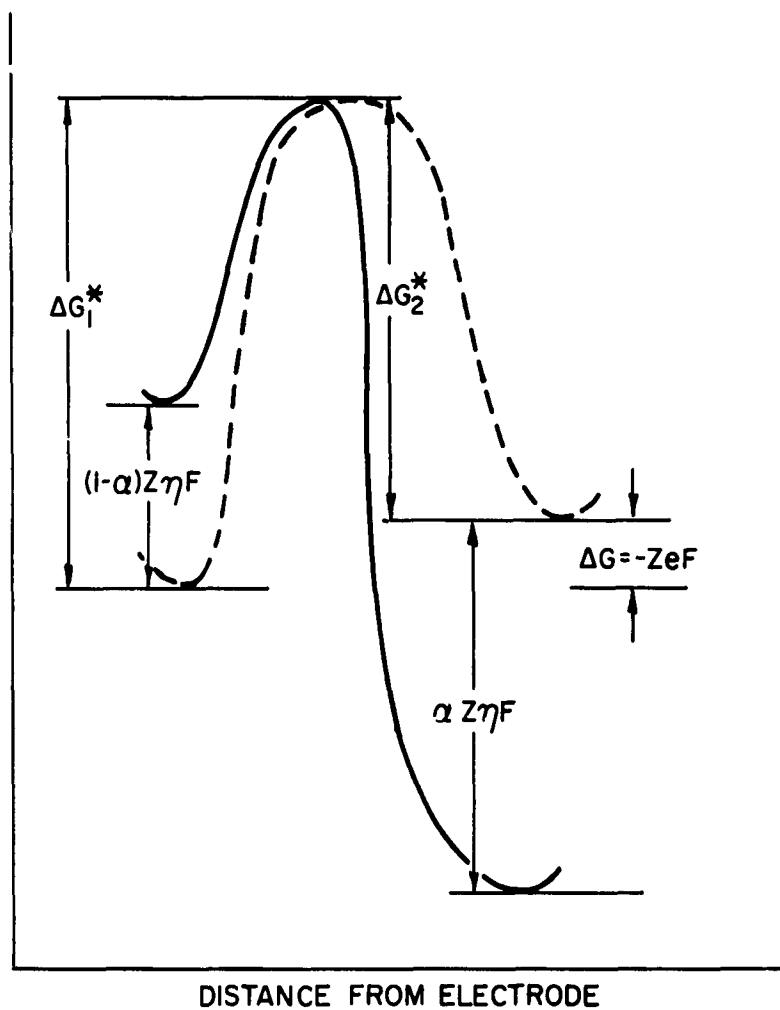


Fig. 3 Effect of Overpotential on Irreversible Energy Barrier at Electrode.

(metal + e⁻), H₃O⁺ indicate the α is a function of the work function of the metal but will not vary greatly from $\frac{1}{2}$.⁴⁶

The term "Z" can be separated from "a" by considering the relation between I and η at low overpotentials (η less than -20 mv.).^{3 35} In this case, equation (28) can be expanded and all but the first terms of the expansion dropped. This gives the relation,

$$I = - \frac{Z I_0 \eta F}{RT} \quad (33)$$

To reduce the errors due to the expansion of terms

$$Z = - \frac{RT}{F I_0} \left(\frac{\partial I}{\partial \eta} \right)_{\eta \rightarrow 0} \quad (34)$$

3. Chronopotentiometry

a. Basic Theory

Chronopotentiometry is the study of the voltage time behavior at a single electrode when a constant current is applied and transport of reactant is controlled by diffusion only. In order to develop the important equations for chronopotentiometry, consider a reaction



where substance A is oxidized to B yielding n electrons. The following treatment of the basic relationships will follow that of Delahay.¹⁷

Since the current density, i_0 , is constant and the total current is assumed to be due to the reaction of A, the flux of substance A at a plane electrode surface can be written as

$$i_0 = n F D_A \left(\frac{\partial C_A(x,t)}{\partial x} \right)_{(x=0)} \quad (36)$$

where F is Faraday's number, D_A is the diffusivity of A and $C_A(x,t)$ represents the concentration of A at a distance x from the electrode and t in time. The

notation $x=0$ signifies that the derivative $\left(\frac{\partial C_A(x,t)}{\partial x}\right)$ should be taken at $x=0$, which represents the electrode surface. The following boundary conditions can also be established:

$$C_A(x,0) = C_A. \quad (37)$$

where $C_A.$ is the bulk concentration of A.

$$C_A(x,t) = C_A. \quad x \rightarrow \infty \quad (38)$$

The three conditions stated above are sufficient to solve Fick's law of diffusion,

$$\frac{\partial C_A(x,t)}{\partial t} = \frac{\partial}{\partial x} D_A \frac{\partial C_A(x,t)}{\partial x} \quad (39)$$

if D_A is independent of both the distance x and time. In electrolyte solutions, the diffusivity of a species is a function of the ionic strength of the solution. In an electrochemical half cell reaction at least one of the reactants or products must be an ion. Thus, there would be a buildup or depletion of ions in the vicinity of the electrode as the reaction proceeded and D_A would be a complex function of both distance and time. If, however, the half cell reaction is carried out in a large excess of an inert electrolyte, the diffusivity is independent of the distance and time in spite of changes in C_A .¹⁷

The concentration of B can be solved for because the following boundary conditions are known. The sum of the fluxes for A and B must equal zero at the electrode surface,

$$D_A \frac{\partial C_A(0,t)}{\partial x} + D_B \frac{\partial C_B(0,t)}{\partial x} = 0 \quad (40)$$

At time zero,

$$C_B(x,0) = C_B. \quad (41)$$

and

$$C_B(x,t)_{x \rightarrow \infty} = C_B. \quad x \rightarrow \infty \quad (42)$$

The solution of equation (39) for A was reported first by Weber⁵³ while Karaoglanoff³¹ was the first to calculate the concentrations of both A and B as functions of x and t. These concentrations are:

$$C_A(x,t) = C_{A^0} - \frac{2\lambda D_A^{1/2} t^{1/2}}{\pi^{1/2}} \exp\left(-\frac{x^2}{4D_A t}\right) + \lambda x \operatorname{erfc}\left(\frac{x}{2D_A^{1/2} t^{1/2}}\right) \quad (43)$$

$$C_B(x,t) = \frac{2\lambda D_A t^{1/2}}{D_B^{1/2} \pi^{1/2}} \exp\left(-\frac{x^2}{4D_B t}\right) - \frac{\lambda x D_A}{D_B} \operatorname{erfc}\left(\frac{x}{2D_B^{1/2} t^{1/2}}\right) \quad (44)$$

for the case where $C_{B^0} = 0$, and where λ is defined as

$$\lambda = \frac{1_0}{nFD_A} \quad (45)$$

1. Reversible Process

The electrode potential for a reversible process can be determined easily by setting $x=0$ and substituting the values of $C_A(x,t)$ and $C_B(x,t)$ into equation (20).

$$E = E^0 - \frac{RT}{nF} \ln \frac{f_A D_B^{1/2}}{f_B D_A^{1/2}} - \frac{RT}{nF} \ln \frac{C_{A^0} - \gamma t^{1/2}}{\gamma t^{1/2}} \quad (46)$$

where f_A is the activity coefficient of A and γ is defined as

$$\gamma \equiv \frac{21_0}{\pi^{1/2} nFD_A^{1/2}} \quad (47)$$

It can be seen from equation (46), that the numerator of the logarithmic term goes to zero, which means that the voltage goes to infinity, when the time has the value τ , defined as

$$t^{1/2} = \frac{C_{A^0}}{\gamma} \equiv \tau^{1/2} \quad (48)$$

The significance of this sudden rise of the voltage to infinity, is that the reaction of A can no longer be supported at this current. Thus, some other reaction must take place at the electrode surface. In aqueous solutions, for anodic processes, this generally leads to oxidation of the electrode or evolution of oxygen due to the oxidation of water. However, when the time

τ is reached there is a significant change in the voltage, and τ is one of the important responses in chronopotentiometry.

By introducing τ into equation (46), another interesting aspect of the voltage-time behavior is seen,

$$E = E^\circ \frac{RT}{nF} \ln \frac{r_{AB}^{D^{1/2}}}{r_{BA}^{D^{1/2}}} - \frac{RT}{nF} \ln \frac{\tau^{1/2} - t^{1/2}}{t^{1/2}} \quad (49)$$

namely, that the last logarithmic term is zero when

$$t^{1/2} = \frac{\tau}{2}^{1/2} \quad (50)$$

or when

$$t = \frac{\tau}{4} \quad (51)$$

The voltage at this point is called $E_{1/2}$ because when a mercury electrode is used in a cathodic process this potential is equal to the polarographic half wave potential.¹⁷

$$E = E_{1/2} - \frac{RT}{nF} \ln \left[\left(\frac{\tau}{t} \right)^{1/2} - 1 \right] \quad (52)$$

2. Irreversible Processes

For an irreversible reaction the anodic component for a metal electrode of unit activity was shown to be

$$i_a = I_0 \exp \left\{ \frac{(1-\alpha)Z\eta F}{RT} \right\} \quad (53)$$

For the reaction



i_0 can be expressed as

$$i_0 = n F k_f^{\circ} C_A(0, t) \quad (54)$$

in terms of a formal rate constant, k_f° , and the concentration of A at the electrode surface, $C_A(0, t)$. The transition time, τ , is determined by the condition $C_A(0, t) = 0$, just as for the irreversible process. Thus, the voltage-time equation can be written as

$$E = \frac{RT}{(1-\alpha)ZF} \ln \frac{nFC_A^{\circ}k_f^{\circ}}{i_0} - \frac{RT}{(1-\alpha)ZF} \ln \left[1 - \left(\frac{t}{\tau} \right)^{1/2} \right] \quad (55)$$

3. Differentiation of Simple Reversible and Irreversible Processes

From equations (52) and (55) it can be seen that there are two simple methods of testing whether a process is reversible or irreversible.

The first is to plot the value of the potential at $t = \tau/4$ versus $\log i_0$. In the case of the reversible process, $E_{1/2}$ will be independent of the current density, whereas for the irreversible process, a straight line of slope $RT/(1-\alpha)ZF$ will be obtained.

The second is to plot the logarithm $1 - \left(\frac{t}{\tau} \right)^{1/2}$ or $\left[\left(\frac{\tau}{t} \right)^{1/2} - 1 \right]$ against potential at any current density. With a reversible process $\log \left[\left(\frac{\tau}{t} \right)^{1/2} - 1 \right]$ vs. potential yields a straight line of slope $2.3 RT/nF$, whereas for an irreversible process, $\log \left[1 - \left(\frac{t}{\tau} \right)^{1/2} \right]$ vs. potential yields a slope of $RT/(1-\alpha)ZF$ and an intercept of

$$\frac{n F C_A^{\circ} k_f^{\circ}}{i_0}.$$

Such tests have been carried out for both reversible and irreversible processes. The references are given by Delahay.¹⁷

b. Effect of Double Layer Capacity

Because the potential of the electrode is varying during chronopotentiometry and the double layer capacitance is a function of the potential, a certain amount of coulombs must go into the charging of the double layer. If this amount of coulombs is a significant percentage of the total coulombs passed, a great deal of distortion can take place in the potential time curve.

The number of coulombs used to charge the double layer, Q_1 , can be estimated by using an average value for the double layer capacitance, $(\bar{C}_1)$,

$$Q_1 = (\bar{C}_1) (\Delta E) \quad (56)$$

where ΔE is the change in potential. The number of coulombs in the electrochemical reaction is

$$Q_e = i \cdot T \quad (57)$$

After substituting from equation (48) for T , the ratio

$$\frac{Q_1}{Q_e} = \frac{4i \cdot \bar{C}_1 \Delta E}{\pi n^2 F^2 (C_A^\circ)^2 D_A} \quad (58)$$

In order to reduce Q_1/Q_e to one per cent

$$n^2 (C_A^\circ) \geq 2.7 \times 10^{-9} i. \quad (59)$$

where D_A was chosen as 10^{-5} cm²/sec, ΔE as 0.1 volt, and $\bar{C}_1 = 20$ Mf/cm².

In the above calculation the electrode was assumed to be perfectly smooth. This is the case for liquid metal electrodes, such as mercury. However, for metal electrodes, especially electrodes which have been plated to provide an active surface this situation is frequently far from true. In order to correct for this effect in our work we have adopted the method suggested by Rheinmuth.²⁸ This is shown in Figure 4b.

c. Effect of Surface Roughness

If the roughness of the surface of a plain electrode becomes of the order of the thickness of the diffusion layer, the constancy of the product $(i.t^{1/2}/C^*)$ cannot be expected. Since the thickness of the diffusion layer is a function of the transition time, being of the order of magnitude of $\sqrt{Dt}$,⁴⁷ the effect of surface roughness is more important at shorter transition times, or higher current densities. Thus, the diffusion front area is initially large when the surface is rough and becomes smaller as the reactant becomes depleted near the electrode surface. Eventually, the diffusion front area becomes equal to the area that would be expected at a smooth electrode.

The effect of surface roughness is to cause the $(i.t^{1/2}/C^*)$ product to be higher at short transition times or high current densities.¹⁹

d. Effect of Adsorbed Species

If a species is adsorbed on the electrode prior to the start of the chronopotentiometric experiment and this adsorbed species is reactive, a definite number of coulombs must be expended in order to react this species before the reactant dissolved in solution is reacted. Since the number of coulombs consumed in chronopotentiometry is a function of the transition time, this effect will become more noticeable at low transition times.

A coulomb balance on such a system is as follows,

$$\left(\frac{i.t}{C^*}\right)_{\text{obs.}} = \left(\frac{i.t}{C^*}\right)_{\text{diff.}} + \left(\frac{i.t}{C^*}\right)_{\text{ads.}} \quad (60)$$

where obs., diff., and ads., stand for observed, diffusion, and adsorbed species, respectively. Now, $(i.t)_{\text{ads.}}$ is equal to $n F \Gamma$ where Γ is the number of moles adsorbed per square centimeter of projected area. If equation (60) is now divided by $T^{1/2}_{\text{obs.}}$

$$\left(\frac{i_0 \tau^{1/2}}{C^0} \right)_{\text{obs.}} = \left(\frac{i_0 \tau}{C^0} \right)_{\text{diff.}} \times \frac{1}{\tau_{\text{obs.}}^{1/2}} + \frac{n F \Gamma}{C^0 \tau_{\text{obs.}}^{1/2}} \quad (61)$$

However, as $\tau_{\text{obs.}}$ approaches infinity $\tau_{\text{obs.}}$ becomes equal to $\tau_{\text{diff.}}$,

$$\tau_{\text{obs.}} = \tau_{\text{diff.}} \text{ as } \tau_{\text{obs.}} \rightarrow \infty \quad (62)$$

Thus, for long observed transition times,

$$\frac{i_0 \tau^{1/2}}{C^0} \text{ obs.} = \frac{i_0 \tau^{1/2}}{C^0} \text{ diff.} + \frac{n F \Gamma}{C^0 \tau_{\text{obs.}}^{1/2}} \text{ as } \tau_{\text{obs.}} \rightarrow \infty \quad (63)$$

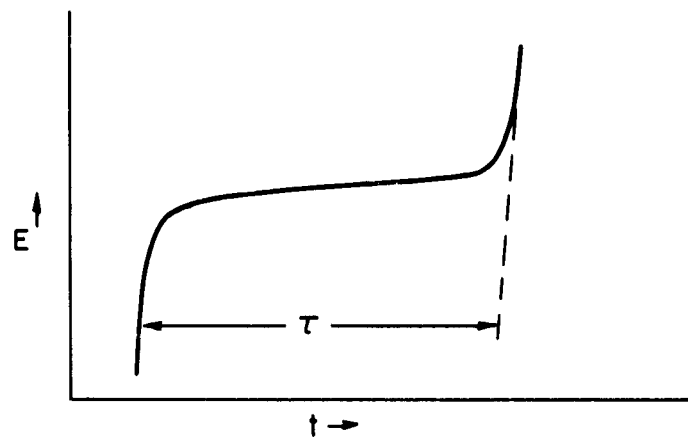
From equation (63) it is seen that Γ can be determined if a plot is made of $(i_0 \tau^{1/2}/C^0)_{\text{obs.}}$ vs. $(1/\tau^{1/2})_{\text{obs.}}$. The intersection of the curve at $(1/\tau^{1/2})_{\text{obs.}} = 0$ is $(i_0 \tau^{1/2}/C^0)_{\text{diff.}}$ which can be calculated and the slope near $(1/\tau^{1/2})_{\text{obs.}} = 0$ is equal to $(n F \Gamma/C^0)$.

e. Complex Processes

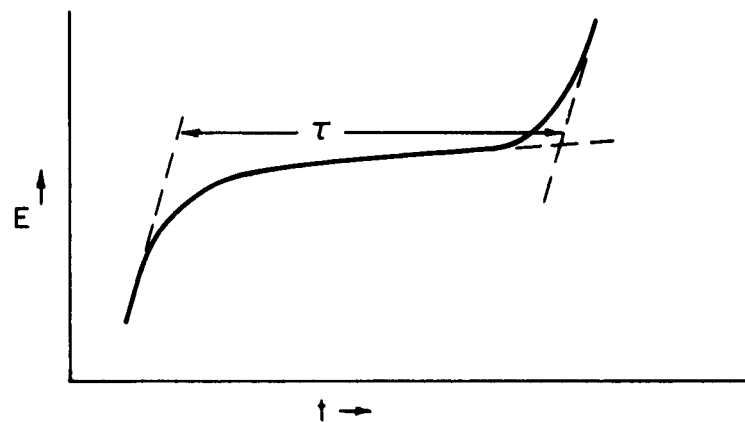
By examining a plot of current density vs. the $(i_0 \tau^{1/2}/C^0)$ product, an insight into the mechanism of the electrochemical process may be obtained. When the $(i_0 \tau^{1/2}/C^0)$ product is independent of the current density, the voltage-time curve may be used for the same purpose. Diagnostic criteria to distinguish different mechanisms have been published by Delahay¹⁷ and Rheinmuth.⁴⁷

4. Double Layer Capacitance

In a recent article, Laitinen³⁶ reviews the methods for determining the amount of substances present on the surface of a metal in an electrolyte solution. In particular, three techniques are examined; coulometry, chronopotentiometry, and double layer capacitance measurements. Coulometry is directly applicable if no side reactions take place and definite potential regions are identifiable. It has been used to demonstrate the existence of oxide films on noble metals (Introduction C2.). The use of chronopotentiometry to determine adsorbed layers is actually an extension of the use of



(a) VOLTAGE-TIME CURVE WHERE DOUBLE LAYER CHARGING IS NEGLIGIBLE



(b) VOLTAGE-TIME CURVE DISTORTED BY DOUBLE LAYER CHARGING

Fig. 4 Effect of Double Layer Charging on Potential Time Curve.

coulometry, except that the number of coulombs in the adsorbed film is determined by extrapolation of the ($i. \tau^{1/2}/C^{\circ}$) product to values of τ equal to infinity (see Introduction B3d.). Double layer capacity measurements are unique since this technique does not require an electrochemical reaction to take place and responds to all substances which change the dielectric properties of the metal solution interface.

When a metal is in contact with an electrolyte solution, the metal acts as a surface of free charge and ions of opposite charge are adsorbed from the bulk of the solution to a region close to the metal surface in order to maintain electrical neutrality. Because the metal and the adsorbed ions are physical entities they must be separated by a finite distance. The effect of this physical situation is exactly analogous to a capacitor. The theories regarding the distribution of ions from the metal surface out to the bulk of the solution lead to the conclusion that the double layer is not simply a single layer of ions held close to the surface of the metal. For details on the double layer structure, the following reviews are recommended,^{5 23 37}

a. Problems of Measurement on Solid Metals

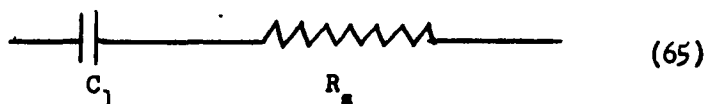
The method most commonly used to measure double layer capacity on mercury electrodes is to determine the change in interfacial surface tension as a function of applied potential. The first derivative of the surface tension-voltage curve gives the surface charge density by the well-known Lippman equation.⁵ The second derivative yields the capacitance.⁵

However, with solid metal electrodes no reliable method has been found by which the interfacial tension of the metal-solution interface can be determined. Thus, the capacitance is measured directly.

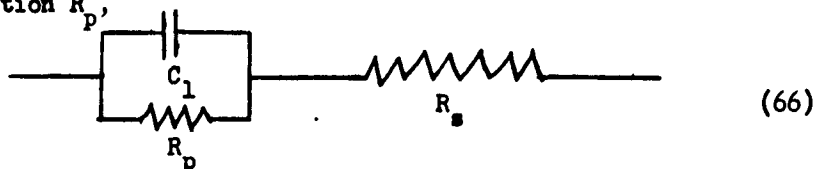
When no electrochemical reaction can take place at an electrode, the circuit for the electrochemical cell can be written simply as:



where C_1 represents the capacitance of the double layer at each electrode and R_s is the solution resistance. Usually one would desire to measure the capacitance of only one electrode, so the area of the electrode that is not to be measured is made much larger than the electrode to be tested. Since the capacitances of the two electrodes are in series, the reciprocal of each capacitance is added and if one capacitance is very large its effect will be negligible. Thus, the circuit, under this condition, can be written as,



However, when an electrochemical reaction can take place on an electrode, another element must be introduced into the circuit, namely the resistance of the reaction R_p ,



This resistance, R_p , is equal to η/i where η is the overpotential and i is the current passing through the resistance. Since alternating current has two possible paths across the electrode one can define two currents. One is caused by the discharge of a reacting species, i.e., across resistance R_p . This is called the faradic current. The other current, is caused by the charging and discharging of the capacitance.

The usual method of measuring metal-solution capacitances is to determine the cell response to a sine wave current or voltage. The amplitude of the sinusoidal voltage response or input is held to a small value since the capacitance is a function of the potential.

Up to this point no complications have been introduced in the determination of the elements of the electrode circuit (66). However, when one

attempts to measure a circuit of type (66), the input alternating current or voltage causes changes in the concentrations of the species involved in the faradic reaction. The effect of this is to change the circuit so that, with the exception of one special case, the electrode cannot be simply represented by a fixed set of resistor and capacitors.²²

Since this complication is brought about by the faradic current, the way to circumvent the problem is to eliminate the faradic current. This situation, the special case referred to above, arises when R_p is infinite. All the alternating current then passes through the capacitance and the electrode is termed ideally polarized. In the case of the ideally polarized electrode the circuit can be represented by (65). However, one must be certain that R_p is infinite before analyzing measurements from a metal-solution interface in terms of circuit (65).

b. Measurement by Square Wave Current

Aside from the measurement of double layer capacitances by passing an alternating sine wave current or voltage, there are other methods of capacitance measurement. One convenient method, suggested by Brodd and Hackerman,⁴¹ is to send a square wave current input to the electrode. The voltage output of the cell will be of the form in Figure 5a for an ideally polarized electrode and as in Figure 5b for a non-ideally polarizable electrode.

The step, in either case, is due to the solution resistance, R_s , which is equal to,

$$R_s = \frac{\Delta V_1}{i \text{ a.c.}} \quad (67)$$

For the ideally polarizable electrode, Figure 5a, the capacitance is simply,

$$C = \frac{i \text{ a.c.}}{\Delta V_2} \Delta T \quad (68)$$

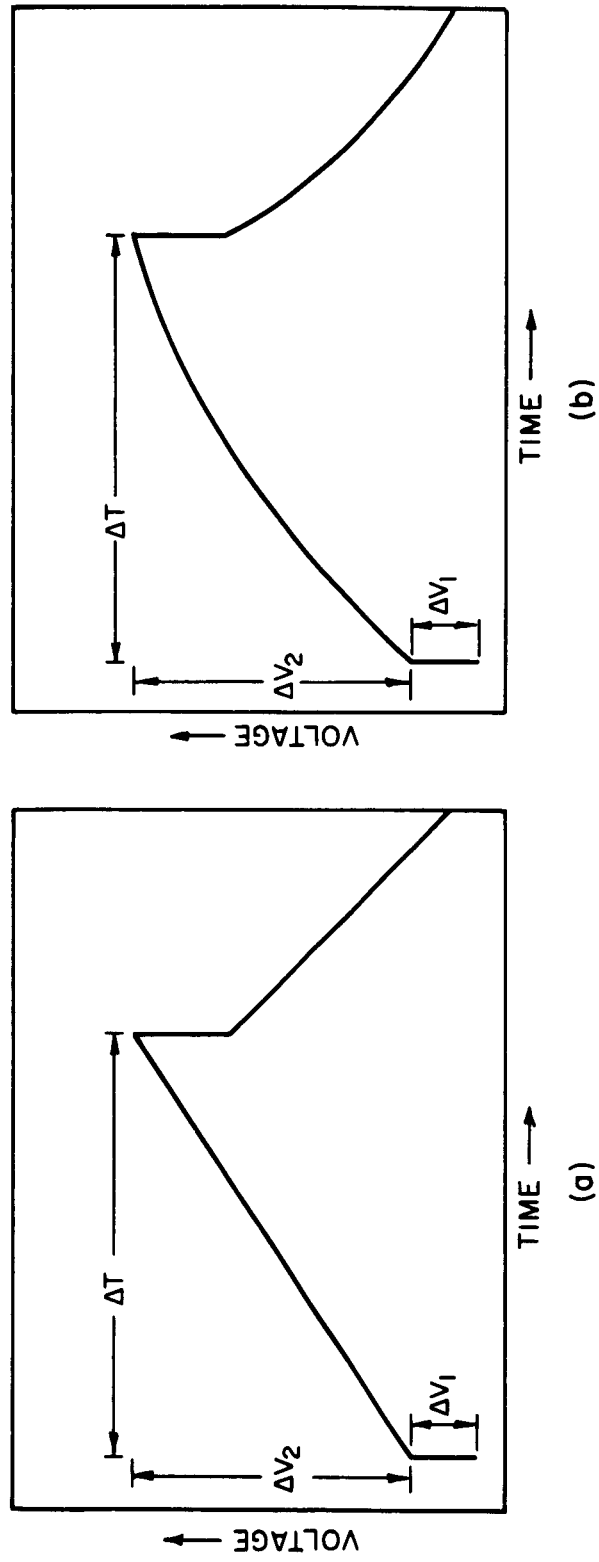


Fig. 5 Voltage Output Resulting from a Square Wave Current Input.

Furthermore, one can check as to whether the assumption that $R_p = \infty$ is valid by examining the curvature as a function of frequency, since at lower frequencies the electrode is more likely to behave as in Figure 5b.

Hackerman and Brodd²⁵ used the square wave input technique to determine the relationship between double layer capacity and surface area at constant potential on solid metal electrodes. Later Hackerman and McMullen³⁶ extended the technique to examine capacitance-potential curves and, more recently, the technique was used by Popat and Hackerman⁴⁴ to determine the adsorption of inorganic anions on platinum electrodes at constant potential. Cahan and Ruetschi¹¹ superimposed a square wave current on a d.c. current in order to examine transient corrosion films on lead in sulfuric acid. They studied the changes in double layer capacity and voltage simultaneously.

c. Quantitative Treatment of Adsorbed Layers

The determination of organic monolayers by double layer capacity measurements is not absolutely straightforward. The simplest explanation which has been applied by several workers, is to assume a parallel capacitor model of the double layer for fractional monolayer adsorption,³² such that

$$C_{\text{double layer}} = \Gamma C_{\text{double layer}}^{\text{sat}} + (1 - \Gamma) C_{\text{double layer}}^{\circ} \quad (67)$$

where Γ = the fraction covered

$C_{\text{double layer}}^{\text{sat}}$ = differential double layer of a saturated monolayer

$C_{\text{double layer}}^{\circ}$ = differential double layer of a clean surface

$C_{\text{double layer}}$ = measured double layer

where all measurements are made at constant potential and various concentrations. An example of the type of data observed was given by Laitinen³² and is shown in Figure 6.

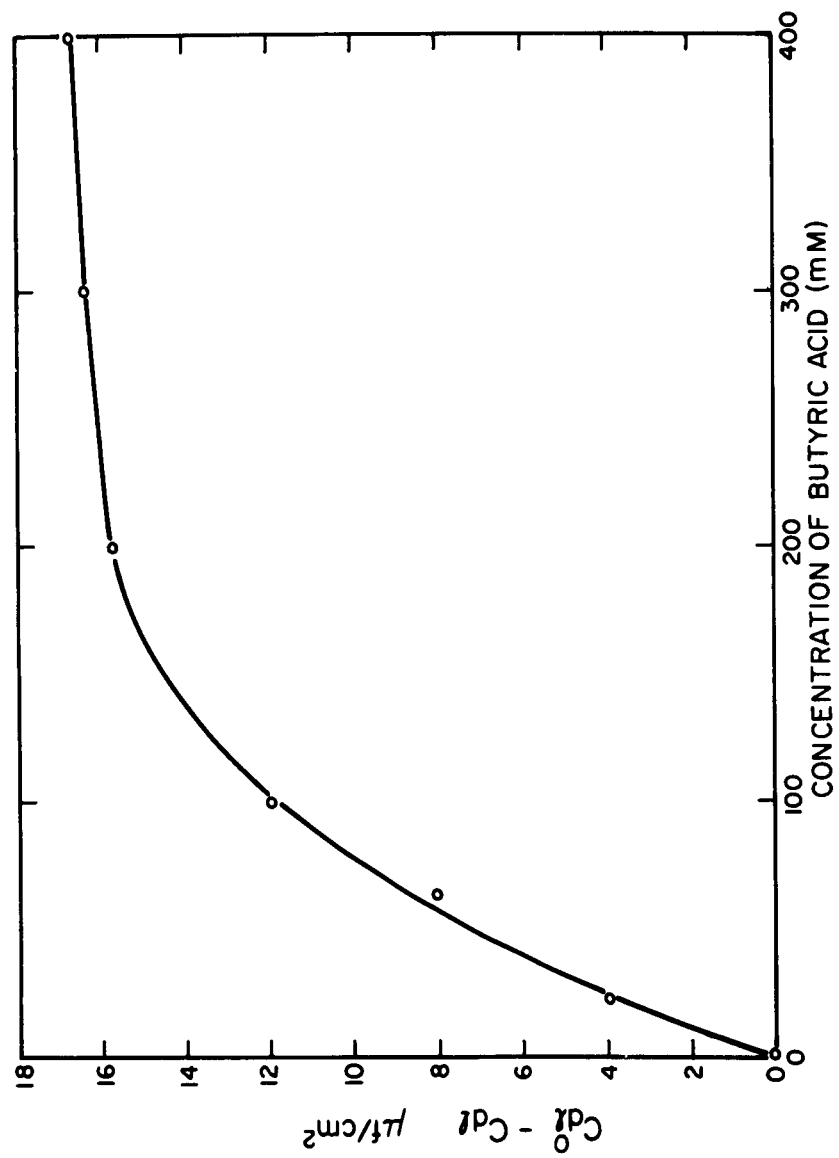


Fig. 6 Adsorption Isotherm for Butyric Acid.

This assumption of a parallel capacitor has been justified in the case of oxide formation on a platinum electrode. In this case, the change in double layer capacity has been found to be linearly related to the millicoulombs of oxide on the surface.³¹ With platinum oxides the double layer capacitance increases with increased oxide coverage. In the case of organic molecules being adsorbed on platinum, the capacitance is found to decrease with increasing coverage.⁴

C. Previous Investigations on the Electrochemical Oxidation of Formic Acid

1. Work of E. Muller

a. Early Theory

The first investigation of the electrochemical oxidation of formic acid where the main purpose of the work was to understand the mechanism of the anodic process was undertaken by Muller in 1923.³⁹ In this work Muller obtained current-potential curves on platinized and rhodenized platinum, pallidized palladium, and on smooth metals including platinum, iridium, and palladium. Current-potential curves were taken with formic acid in acid, neutral, and basic aqueous solutions at temperatures ranging from 20°C to 75°C. Although not stated, the shape of the curves indicate that they were obtained under conditions of constant potential. Typical curves for smooth platinum in 1 Normal sulfuric acid and 1 Molar formic acid are shown in Figure 7. The dotted line in Figure 7 represents the current potential curve obtained when no formic acid was present in the aqueous sulfuric acid.

In the pure sulfuric acid oxygen evolution causes the rise in current after +1.2 volts vs. N.C.E. that is seen in Figure 6. However, when the formic acid is present, the current rises at a lower potential, increases to a maximum, and then falls only to rise again. Furthermore, this maximum is seen in Figure 6 to increase with increasing temperature. On platinized platinum the same general shape was obtained, only in this case higher currents were observed.

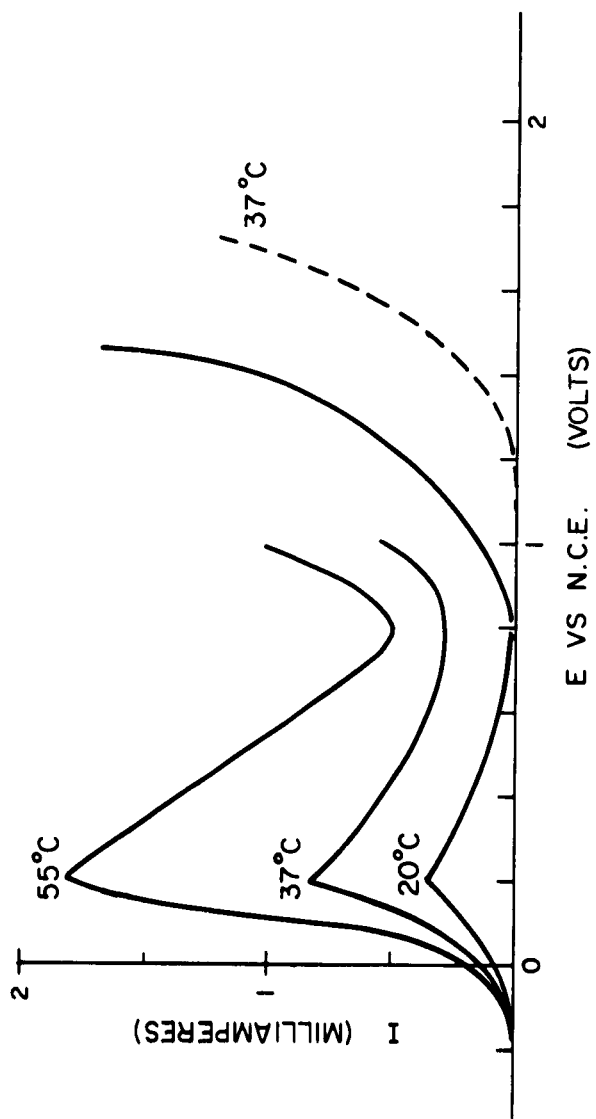
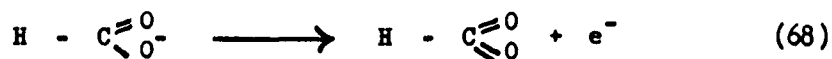


Fig. 7 Current-Potential Curve for 1M Formic Acid in 1N Sulfuric Acid Obtained by Muller on Plain Platinum.

In order to explain the question: what can cause the sudden rise of resistance in the region after the maximum current, Muller suggested the following scheme. First, the formate ion was postulated to be oxidized in a one-step process to an oxidized intermediate:



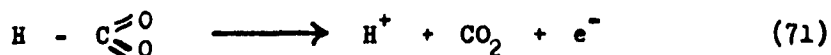
This intermediate was then thought to be catalytically decomposed by the metal anode to hydrogen and CO_2 ,



and the resulting hydrogen atom easily oxidized to a hydrogen ion as follows:



Muller felt that as the potential was increased, the metal became covered with an oxide layer. The oxide-covered metal was not catalytic and hence reaction (69) did not proceed. Hence, the current decreased until the potential for the reaction

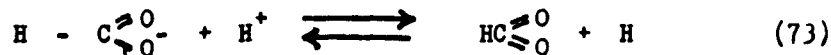


was attained.

Previously, Muller had investigated the electrochemical oxidation of formaldehyde on copper³⁸ and had found that H_2 was given off at the anode. In order to explain this unexpected result Muller suggested that the formaldehyde was in equilibrium with a partially oxidized form in the solution:



In the case of formic acid, he proposed a similar equilibrium,



If such an equilibrium were to exist, Muller expected to find a current peak corresponding to the oxidation of the hydrogen on the surface. Since it was known that palladium was an excellent adsorbent for hydrogen, such a current peak was expected on the palladium electrode. At 20°C only one peak was seen at +0.6 v and no second peak was observed, but at 75°C a small peak current was seen on plain palladium at about +0.2 v besides the peak at +0.6 v. vs. N.C.E. Furthermore, when pallidized palladium was used on the anode at 75°C a strong maximum current at -0.2 v was observed and this corresponded to the potential at which hydrogen itself was electrochemically oxidized.³⁹

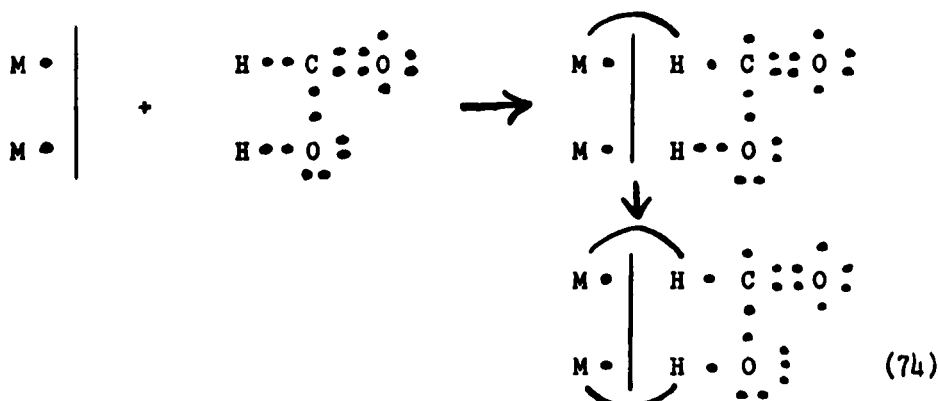
As to the effect of pH Muller observed the same general-shaped curves and with the exception of plain platinum, all the metals exhibited the highest maximum current in neutral solution, rhodium being the most active catalyst. On plain platinum current-voltage oscillations were found in neutral solution.

b. Revised Theory

Muller published further observations and theories on the electrochemical oxidation of formic acid in 1927.⁴⁰ Here, he revised his earlier postulates, such as the existence of an $\text{H} - \text{C} \begin{array}{c} \nearrow \text{O} \\ \searrow \text{O} \end{array}$ molecule, and presented a new theory based on "der neuen Atomtheorie".

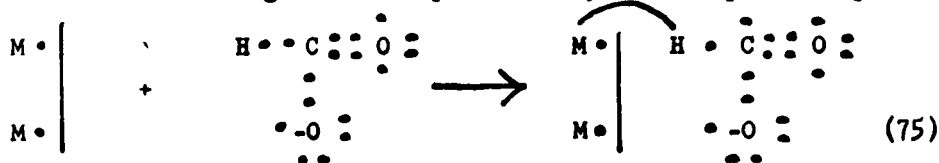
1. Importance of Adsorption

Here, Muller states that the chemical decomposition of the undissociated formic acid proceeds first by an adsorption step as follows:

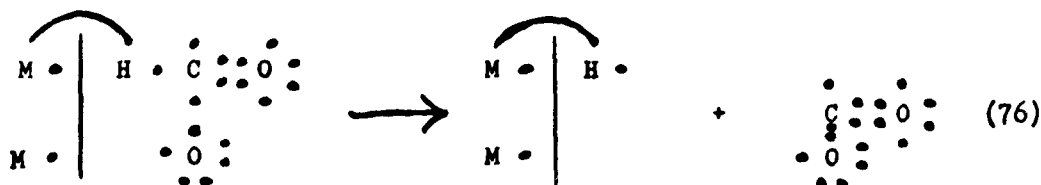


where M represents a metal site and the dots represent electrons, the electrons of the metal being outer electrons. Once the formic acid has been adsorbed, the carbon dioxide can be set free and the hydrogen remains adsorbed by the metal. Muller stated that, because of the surface regularity of smooth metals, reaction (74) proceeds extremely slowly if at all on smooth metals, but can take place on spongy or plated metals. Muller felt that the adsorbed hydrogen accounted for the electrochemical behavior of palladium noted previously.

Once the voltage was raised to sufficiently anodic potentials, the current rose due to the oxidation of the formate ion. Muller thought that the formate ion discharge was also preceded by an adsorption step:



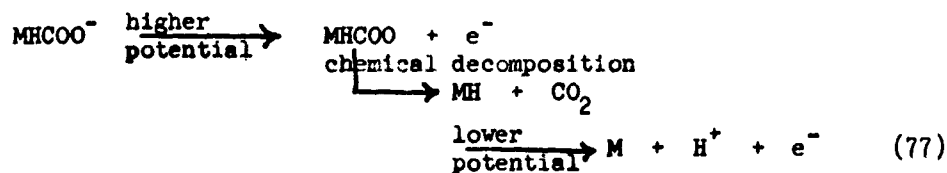
However, the adsorbed formate ion could not further decompose until an electron was removed from the structure, i.e., until the ion was discharged at the surface. Once this occurred, the resulting "CO₂ complex" was decomposed catalytically as follows.



the remaining adsorbed hydrogen atom being easily discharged to hydrogen ion electrochemically. Muller felt that reaction (76), just as (74), occurs very slowly on smooth metals because of the "special position" of the molecule when it hits the surface. Here, Muller is basing his argument more on an underlying assumption of the rigidity of the formic acid or formate molecule than on steric factors such as bond lengths and metal site distances.

11. Explanation of Oscillatory Behavior

By operating in higher formic acid concentrations, Muller⁴⁰ observed current-voltage oscillations on rhodenized platinum and pallidized palladium. The higher potential in the oscillation was assumed to be the potential of the discharge of the formate ion, the lower potential represented the discharge of the hydrogen resulting from the discharge of the formate ion. This scheme can be represented as follows:



This theory he felt was especially borne out by the behavior of pallidized palladium at 18°C. This is shown below in Figure 8. In Figure 8 the region of oscillations is characterized by parallel lines. The initial rise in Figure 8 below 0 volts vs. N.C.E. was previously shown to be due to hydrogen discharge. The fact that the minimum potentials are in this potential region of hydrogen discharge support the view that the electrochemical oxidation of hydrogen plays an important role in the periodic phenomena.

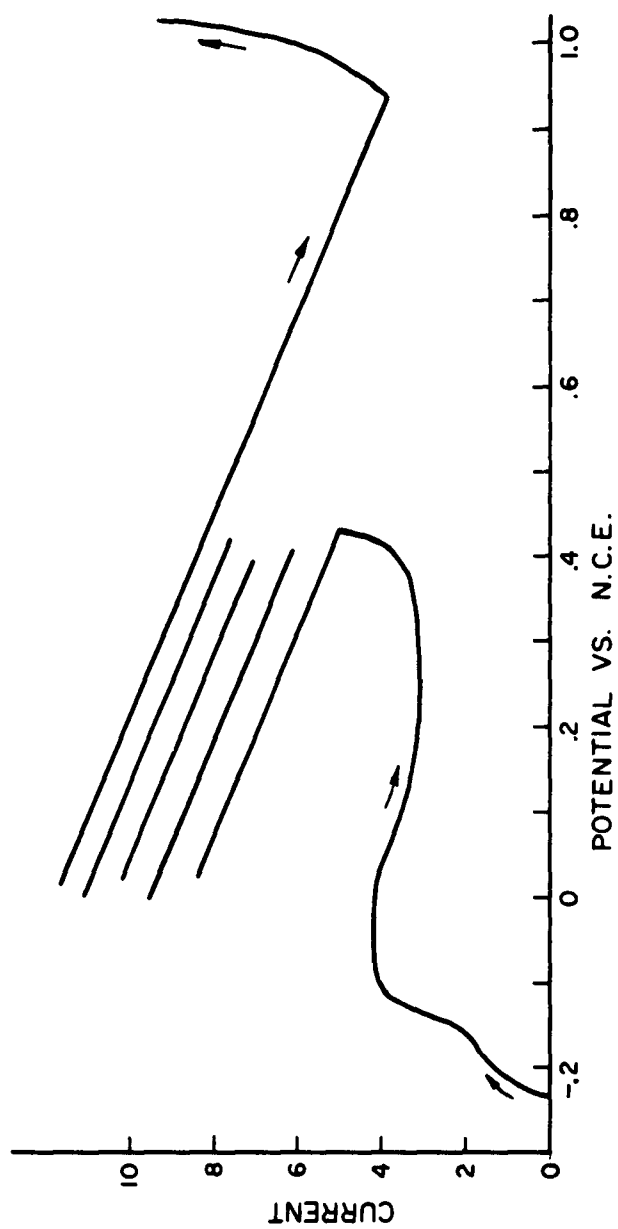


Fig. 8 Behavior of Palladized Palladium in Formic Acid after Muller.

In a later publication Muller reported on oscillations observed with a 1M NaOOCH and formic acid solution on a rhodenized platinum electrode.⁴¹ Under the conditions of this experiment the oscillations exhibited a constant period at a given current density. The product of the current density and the time of a period was found to be constant. This amount of coulombs was interpreted to be the amount of coulombs necessary to discharge enough formate so that the surface would be saturated with adsorbed HCOO.

iii. Evidence for Oxide Layer Inhibition

By first increasing the potential to voltages higher than +1.2 v vs. N.C.E. and then decreasing the voltage, Muller⁴⁰ found a significant hysteresis effect in the current potential curve. This is shown below in Figure 9. The arrows in Figure 9 indicate the direction in which the potential was changed. Once the potential was raised to about +1.1 v vs. N.C.E. the electrode was felt to be covered with an oxide layer, which in the case of a rhodium electrode, could not be removed until low potentials were attained. The fact that different currents were attained at the same potential depending on whether the oxide was present, was attributed to the non-catalytic nature of the oxide surface.

iv. Products of Electrochemical Oxidation

Muller^{40 41} also showed that the products of the potential region, which includes the oscillations, and the high potential region near +1.2 v. vs. N.C.E. where the metal is covered with oxide yield the same reaction products. Namely in 10 molar HCOOH and 1 molar NaCOOH with a rhodinized platinum anode and platinum cathode at 19°C, the formic acid was electrolyzed quantitatively to carbon dioxide and hydrogen in both potential regions.

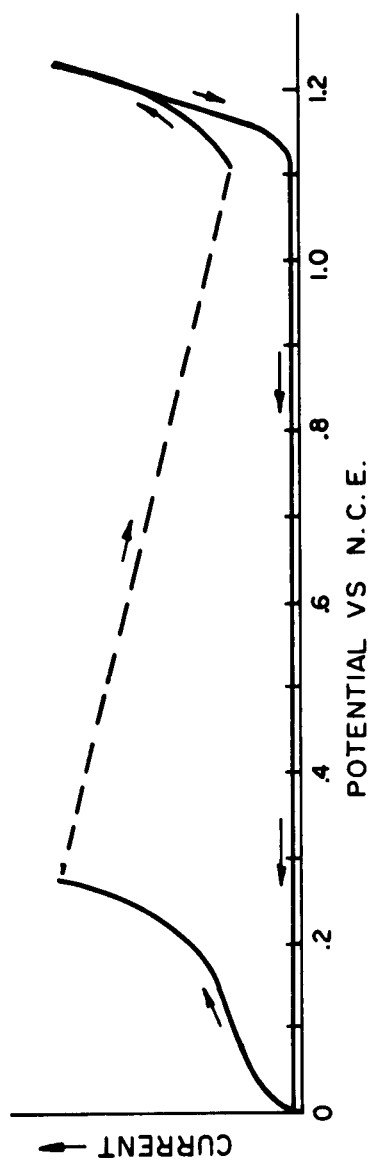


Fig. 9 Behavior of Rhodium in Formic Acid after Muller.

2. Oxide Formation on Noble Metals

Whereas the existence of oxides on noble metals had been assumed for many years, the proof of oxides on a noble metal such as platinum was not obtained until fairly recently. It was not until 1947 when Hickling²⁸ performed experiments on platinum at constant current in neutral, acid, and basic solution that the existence of oxides on platinum was on a firm basis. Hickling counted the coulombs passed in different potential stages of the oxidation. In particular, three stages were found. The first was due to adsorbed hydrogen put on the surface by an initial cathodic polarization. The second was due to the charging of the double layer. The onset of the third stage, noted by a bend in the potential time curve, occurred at the same potential which had been estimated for platinum oxide. Furthermore, Hickling calculated that the coulombs passed in the third potential stage corresponded roughly to one oxygen atom per atom of platinum on the surface.

Anson and Lingane¹ show more conclusive proof when they compared the coulombs passed not only in the anodic charging curve but also the coulombs needed to cathodically strip the oxides from the platinum. These authors also reduced the oxides by chemical means and found the same number of equivalents of oxide independent of whether the electrochemical or chemical technique was used.

Lingane³⁴ showed that platinum oxide was formed in the oxidation of oxalic acid. Lingane oxidized the oxalic acid chronopotentiometrically and found that it was necessary to subtract a constant number of coulombs from the $i \cdot t^{1/2}$ product in order to correlate the transition times obtained at different currents. This number of coulombs, Lingane found, was due to the formation of platinum oxides on the electrode.

3. Recent Work on the Electrochemical Oxidation of Formic Acid

Pavela⁴³ examined the limiting current densities of methanol, formaldehyde, and formic acid on platinized platinum in 1954. The limiting current density is the highest current density that can be supported before electrode oxidation takes place. This current density was measured by increasing an externally controlled current in steps until the voltage rose to the platinum oxide potential. No steps were taken to avoid "concentration polarization" so that it was not surprising to find that the results were "generally good to ten per cent". The appearance of concentration polarization would be most likely to occur at low concentrations on a plated electrode. Because of the galvanostatic voltage oscillations, Pavela was only able to measure the limiting current densities at concentrations below 0.5M HCOOH in 1N H₂SO₄.

The limiting current densities reported for formic acid were all obtained in 1N H₂SO₄. Pavela's results show increased performance as temperature increased from 1°C to 48°C and as concentration increased from 0.05 to 0.5M HCOOH. These trends agree with the results found by Muller³⁹ at constant voltage.

More recently, Buck, et al,^{6 to 10} have been investigating the electrochemical oxidation of methanol, formaldehyde, and formic acid on platinized platinum with the aim of ascertaining the mechanisms of these oxidations in basic, neutral, and acid solutions. These authors carried out chronopotentiometric experiments of 0.1M HCOOH in 2.5M H₂SO₄.^{8 10} It was found that the shape of the chronopotentiogram was affected by the length of time the platinized platinum electrode was left in solution between experiments. In particular, when the electrode was left in solution for ten minutes the voltage exhibited a maximum at the beginning of the chronopotentiogram. On the other hand, when the electrode was left in the solution only thirty seconds, the voltage rises slowly at first indicating the

oxidation of some species more easily oxidized than formic acid. This phenomena was explained in the following manner: "Upon standing at open circuit for short times, a material forms on the electrode which oxidizes at more negative potentials than the electrochemically active species of formic acid. At longer times, a material is formed on the electrode which oxidizes at more positive potentials than formic acid. This latter material is oxidized and removed from the electrode before the oxidation of formic acid can proceed because it effectively blocks the electrode while it is there."⁸ The transition time on platinized platinum was not noticeably different in the two cases at the same current.

Buck, et al,^{8 9 10} also used cyclic voltammetric scans of formate and formic acid to examine the electrochemical oxidation of formic acid. In this technique the voltage between the test electrode and the reference electrode is controlled so that it varies linearly with time. At the same time the current passed through the test electrode is measured on a recorder. When the potential at which an electrochemical reaction can take place is reached, the current increases. If the reactant is present in solution in only a small amount, the current will decrease due to the fact that the supply of reactant will diminish as it reacts.

The mathematical equations for cyclic voltammetry have been solved only for simple one-step reversible and irreversible processes.¹⁷ However, much useful information can be obtained by examining the current voltage traces. A multiplicity of current peaks indicate multistep processes. The height of the first current peak gives a measure of the rate of the reaction, if the reaction is irreversible.

Buck, et al,^{9 10} found that a doublet peak was in evidence in the oxidation of formic acid between pH 10 and 5M H_2SO_4 . This doublet was composed of two peaks very close together in potential. The first peak appears at about +0.5, the second at about +0.7 v vs. a H_2 electrode in the same

solution. The more negative peak predominates in the more basic solution. At pH 10 the +0.7 v peak appears just as a shoulder on the tail end of the 0.5 v peak. As the solution is made more acid, this more positive current peak grows while the more negative one decreases. In 9M H_2SO_4 no trace of the +0.5 v peak remains. Vielstich⁵² also found two peaks between +.4 and +1.0 v vs. H_2 in a cyclic voltage scan of formic acid in sulfuric acid. This doublet formation indicates either that the formic acid can be oxidized in two ways or that the process occurs in two steps.

Another current peak was observed by Buck, et al, at about +1.1 v vs. a H_2 electrode in the same solution. This peak was first noted at pH 10 and grew steadily with increasing acidity. In 9M H_2SO_4 it is the largest current peak observed. Buck, et al,⁹ interpreted this peak as an acid and platinum oxide-catalyzed oxidation of formic acid.

By comparing the height of the first current peak, it can be seen that formic acid is most easily oxidized in neutral solutions from pH 10 to pH 3.

Other investigations of the electrochemical oxidation of formic acid are being carried out by Heath, et al,²⁷ and Hael, ²⁶ et al.

D. Present Investigation

The present investigation was undertaken in order to obtain a better understanding of the mechanism of the electrochemical oxidation of formic acid on plain platinum. In particular, it was desired to gain more insight into the unusual voltage behavior exhibited by formic acid. An attempt was made to ascertain the significance of the minimum potential observed after oxide reduction and the causes for the rise of potential at open circuit after this minimum was observed, and insight about the galvanostatic voltage oscillations observed in the electrochemical oxidation of formic acid.

The mechanism of the electrochemical oxidation of formic acid was to be determined by chronopotentiometry. Unexpected results obtained by that technique, however, led us to the use of double layer capacitance measurements

by square wave current. Observations of the open circuit voltage behavior were examined as a function of pH, electrode pretreatment, and the presence of certain gases.

III. APPARTUS AND EXPERIMENTAL PROCEDURE

A. Materials Used

1. Platinum Electrodes

The platinum sheet and wire from which platinum electrodes were fabricated was 99.8% pure and obtained from the Baker Platinum Division of Englehard Industries. Electrode fabrication was carried out in the following manner. Platinum sheet 0.010 inches thick was cut into a 0.50 CM. by 1.0 CM. rectangle. A 0.008 inch diameter platinum wire was spot welded to the platinum sheet.

When an electrode was not being tested it was kept in distilled water placed in a covered beaker. Before using the electrode the following cleaning procedure was followed:

1. The electrode was placed in benzene,
2. then immersed in acetone,
3. then rinsed thoroughly in distilled water.
4. next the electrode was immersed in concentrated sulfuric acid and finally
5. rinsed again with distilled water.

This procedure was used unless otherwise noted. Once the electrode was in solution, the electrode was cleaned by brief anodic oxidation.

2. Chemicals

The chemicals used along with their manufacturer and purity are listed below.

<u>Chemical</u>	<u>Manufacturer</u>	<u>Purity</u>
Acetone	Baker	A.R.
Benzene	Fisher	C.R.
Formic Acid	Baker	A.R.
Phosphoric Acid	Baker	A.R.
Potassium Chloride	Baker	A.R.
Potassium Hydroxide	Baker	A.R.
Sodium Formate	Merck	Reagent
Sodium Nitrate	Baker	A.R.
mono-Sodium Phosphate	Baker	A.R.
di-Sodium Phosphate	Fisher	C.R.
tri-Sodium Phosphate	Fisher	C.R.
Sulphuric Acid	DuPont	Reagent

<u>Gas</u>	<u>Manufacturer</u>	<u>Purity</u>
Air	Air Company	?
Carbon Dioxide	Pure Company	?
Carbon Monoxide	Matheson	?
Nitrogen	Air Company	Prepurified

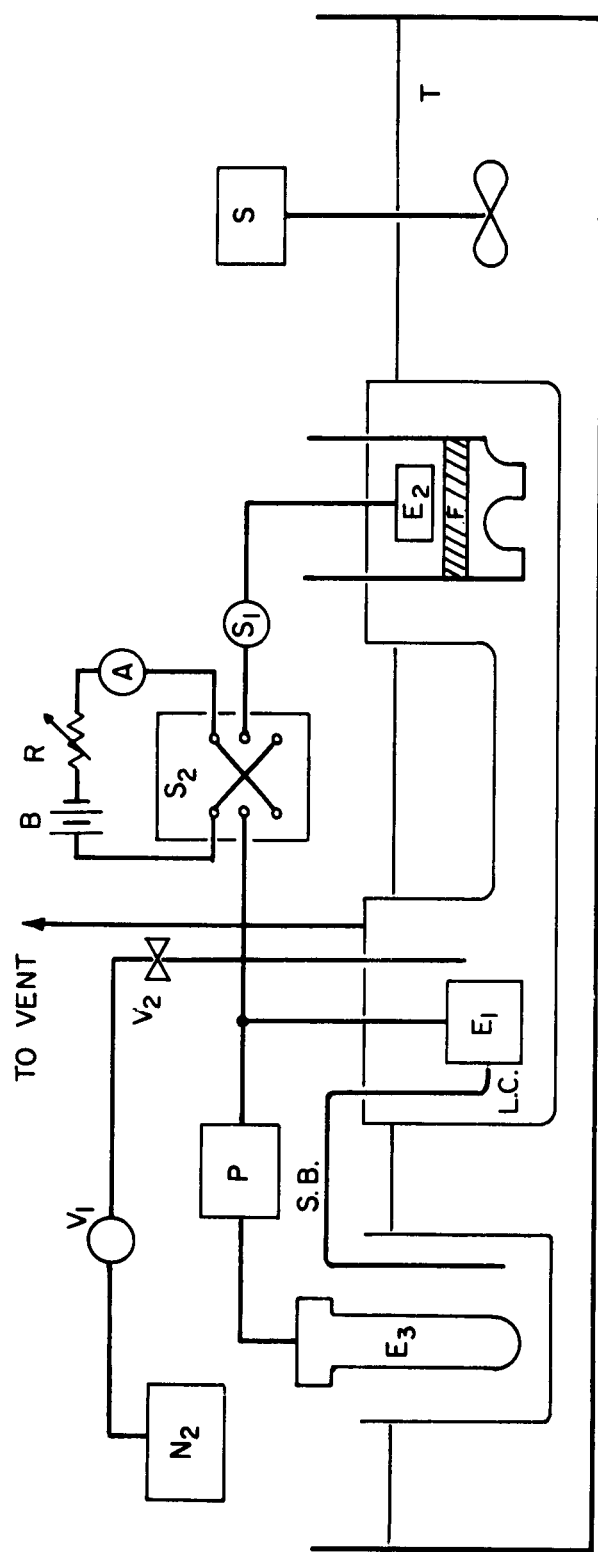
B. Apparatus

1. Chronopotentiometry

The chronopotentiometric experiments were carried out in an all glass cell. The apparatus is shown in Figure 10. Three 12 volt batteries in series with a large decade resistor were employed to maintain the current constant to within three per cent. Before a typical run, the electrode was cleaned by brief oxidation. Then nitrogen was bubbled through the solution for one minute to remove traces of oxygen and to maintain a blanket of nitrogen above the solution. This inert atmosphere was necessary since the oxidation of formic acid by dissolved oxygen is catalyzed by platinum. Such reaction would not necessarily cause a large change in the bulk concentration of the formic acid in the cell during the time of the experiments, but it might cause a concentration gradient near the surface of the electrode. A depletion of formic acid near the electrode would seriously impair the accuracy of the results by causing shortened transition times. The nitrogen bubbling also served to stir the solution and thus insure the mixing of the formic acid.

Since the technique of chronopotentiometry requires that diffusion must be the only method of transport of the reactant from the bulk solution to the electrode, at least one minute of waiting time was provided after the nitrogen was stopped. During this time the stirrer in the constant temperature bath was turned off to minimize convection currents. The whole apparatus was carefully constructed so that no vibrations could be felt on the cell even when the stirrer was on. However, it was felt that to be sure of eliminating convection currents the stirrer should be turned off before and during the actual runs.

During a run, a constant current was set by adjusting the decade resistance and read from the Weston 911 ammeter. The voltage-time behavior



- | | | | |
|----------------|---------------------------------------|----------------|---------------------------|
| A | AMMETER | R | DECADE RESISTANCE |
| B | BATTERIES | S | STIRRER |
| E ₁ | TEST ELECTRODE | S.B. | SOLUTION BRIDGE |
| E ₂ | DUMMY ELECTRODE | S ₁ | ON-OFF SWITCH |
| E ₃ | SATURATED CALOMEL REFERENCE ELECTRODE | S ₂ | CURRENT REVERSAL SWITCH |
| F | GLASS FRIT | T | CONSTANT TEMPERATURE BATH |
| L.C. | LUGGIN CAPILLARY | V ₁ | PRESSURE REGULATING VALVE |
| N ₂ | NITROGEN CYLINDER | V ₂ | CONTROL VALVE |
| P | VOLTAGE RECORDER | | |

Fig. 10 Apparatus for Chronopotentiometry.

was recorded on the Sargeant MR recorder. The current was turned off when the voltage had risen to the point where metal oxide existed on the electrode.

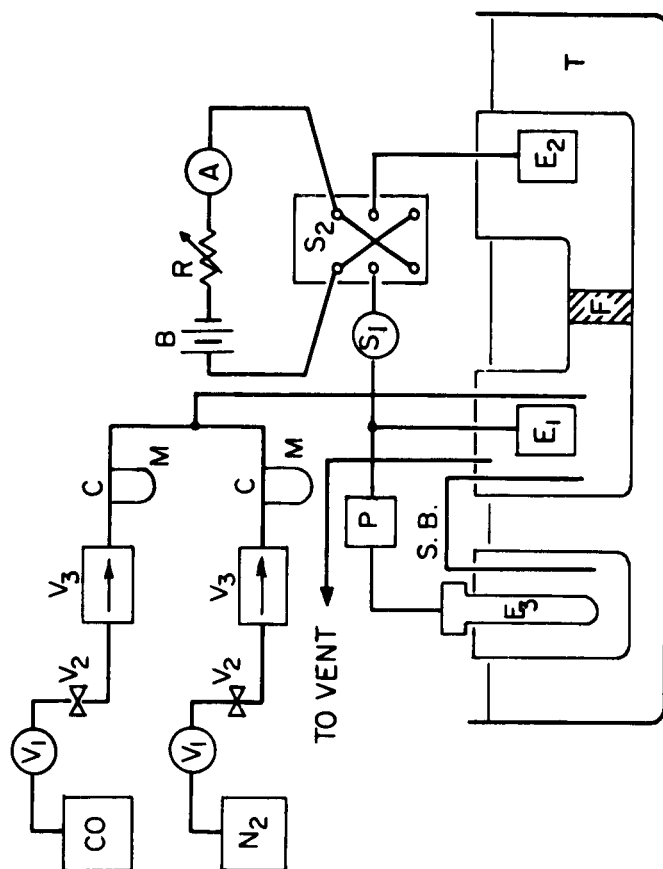
Although formic acid depolarizes noble metal oxides at the lower concentrations used in the chronopotentiometric experiments, the oxide could not be reduced in a reasonable length of time. In these cases, the current was decreased to a small value between 10 and 50 $\mu\text{A}/\text{cm}^2$, and the current reversal switch was thrown to reduce the oxides electrochemically.

Care was taken to insure that the voltage of the test-electrode did not reach that point where hydrogen would be evolved since the test-electrode became a cathode when the current was reversed. If significant amounts of hydrogen were generated near the electrode, the accuracy of the next chronopotentiogram would be in question. Thus, the voltage of the test-electrode was closely watched while the cathodic current was used and the current was turned off when the potential dropped just below the point at which the oxide was no longer stable. The application of a small cathodic current insured close control in this operation.

At this point the nitrogen was turned on and a new run was started. Although a number of runs were made in the same solution, the bulk concentration of formic acid did not change appreciably during this time (see Appendix C).

2. Minimum Open Circuit Potentials

The minimum open circuit potential at a planar platinum electrode was determined in an all glass cell having two compartments separated by a glass frit. The platinum electrode was connected to a constant current electrical network. The potential of the electrode was measured on the Sargeant MR voltage recorder against a saturated calomel electrode which was placed in a separate beaker and connected to the cell by means of a solution bridge. The experimental apparatus for determining the effect of carbon monoxide is shown in Figure 11. When only nitrogen or carbon dioxide was being bubbled through the solution, the flow rate of the gas was not



- A AMMETER
 B BATTERIES
 C CAPILLARY
 E₁ TEST ELECTRODE
 E₂ DUMMY ELECTRODE
 E₃ SATURATED CALOMEL REF. ELECTRODE
 F GLASS FRIT
 M MANOMETER
 P VOLTAGE RECORDER
 R DECADE RESISTANCE
 S₁ ON-OFF SWITCH
 S₂ CURRENT REVERSAL SWITCH
 S.B. SOLUTION BRIDGE
 T CONSTANT TEMP. BATH
 V₁ PRESSURE REGULATING VALVE
 V₂ CONTROL VALVE
 V₃ CHECK VALVE

Fig. 11 Equipment for Examining Effect on Carbon Monoxide on Minimum Potential.

metered. However, the results obtained were not sensitive to changes in flow rate as long as a steady stream of bubbles was present.

In a typical run an anodic current pulse of from 10 to 80 milliamperes per square centimeter in amplitude and less than one second in time was put through the electrode. The voltage behavior of the test electrode against the saturated calomel electrode was followed on the Sargeant MR recorder. The minimum potential after current cut off was noted.

3. Double Layer Capacitance

Double layer capacitance measurements were obtained either at constant current or at constant voltage. The square wave input type of measurement originated by Hackerman (see Introduction B4b.) was used.

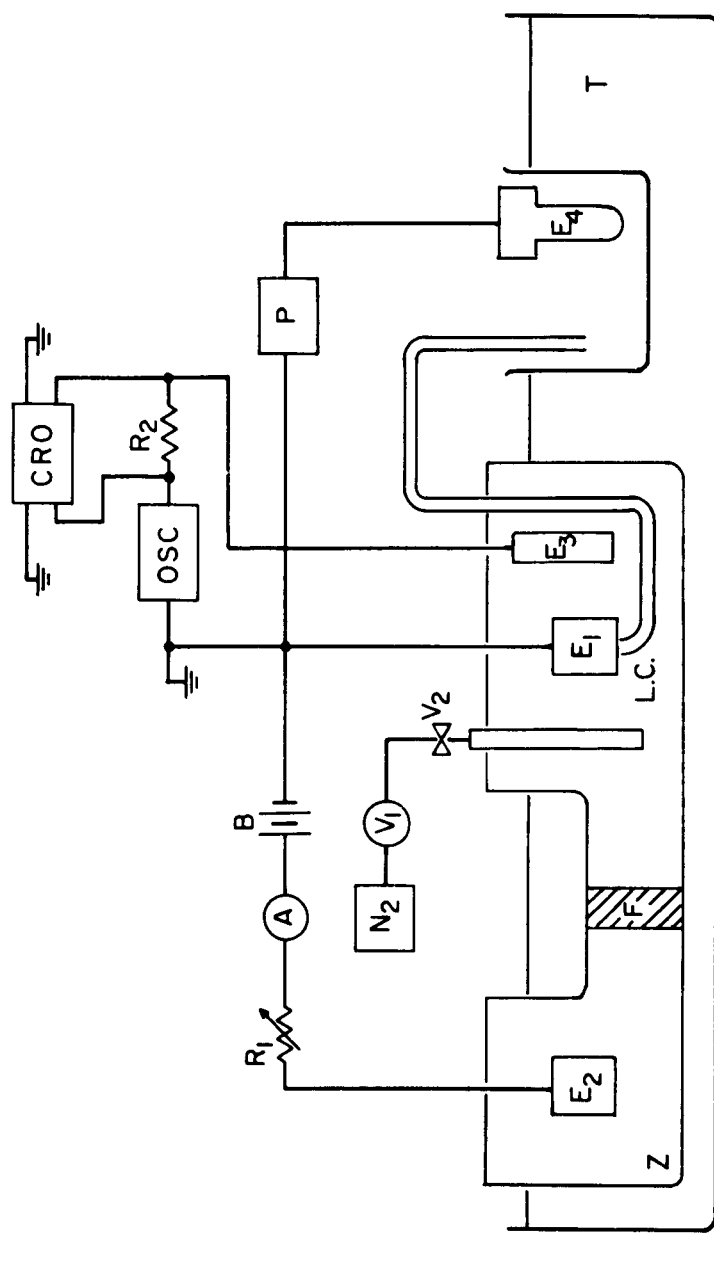
a. Constant Current

The apparatus used at constant current is shown in Figure 12. The square wave current input was obtained from a Hewlett-Packard 202A function generator (Osc. in Figure 12). Generally, frequencies of 1000 or 1200 cycles per second were used. The voltage oscillation from the generator was passed through a 10^4 ohm resistor, R_2 , and to an a.c. dummy electrode, E_3 , which was a large platinum electrode, about 8 cm² apparent area, heavily platinized.

The voltage output from the cell was displayed on a Tektronix 502 double beam oscilloscope. A Tektronix C-12 camera with a Polaroid back was used to take pictures of the output when studies were made during the rise of potential at open circuit or during oscillations.

The voltage of the test electrode was measured on the Sargeant MR recorder vs. a saturated calomel reference electrode. The voltage recorder was unaffected by the 1000 c.p.s. input to the test electrode.

The square wave current was measured by displaying the voltage drop across the 10^4 ohm resistor on one beam of the oscilloscope.



- A AMMETER
 B 36 VOLT BATTERY
 C.R.O. OSCILLOSCOPE
 E₁ TEST ELECTRODE
 E₂ DUMMY ELECTRODE (D.C.)
 E₃ PLATINIZED PLATINUM DUMMY ELECTRODE (A.C.)
 E₄ SATURATED CALOMEL REFERENCE ELECTRODE
 F GLASS FRIT
 L.C. LUGGIN CAPILLARY
 N₂ NITROGEN CYLINDER
 OSC OSCILLATOR
 P VOLTAGE RECORDER
 R₁ VARIABLE RESISTOR
 R₂ 10⁴ Ω RESISTOR
 T CONSTANT TEMPERATURE BATH
 V₁ PRESSURE REGULATOR VALVE
 V₂ CONTROL VALVE
 Z GLASS CELL

Fig. 12 Apparatus for Measuring Double Layer Capacitance at Constant Current.

Three 12 volt batteries connected in series with a large variable resistance, R_1 , afforded a constant current source between the test electrode, E_1 , and the d.c. dummy electrode, E_2 . A glass frit separated the anode compartment from the cathode, so that the hydrogen generated at the d.c. dummy would not interfere with the oxidation of formic acid.

b. Constant Voltage

The apparatus used to measure double layer capacitance at constant voltage is shown in Figure 13. In this apparatus the voltage was held constant by means of a voltage divider, R_1 , R_2 . The constancy of the voltage was verified by measuring the voltage vs. a saturated calomel electrode.

The square wave current was generated by the Hewlett-Packard 202A function generator at a frequency of 1000 c.p.s. In order to prevent the square wave current from passing to ground through the voltage divider, (R_1 see Figure 13), a 500 mH inductance was placed between the oscillator and the voltage divider. The inductance not only stopped the a.c. signal but proved to be the most noise free method of measuring the cell response to the square wave input. The square wave current was adjusted so that the cell response was always less than 10 mv.

The cell used in the controlled voltage measurements was somewhat different than that employed in the controlled current experiments. In order to insure uniform current density a platinum wire was used as a test electrode, E_1 . This wire was placed inside a cylindrical platinum wire screen dummy electrode. The dummy electrode had 90 times the area of the platinum wire.

All experiments at constant potential were carried out in the following manner. The potential was raised to a point where oxides existed on the platinum wire, 1.7 v vs. S.C.E. in 1N H_2SO_4 , and held there for 60 seconds.

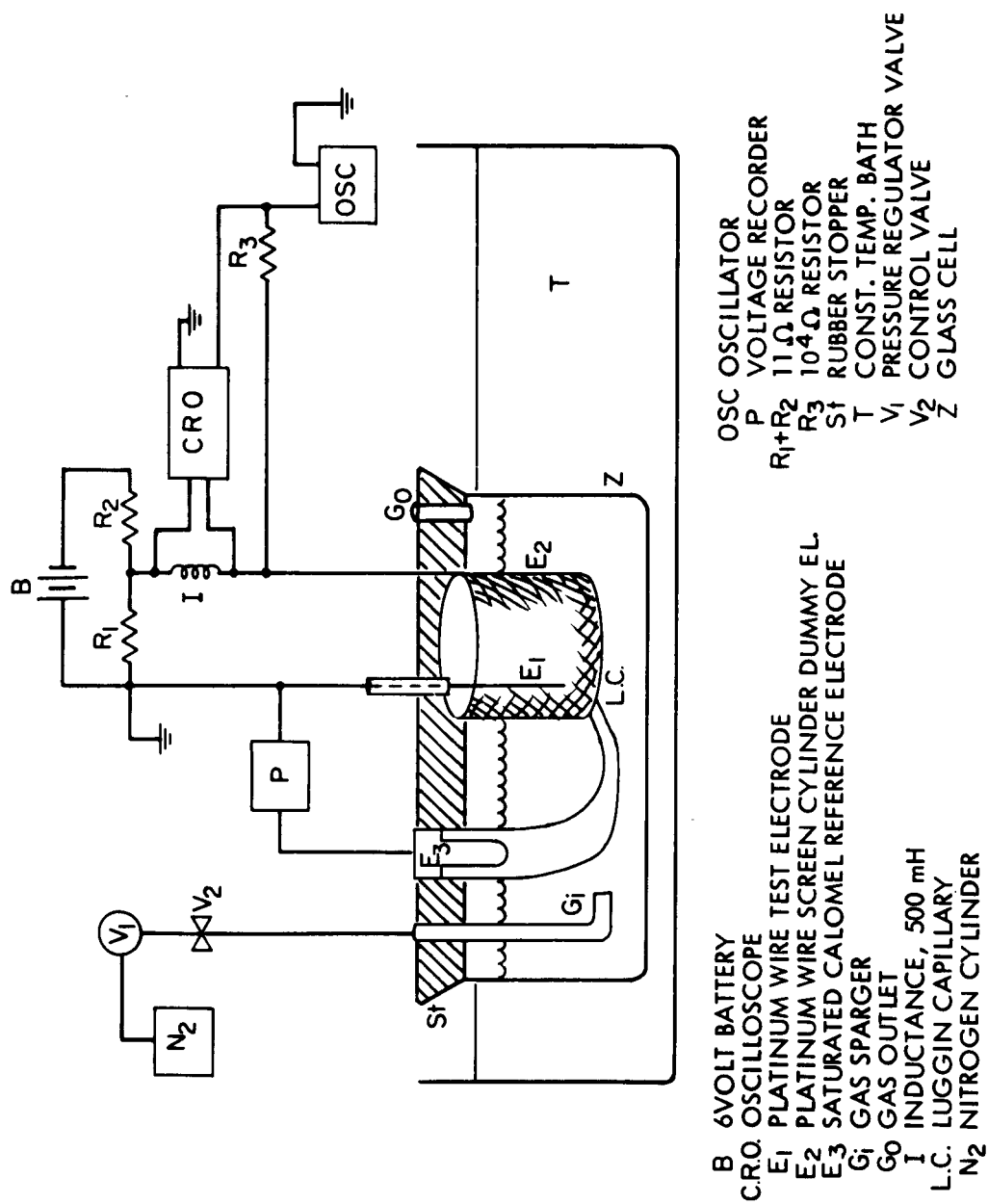


Fig. 13 Apparatus for Measuring Double Layer Capacitance at Constant Potential.

Then open circuit was established and the potential rapidly dropped to the minimum potential. After about 10 seconds the potential was set. Capacitance measurements were read from the oscilloscope. The capacitance changed with time at first, but became constant within fifteen minutes. However, twenty minutes was taken on each run to be sure that the capacitance was at a constant value. The steady state capacitance and the fixed voltage were then recorded.

Nitrogen was bubbled through the solution at all times to prevent diffusion from becoming a determining factor in the capacitance-potential data.

c. Establishment of the Ideally Polarized Electrode

The success of measuring the double layer capacitance was entirely dependent on the ability to establish or approximate an ideally polarizable electrode (see Introduction B4a.). The square wave current technique allows the experimenter to estimate when this condition is fulfilled. If the cell voltage response is curved (see Figure 5) then the electrode is not ideally polarized. However, it is a problem to determine when the slope of the cell voltage response corresponds to a straight line.

In order to check whether a typical case at constant current was "ideally polarized" the following test was made. In a double layer measurement where no curvature in the ramp portion of the a.c. cell voltage response was detected, a sine wave current input at the same frequency was put on the electrode. The voltage response of the cell was presented on the ordinate of the oscilloscope screen and the voltage drop across a large known resistance was presented on the abscissa. The latter voltage drop was directly proportional to the sine wave current.

The presentation on the oscilloscope is a Lissajous figure and the impedance and phase angle of the cell circuit can be simply computed as follows:

$$i = i^{\circ} \sin \omega t \quad (78)$$

$$v = v^{\circ} \sin (\omega t + \phi) \quad (79)$$

$$v = v^{\circ} \sin (\omega t + \phi) = v^{\circ} [\sin \omega t \cos \phi + \cos \omega t \sin \phi] \quad (80)$$

$$\sin \omega t = i/i^{\circ} \quad (81)$$

$$\sin^2 \omega t + \cos^2 \omega t = 1 \quad (82)$$

$$\cos \omega t = \sqrt{1 - (i/i^{\circ})^2} \quad (83)$$

$$v = v^{\circ} [i/i^{\circ} \cos \phi + \sqrt{1 - (i/i^{\circ})^2} \sin \phi] \quad (84)$$

When $i = 0$

$$\frac{v_{i=0}}{v^{\circ}} = \sin \phi \quad (85)$$

Or by similar analysis

$$\frac{i_{v=0}}{i^{\circ}} = \sin \phi \quad (86)$$

where v represents the a.c. voltage component.

The trace appeared as in Figure 14. From measurements of V° and i° the impedance, Z , could easily be calculated

$$\frac{V^{\circ}}{I^{\circ}} = Z \quad (87)$$

By assuming a series circuit

$$R_s = Z \cos \phi \quad (88)$$

and

$$C = \frac{1}{\omega Z \sin \phi} \quad (89)$$

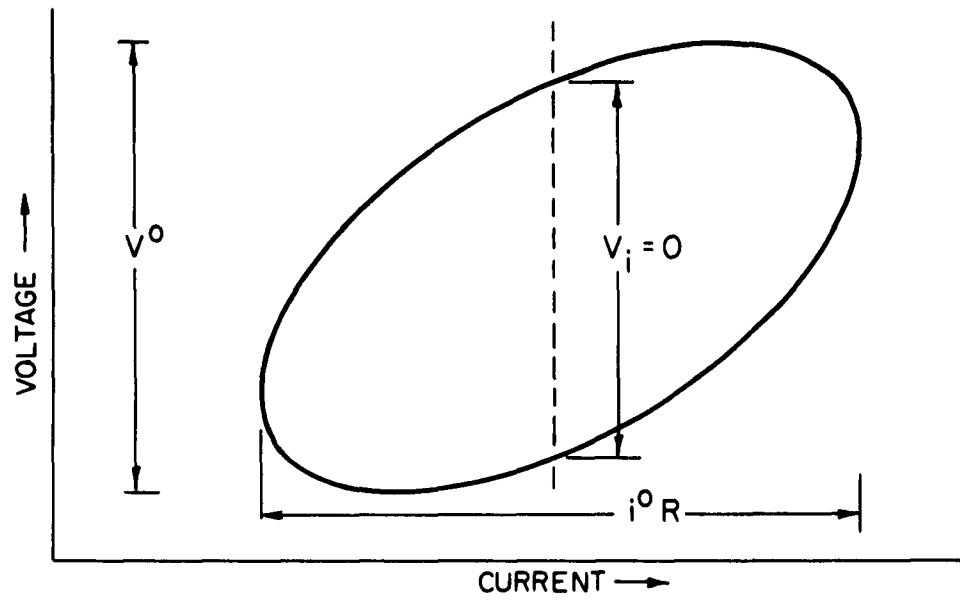


Fig. 14 Oscilloscope Trace.

When this was done, the resistance, R_g , was found to be equal to the solution resistance calculated from the step of the square wave current response and the capacitance was found to be equal to the capacitance calculated from the ramp of the square wave current response. Thus, justifying the assumption that $R_p = \infty$, and that the electrode was "ideally polarized".

Since it might be argued that some charging of the double layer occurs because of the rise time of the square wave, measurements of the rise time were taken. The rise time of the square wave was 13μ sec., but when the initial rise of the square wave across the large resistor set on one beam of the oscilloscope was compared to the initial rise of the step of the output voltage traced on the second beam by adjusting the individual voltage scale factors, no difference could be seen at 2.5μ sec/cm.

IV. RESULTS AND DISCUSSION

A. Chronopotentiometry on Smooth Platinum Electrodes

1. Dependence of Transition Time on Pretreatment

Since other investigators^{8 31} had found that formic acid oxidation proceeded most easily in neutral solutions, chronopotentiometry on plain platinum in NaH_2PO_4 solution was attempted. A solution of $2.50 \times 10^{-2}\text{M}$ HCOOH and 1.33M NaH_2PO_4 was prepared and the temperature held at 26.1°C .

Under these conditions three different pretreatment operations were applied to the electrode. In the first case, the electrode was oxidized at the oxide potential at 2.0 milliamperes for 25 seconds, the oxide was reduced by reversing the current, then nitrogen was bubbled through the solution for 60 seconds. After this the nitrogen was turned off and the solution allowed to equilibrate for 60 seconds before the current was turned on.

In the second case, the pre-oxidation and current reversal steps were eliminated, the oxide formed during the last chronopotentiometric run being reduced by the formic acid itself. After oxide reduction the nitrogen bubbling was continued for 60 seconds and the solution allowed to equilibrate 60 seconds as in Case I. When the oxide reduction was carried out by the formic acid itself, the potential dropped to very low values and then slowly rose. This potential rise was rapid when nitrogen was being bubbled, but much slower when the nitrogen was turned off. Because of this potential rise (see Introduction A2.), it was felt that some species was being adsorbed on the surface. Thus, in the third case nitrogen was bubbled only until the oxide was reduced. Then only 15 seconds was allowed for the solution to equilibrate, longer times causing the potential to rise. The results for these three cases are shown in Table II.

TABLE II

Results of Chronopotentiometry on Plain Platinum for
Different Electrode Pretreatment

Case I

Run	Vo.c. v. vs. S.C.E.	$V_t = 0$	i ma.	τ sec.
20-C-3	-.243	+.213	5.60	12.8
20-C-5	-.243	+.217	5.60	12.0
20-C-7	-.232	+.223	5.60	11.3
20-C-8	-.245	+.218	5.60	12.3

Case II

20-C-9	-.240	+.200	5.60	16.9
20-C-10	-.239	+.183	5.60	18.3
20-C-11	-.226	+.175	5.60	19.0
20-C-12	-.234	+.196	5.60	18.3
20-C-13	-.239	+.194	5.60	18.7

Case III

22-C-1	-.433	+.050	5.60	22.5
22-C-2	-.440	+.010	5.60	22.2
22-C-20	-.441		5.60	21.6
22-C-21	-.441		5.60	21.3

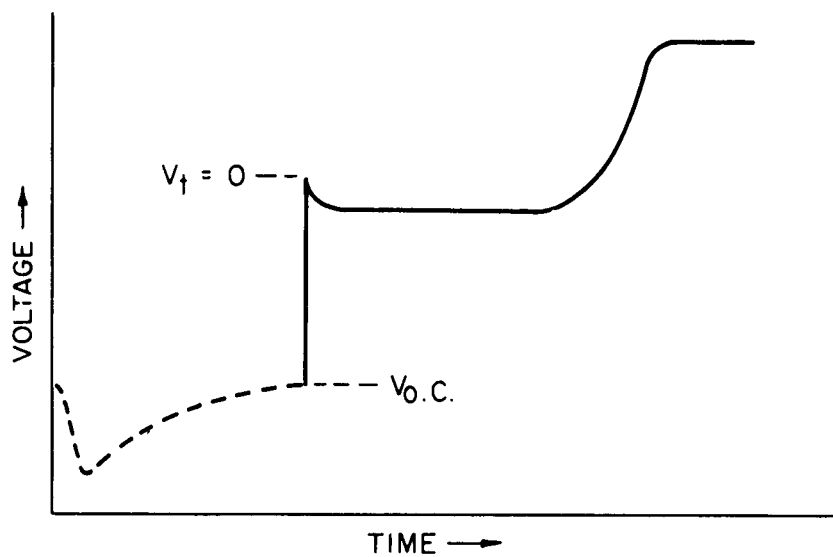
TABLE II (Continued)

Average Values

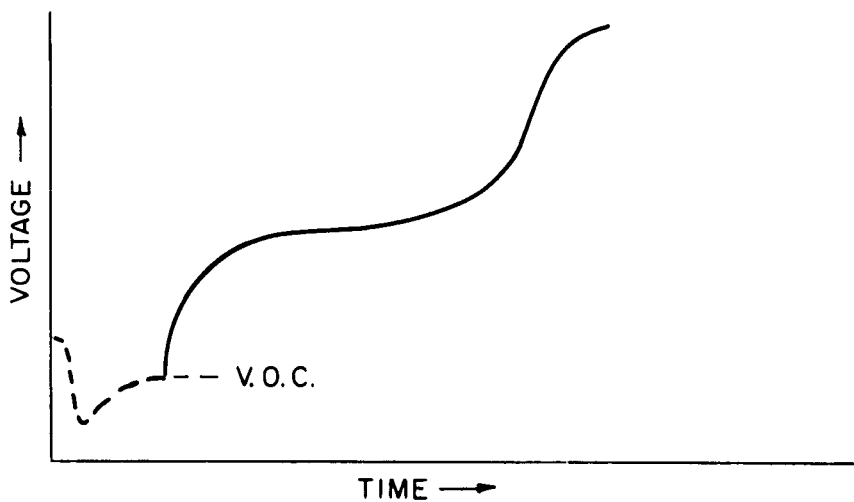
Run	Vo.c. v. vs. S.C.E. ^t	$V_t = 0$	i ma.	τ sec.
Case I	-.241	+.218	5.60	12.1
Case II	-.236	+.190	5.60	18.2
Case III	-.441	+.030	5.60	21.7

Vo.c. is voltage just before current turned on.

$V_t = 0$ is voltage just after current turned on.



(a) VOLTAGE-TIME CURVE FOR CASE I AND CASE II



(b) VOLTAGE-TIME CURVE FOR CASE III

Fig. 15 Voltage-Time Curve as a Function of Pretreatment.

Not only the transition time but also the shape of the voltage-time curve was a function of the pretreatment. With Case I and Case II a maximum was observed initially as is shown in Figure 15a. In Case III the maximum has virtually disappeared. The shape of the voltage time curve for Case III is shown in Figure 15b.

If the transition time were seen to increase with increasing time between experiments, the explanation would be straightforward. Adsorption of a reactive species presumably would be taking place. However, since the transition time was decreasing with increasing time between experiments, this could not be the case. In order to account for this phenomena, three possibilities were considered. First, dissolved oxygen in the solution could be reacting with the formic acid. If this reaction were catalyzed by the platinum electrode, the concentration of formic acid near the electrode would be reduced. This would result in shorter transition times. Furthermore, the longer the time between runs, the more the concentration of formic acid would be reduced and the shorter the transition time would become.

The second possibility considered was that an impurity present in the solution was being adsorbed on the platinum electrode. It had been observed by Gierst and Juliard²⁰ that transition times decrease markedly when a strongly adsorbable substance was present in solution. This effect was observed with very low concentrations of gelatin. This was accounted for by assuming that the adsorption of gelatin on the electrode decreases the effective area of the electrode. If this impurity were difficult to oxidize, a similar effect should be noted.

The third possibility was that a blocking agent might be formed from the chemical decomposition of the formic acid itself.

In order to clarify the situation, further experiments were undertaken.

2. Highly Purified System

In order to determine whether the phenomena of decreasing transition time was due to impurities in the system which were being adsorbed on the electrode, a highly purified solution was prepared. A liter of solution of 1.33M NaH_2PO_4 was pre-electrolyzed for 24 hours at over 25 ma. and then boiled to remove dissolved H_2 and O_2 . Part of this solution was added to 20 ml. of a 0.25M NaCOOH solution made from recrystallized sodium formate and distilled de-ionized water. The total volume prepared was 250 ml., so the molarity of the formate was 2.0×10^{-2} . All glassware was washed in chromic acid cleaning solution and thoroughly rinsed in distilled de-ionized water.

To avoid chloride contamination, a glass electrode was used for a reference electrode. The potential difference was read on a Beckman Zero-matic pH Meter. Although the output from this instrument can be read out on a recorder, trouble with noise was experienced in attempting to hook up the Sargeant MR recorder. Thus, all that was measured in the following runs was the open circuit potentials and transition times.

In the following set of runs no pre-oxidation was used other than the small amount of oxide formed at the electrode at the end of the chronopotentiometry experiments. The same phenomena were observed in the highly purified system that were observed in the system of normal purification. After reduction of the oxide by formic acid the potential of the platinum anode dropped to very low values and rose with nitrogen bubbling. The transition time was a function of the time between runs. These results are shown in Table III.

The results for one minute of nitrogen bubbling and one minute of waiting yield an $(i, \tau^{1/2}/C)$ product near 520 ma. sec.^{1/2} l./m. A reactant undergoing a two electron process with a diffusivity of $10^{-5} \text{ cm}^2/\text{sec.}$ would yield an $(i, \tau^{1/2}/C)$ product of 540 ma. sec.^{1/2} l./m. Thus, the transition time at low time between runs is the transition time that is expected.

TABLE III

Results of Chronopotentiometric Experiments in the
Highly Purified System at 26.1°C

Run	Vo.c. vs. glass electrode	i ma/cm ²	τ sec.	N ₂ on min.	N ₂ off min.
33-C-6	-.387	4.00	14.8	0	16
33-C-7	-.420	4.00	14.1	4	1
33-C-9	-.382	4.00	25.9	1	1
33-C-10	-.371	4.00	26.3	1	1
33-C-11	-.369	4.00	26.4	1	1
33-C-12	-.370	4.00	26.0	1	1
33-C-13	-.370	4.00	26.3	1	1

TABLE IV

Results of Experiments in Highly Purified System with
Air Bubbling at One Current Density Run

Run	Vo.c. vs. glass electrode	i ma/cm ²	τ sec.	Air on min.	Air off min.
35-C-49	-.411	4.00	23.2	1	1
35-C-50	-.413	4.00	24.6	1	1
35-C-51	-.409	4.00	24.2	1	1
35-C-52	-.411	4.00	23.8	1	1
35-C-62	-.380	4.00	15.6	4	1

It was felt that minute traces of dissolved oxygen might be causing this phenomena, so air was bubbled through the solution instead of nitrogen. The same general trend was noted in the case of air bubbling. This is shown in Table IV.

Furthermore, the values of the $(i \tau^{1/2})$ product at different current densities were virtually identical between the two cases, indicating that the dissolved oxygen cannot be an important factor in the shortened transition times observed with increasing time between runs. These data are shown in Table V.

It is seen in Table V that the values for the air-bubbling were slightly lower than those for nitrogen bubbling. This is probably due to a reaction between the dissolved oxygen and the formic acid which is catalyzed by the platinum electrode. The decomposition of the formic acid by this chemical oxidation would decrease the formic acid concentration near the electrode slightly and, hence, the transition time would be decreased. However, the facts that the dependence of transition time on pretreatment was so similar in the two cases and the magnitude of the change in transition time was so small when air was substituted for nitrogen, indicate that dissolved oxygen cannot be playing an important role in this phenomena. Thus, platinum catalyzed oxidation of formic acid by dissolved oxygen could not cause the decrease in transition time. The one remaining possibility was that something was being formed by the formic acid itself that was being strongly adsorbed on the platinum electrode and inhibiting reaction.

3. Study of Dependence of Transition Time on Pretreatment in Neutral Solution

A number of runs were made on a plain platinum electrode at 35°C in a solution of 0.0100M HCOOH, 0.100 Na₂HPO₄, at a current of 0.620 ma. The electrode was about 1 cm² apparent area. In these runs, the electrode was left at the oxide potential for a time θ with the current on. Then the

current was reversed until a potential below the oxide reduction potential but above the hydrogen potential was reached. After this, the electrode was left in the solution for a time, T , where no current was passing. After the time, T , anodic current was started and a transition time, τ , was measured. This is shown schematically in Figure 16.

During a set of runs θ and T were held constant until an asymptotic value of τ was approached. Then either θ or T was changed and another set was run. The asymptotic values of $(i\tau^{1/2}/C)$ are shown below in Table VI.

The trends in Table VI were evident in the trend in $(i\tau^{1/2}/C)$ when T was changed at constant θ in a set of runs. When T was increased, τ would decrease in the set, whereas when T was decreased, τ would increase. This is shown in Table VII. The summary of all of this data is shown in Appendix D.

4. pH Effects

In a more acidic solution the effect of the dependence of the time between runs was even more marked. In a solution composed of 0.226N NaNO_3 , 3.52×10^{-2} H_2SO_4 , and 1.78×10^{-2} NaCOOH the results in Table VIII were obtained on a plain platinum electrode of about 1 cm^2 at 26.3°C .

The experiments of chronopotentiometry on plain platinum electrodes showed that the transition time was a function of the length of time that the electrode was left in solution between experiments. While the electrode was left in the solution undisturbed at open circuit, there was a rise in the open circuit potential from a minimum value. In order to further investigate this phenomena, three courses of action were taken:

1. The value of the minimum potential was to be observed as a function of pH and of N_2 , CO_2 and CO .
2. The shape of the potential-time curve at open circuit was examined.

TABLE V

Results of Chronopotentiometry on Plain Platinum
in a Highly Purified System

Case I: N₂ bubbled 1 minute, off 1 minute

Run	i° ma/cm ²	τ sec.	Run	i° ma/cm ²	τ sec.
33-C-9	4.00	25.9	34-C-24	2.86	58.9
33-C-10	4.00	26.3	34-C-25	2.86	58.7
33-C-11	4.00	26.4	34-C-26	2.86	59.0
33-C-12	4.00	26.0	34-C-27	2.50	78.6
33-C-13	4.00	26.3	34-C-28	2.50	84.9
33-C-14	3.34	40.3	34-C-29	2.50	80.1
33-C-18	3.34	37.6	34-C-30	2.50	81.9
34-C-19	3.34	38.2			
34-C-20	3.34	38.1			
34-C-21	3.34	38.4			
34-C-22	3.34	38.6			
34-C-23	3.34	38.7			

Case II: Air bubbled 1 minute, off 1 minute

34-C-34	2.50	66.7	35-C-48	2.50	70.6
34-C-35	2.50	68.5	35-C-49	4.00	23.2
34-C-36	2.50	67.8	35-C-50	4.00	24.6
34-C-37	2.86	50.5	35-C-51	4.00	24.2
34-C-38	2.86	51.8	35-C-52	4.00	23.8
34-C-39	2.86	51.9	35-C-53	4.40	16.9
34-C-40	2.86	58.4	35-C-54	4.40	18.6
34-C-41	2.86	54.1	35-C-55	4.40	19.6

TABLE V (Continued)

Run	i° ma/cm ²	τ sec.	Run	i° ma/cm ²	τ sec.
34-C-42	3.34	36.0	35-C-56	4.40	18.6
34-C-43	3.34	36.1	35-C-57	2.66	61.2
34-C-44	3.34	38.1	35-C-58	2.50	70.9
34-C-45	3.34	37.9	35-C-60	2.50	65.0
34-C-46	3.34	36.9	35-C-61	2.50	65.2
34-C-47	3.34	39.8			

Average Values

i° ma/cm ²	τ sec.		$i^{\circ}\tau^{1/2}$ ma-sec ^{1/2} /cm ²	
	N ₂	Air	N ₂	Air
2.50	75.1	68.6	21.7	20.7
2.86	58.9	53.3	21.9	20.9
3.34	38.6	37.8	20.8	20.6
4.00	26.2	24.0	20.4	19.6
4.40		18.4		18.9

TABLE VI

Asymptotic Values of $(i\tau^{1/2}/C)$ in $(ma\text{-sec}^{1/2}/m/e)$

		9	
		15 sec.	50 sec.
T	90 sec.	350	395
	180 sec.	270	360
	360 sec.	100	120
	90 sec.	345	340

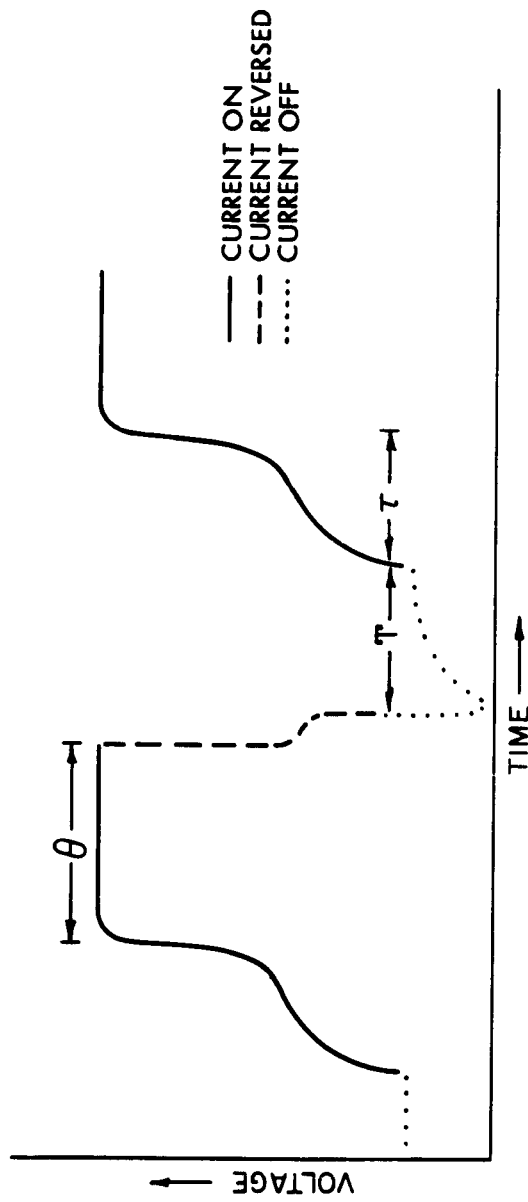


Fig. 16 Definition of θ and T .

TABLE VII

Effect of Changing T on Subsequent Set of Runs

Q = 15 sec.

Run	T changed from 15 sec. to 90 sec. $1 \tau^{1/2}/C$	Run	T changed from 90 sec. to 15 sec. $1 \tau^{1/2}/C$
32-X-28	185	32-X-33	236
32-X-29	135	32-X-34	271
32-X-30	106	32-X-35	281
32-X-31	100	32-X-36	295

TABLE VIII

Effect of Pretreatment in Acid Solution

Run	i ma	τ sec.	N ₂ on	N ₂ off
56-B-6	0.216	26.1	60	60
56-B-7	0.216	21.1	60	60
56-B-11	0.216	24.0	60	60
56-B-12	0.216	28.8	60	60
56-B-13	0.216	21.6	60	60
56-B-19	0.216	158	0	3
56-B-20	0.216	159	0	3
56-B-21	0.216	161	0	3
56-B-22	0.216	157	0	3

3. The double layer capacitance of the electrode was determined at a given voltage as a function of electrode pretreatment under conditions where diffusion was not important.

B. Minimum Potential at Open Circuit

In order to determine what was causing the drop in potential to low values after oxide reduction by formic acid, a series of experiments were performed at 1.0M HCOOH on a plain platinum electrode of about 1.0 cm² apparent area. The pH of the solutions used was varied by the use of phosphate buffers and measured by the Beckman Zeromatic pH Meter. The temperature was held constant at 35.0°C. All voltages were measured vs. a saturated calomel electrode.

The minimum potential was attained by passing a short pulse of anodic current. The pulse was less than one second duration and the current was varied from 10 to 80 milliamperes. The minimum potential was measured after current cut off.

At first, nitrogen was bubbled through the solutions for about twenty minutes before the minimum potentials were obtained. No gas was bubbled through the solution during or after the current pulse. The results obtained under these conditions are shown in Table IX. In Table IX, E_{max}. represents the highest minimum potential obtained, E_{min}. the lowest minimum potential, and E_{ave}. the average value. N signifies the number of minimum potentials taken and the Runs column indicates the run series number. The detailed data can be found in Appendix D, where the data are arranged by run series number.

The solutions were made up in the following manner:

pH

5M H_2SO_4	1M HCOOH	5M H_2SO_4
0.68	1M HCOOH	1M H_3PO_4
2.61	1M HCOOH	1M NaH_2PO_4
3.03	1M HCOOH	adjusted with H_3PO_4 and Na_2HPO_4
3.50	1M HCOOH	adjusted with NaH_2PO_4 and Na_2HPO_4
4.39	1M HCOOH	1M Na_2HPO_4
5.72	1M HCOOH	0.5M Na_3PO_4
11.32	1M HCOOH	adjusted with KOH

It can be seen from Table IX that the average values of the minimum potential vary irregularly with pH when no gas was bubbled during and after the current pulse.

1. Effect of Nitrogen Bubbling

When nitrogen was bubbled through the solution during and after the current pulse, the minimum potential became significantly lower and varied regularly with pH. These results are shown in Table X.

From the data at pH 0.68, 2.61, 4.39, and 5.72 in Table X, it can be seen that the current density of the pulse had no apparent effect on the well potential within the limits of error when nitrogen was bubbled through the solution. Furthermore, varying the rate of bubbling had no effect as long as a steady stream of bubbles was present.

Since nitrogen is an inert gas, it cannot be expected to exert any direct effect on the well potential. However, two possible indirect effects are possible. One is that the bubbling of nitrogen causes increased mass transfer of formic acid to the electrode by stirring the solution. If the minimum potential is due to the formic acid in the solution or a product of

TABLE IX

Minimum Potentials in Formic Acid: No Gas Bubbled

pH	E _{max}	E _{ave} v. vs. S.C.E.	E _{min}	N	Runs	$\frac{i}{ma/cm^2}$
0.68	-.103	-.129	-.160	14	64-X	28-30
2.61						
3.03	-.282	-.302	-.321	20	63-X	40-45
3.50	-.283	-.290	-.307	11	62-X	62-67
4.39	-.334	-.355	-.377	20	58-X	10
5.72	-.340	-.347	-.353	5	59-X	70-80
11.32	-.679	-.694	-.703	6	61-X	75-85

TABLE X

Minimum Potentials in Formic Acid: Nitrogen Bubbled

pH	E _{max}	E _{ave} v. vs. S.C.E.	E _{min}	N ^b	Runs	$\frac{i}{ma/cm^2}$
SM H ₂ SO ₄	+.039	+.035	+.030	5	65-X	45-50
0.68	-.150	-.166	-.193	8	68-X	11
0.68	-.150	-.161	-.165	6	64-X	28-30
2.61	-.350	-.357	-.365	12	69-X	20
2.61	-.331	-.350	-.359	14	60-X	44-49
3.03	-.377	-.383	-.390	13	63-X	40-45
3.50	-.409	-.420	-.444	17	62-X	62-67
4.39	-.464	-.467	-.470	8	87-D	10
4.39	-.468	-.473	-.479	11	58-X	70
5.72	-.525	-.533	-.540	10	71-X	11
5.72	-.537	-.543	-.550	13	59-X	70-80
11.32	-.750	-.750	-.750	6	61-X	75-85

formic acid decomposition then the depth of the well potential would depend on the concentration of the formic acid at the electrode. The current pulse destroys the blocking agent but a certain amount of formic acid is oxidized. This amount of formic acid will depend on the current density and amount of coulombs in the current pulse. Thus, when the solution is not stirred the concentration of formic acid, and hence the well potential will be a function of the current and time of the current pulse. This accounts for the irregularity of the variation of well potential with pH when no nitrogen was bubbled since different current densities were used in these experiments. However, when nitrogen was bubbled, the minimum potential did not seem to depend on either current density or bubbling rate.

2. Effect of Carbon Dioxide Bubbling

The second possibility is that carbon dioxide formed during oxidation is adsorbed and is slow to diffuse away from the electrode. Bubbling nitrogen decreases the partial pressure of carbon dioxide near the electrode and hence speeds the removal of CO_2 . This latter possibility was investigated by bubbling CO_2 instead of nitrogen through the solution. The results, shown in Table XI, are not significantly different than those obtained when nitrogen was bubbled (see Table X). Thus, it can be concluded that carbon dioxide does not play an important role in the minimum potential. The important effect of gas bubbling is that of increased mass transfer.

3. Effect of pH

The question now arises as to what species is responsible for the well potential. The average well potential observed when nitrogen or carbon dioxide was bubbled is plotted against pH in Figure 17. Also shown in Figure 17 are the potentials for formic acid and hydrogen. The formic acid potential was calculated assuming a partial pressure of carbon dioxide equal to one atmosphere. The values for the hydrogen potential were calculated assuming hydrogen gas at one atmosphere.

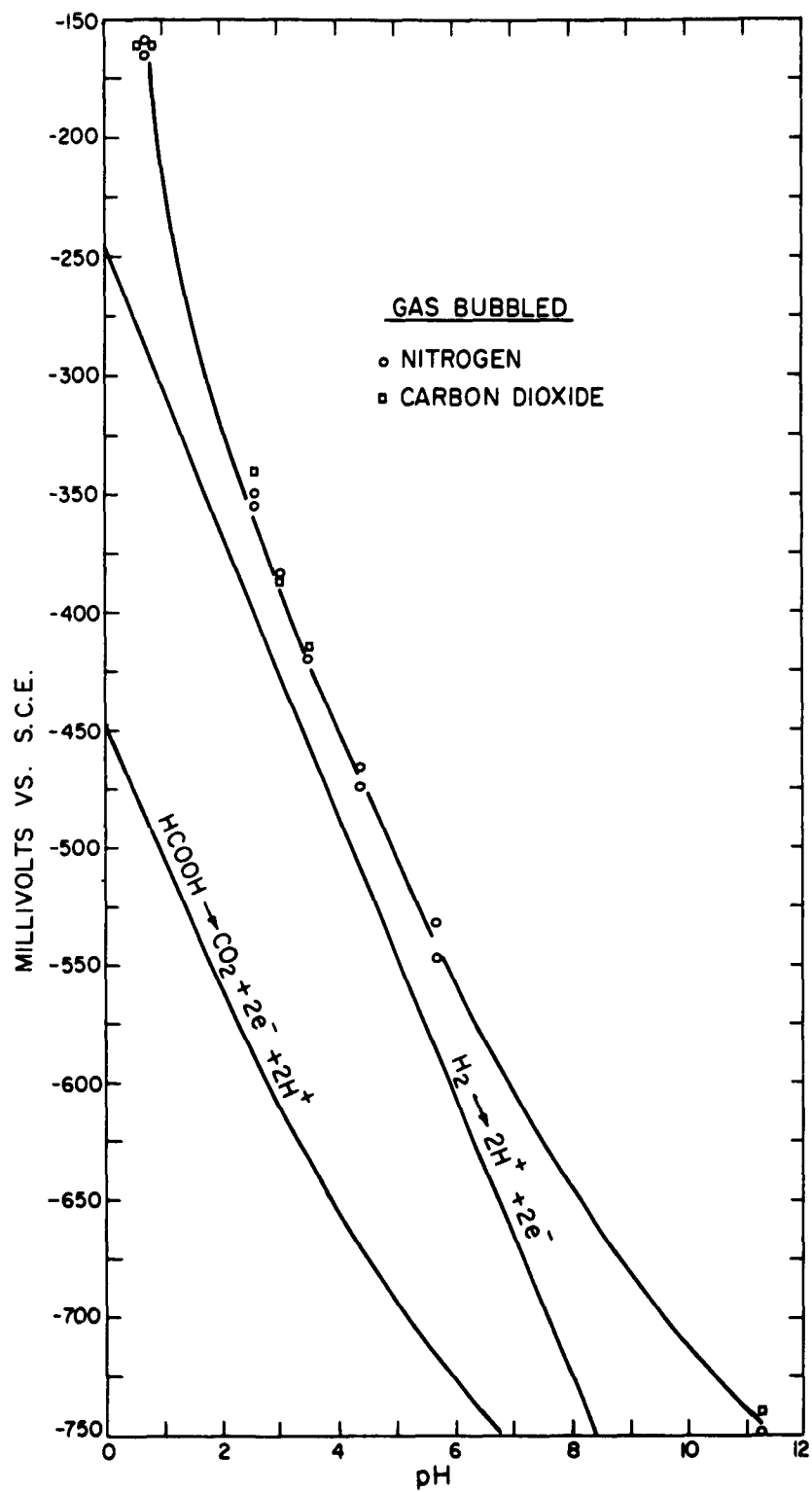


Fig. 17 Average Minimum Open Circuit Potentials as a Function of pH.

TABLE XI

Minimum Potentials in Formic Acid: Carbon Dioxide Bubbled

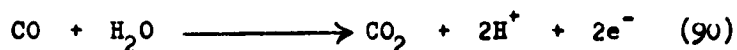
pH	E _{max}	E _{ave} v. vs. S.C.E.	E _{min}	N	Runs	¹ ma/cm ²
0.68	-.152	-.158	-.162	3	64-X	28-30
2.61	-.315	-.341	-.352	16	60-X	44-49
3.03	-.378	-.386	-.392	13	63-X	40-45
3.50	-.410	-.414	-.420	7	62-X	62-67
4.39						
5.72						
11.32	-.735	-.739	-.750	8	61-X	75-85

It can be seen from Figure 17 that the voltages of the minimum potential approach the calculated hydrogen potential at intermediate values of pH and tend to bend away from the hydrogen potential at extremely low values of pH. Under no circumstances does a value of the minimum potential approach the theoretical value for the formic acid potential. Thus, the minimum potential is probably due to the formation of hydrogen on the electrode from formic acid.

In strongly acid solution, two complications occur. First of all, formic acid is known to be highly associated by hydrogen bonding in acid solutions.¹² Secondly, carbon monoxide is produced by the decomposition of formic acid in acidic solutions. This reaction has been shown to be an acid catalyzed reaction.⁴⁹

4. Effect of Carbon Monoxide

Since carbon monoxide might be present because of formic acid decomposition, carbon monoxide was bubbled through the solutions of formic acid at various pH values in order to determine its effect on the minimum potential. In these experiments nitrogen was first bubbled through a solution of formic acid at a certain pH and minimum potentials were determined. Then carbon monoxide was introduced along with the nitrogen and more minimum potentials were taken. The results are tabulated in Table XII along with the percentage of carbon monoxide in the gas stream fed to the cell. These results show that carbon monoxide seems to lower the potential at the minimum. This effect may be due to the establishment of a mixed potential of the reaction involving carbon monoxide



and the reaction

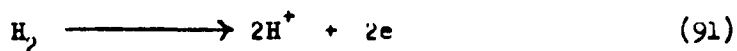


TABLE XII

Effect of Presence of Carbon Monoxide on Minimum Potential

pH	% CO	E _{max}	E _{ave}	E _{min}	N
0.68	0	-.150	-.166	-.193	8
	25.6	-.241	-.248	-.251	4
	61.5	-.259	-.262	-.270	8
	100%	-.281	-.282	-.285	6
2.61	0	-.350	-.357	-.365	12
	37.5%	-.355	-.362	-.369	8
	52.4%	-.365	-.371	-.376	7
	68.7%	-.375	-.378	-.381	6
	100%	-.377	-.388	-.393	11
5.72	0	-.525	-.533	-.540	10
	19.3%	-.560	-.566	-.574	17
	100%	-.542	-.574	-.625	18
4.39	0	-.464	-.467	-.470	5
	100%	-.480	-.492	-.505	10

which is due to hydrogen present from formic acid decomposition. The carbon monoxide potential, equation (90), is shown on Figure 18 along with the results of pure carbon monoxide bubbling. It can be seen from Figure 18 that the carbon monoxide potential is lower than the hydrogen potential and hence a mixed potential would be lower. However, none of the observed minimum potentials for carbon monoxide bubbling are lower than the calculated hydrogen potential. Furthermore, Havel, et al,²⁶ found that carbon monoxide is not easily oxidized on a platinized carbon electrode at room temperature. In fact, Havel, et al, found that introduction of carbon monoxide into a hydrogen burning fuel cell caused polarization of the cell. Thus, a mixed potential of carbon monoxide and hydrogen seems quite unlikely.

Although the lower potentials observed when carbon monoxide was introduced remained unexplained, the polarizing ability of carbon monoxide was apparent in the rise of the potential after open circuit. When carbon monoxide was present in the cell the rate of rise of the potential at open circuit was much more rapid. Also the final steady state potential was seen to be a few tenths of a volt higher than when only nitrogen was bubbled. This is discussed further in the next section.

Since the minimum potentials observed with carbon monoxide bubbling were not lower than the hydrogen potential, a possible explanation is as follows: Because a current pulse was used to "clean" the surface, it was possible that all the adsorbed species was not completely removed. In order to be certain of removing all the organic species on the electrode, the following experiment was set up. The potential of the platinum electrode was held higher than +1.6 v. vs. a H_2 electrode in the same solution for 60 seconds. The potential was maintained by the use of a voltage divider, the circuitry and equipment was the same as that shown in Figure 13. At this potential it is well known that no organic species can remain on an electrode surface.

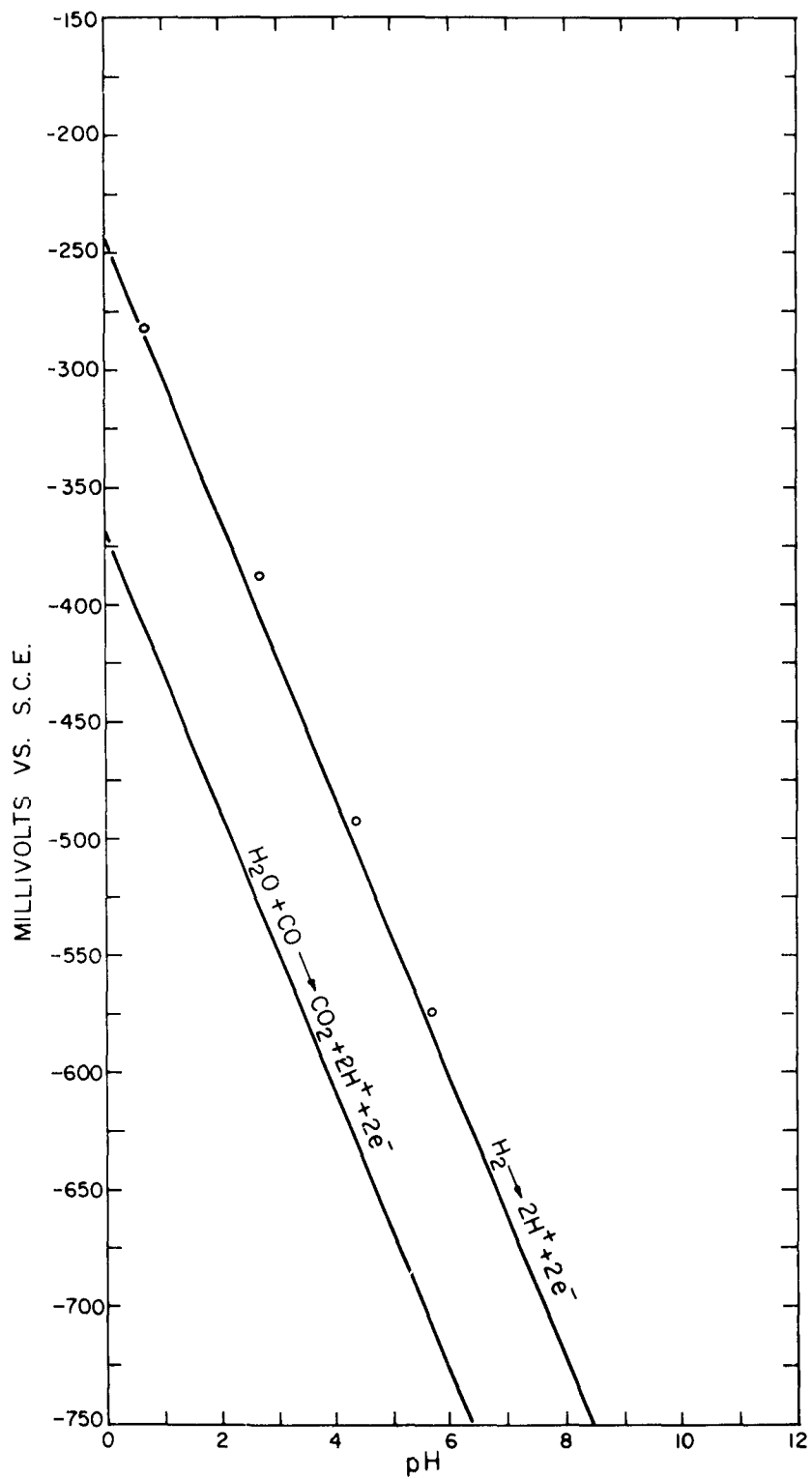


Fig. 18 Average Minimum Open Circuit Potentials as a Function of pH in the Presence of Carbon Monoxide.

After the potential had been held for 60 seconds, the circuit was broken. The potential at open circuit was followed with the Sargeant recorder. Nitrogen was bubbled through the solution at all times. The results obtained are shown in Table XIII.

By comparing the results in Table X with those obtained by the current pulse technique in Table XIII, it is readily seen that the minimum potentials obtained by pretreatment at a high potential are significantly lower. In fact, the highest minimum potential obtained in 1M H_2SO_4 in Table XIII, $-.201$ v. vs. S.C.E., is lower than the lowest potential obtained at a pH of 0.68 by the current pulse technique, $-.193$ v. vs. S.C.E.

The pulse technique probably worked better at higher pH values because the "blocking agent" did not form as rapidly. Although the lower minimum values obtained with carbon monoxide present are still not explained, the pulse technique, especially in acid solution is shown to yield questionable results.

5. Rise of Potential at Open Circuit

The rise of the potential from the minimum value was much more sensitive to the physical conditions at the plain platinum electrode than was the value of the minimum potential itself. Although the rate of rise was reproducible when gas was bubbled at a given gas flow rate, when bubbling rate or position of the sparging tube with reference to the electrode was changed, the rate of rise would change also. This is presumably due to the differences in local stirring at the electrode surface. Because of this no detailed study of this phenomenon was undertaken. However, qualitative effects were noted.

a. Effect of Nitrogen Bubbling

Nitrogen bubbling invariably increased the rate of rise of potential at open circuit and while the nitrogen was bubbled the potential leveled off at a higher value than occurred when no nitrogen was bubbled. This is shown in Figure 19 for 2.5×10^{-2} N HCOOH in 1.33M H_2NaPO_4 .

TABLE XIII

Minimum Potentials Obtained by Pretreatment
at Constant Potential with Nitrogen Bubbled

107D Runs		
1M HCOOH	35°C	pH 2.61
Voltage of Pretreatment v. vs. S.C.E.	Minimum Potential v. vs. S.C.E.	
+1.610	-.371	
+1.661	-.371	
+1.614	-.370	
+1.603	-.375	
+1.657	-.382	
+1.583	-.382	
+1.602	-.381	
+1.590	-.382	
<u>E_{max}</u>	<u>E_{ave}</u>	<u>E_{min}</u>
-.370	-.377	-.382
108D Runs		
1.56M HCOOH	35°C	1M H ₂ SO ₄
Voltage of Pretreatment v. vs. S.C.E.	Minimum Potential v. vs. S.C.E.	
+1.800	-.232	
+1.728	-.238	
+1.800	-.234	

TABLE XIII (Continued)

Voltage of Pretreatment v. vs. S.C.E.		Minimum Potential v. vs. S.C.E.
+1.709		-.205
+1.770		-.220
+1.640		-.180
+1.722		-.211
+1.719		-.208
+1.739		-.209
+1.748		-.201
<u>E_{max}</u>	<u>E_{ave}</u>	<u>E_{min}</u>
-.201	-.214	-.238

b. Effect of pH

In strongly acid solutions such as 5M H_2SO_4 the rate of rise of potential was so rapid that it was difficult to ascertain whether the observed minimums were really minimum potentials. As the solutions were made more basic the rate of rise of potential at open circuit became slower.

c. Effect of Carbon Monoxide Bubbling

Introduction of carbon monoxide into the cell invariably increased the rate of rise of the potential and caused the potential to level off at higher values than would be the case when nitrogen was bubbling. This effect of increasing the rate of rise of potential at open circuit after the minimum potential was most marked in neutral solutions. In particular, at pH 5.72, when nitrogen was bubbled through the solution the potential rose slowly at a steady rate as is shown in Figure 20a. However, when some carbon monoxide was bubbled through the solution there was a short induction period and then a sudden rise of potential as is shown in Figure 20b. The shape of the potential-time curve at open circuit in Figure 20b is similar to the potential-time curve at open circuit in Figure 19, where only nitrogen was bubbled in a more acid solution.

By maintaining the total gas rate constant comparative data could be taken regarding the effect of carbon monoxide bubbling at open circuit. These data at pH 5.72 are shown in Table XIV. In Table XIV, τ is the length of time in the region of slow potential rise (induction period), $(dE/dt)^*$ is the maximum rate of potential rise measured at the inflection point. The other gas present besides CO was N_2 . The temperature was 35°C and the formic acid concentration was 1N as usual.

a. Explanation

The qualitative effect in the rise of potential at open circuit caused by nitrogen bubbling in neutral solution can be most easily explained by the hydrogen theory, namely that the formic acid dissociates on a clean

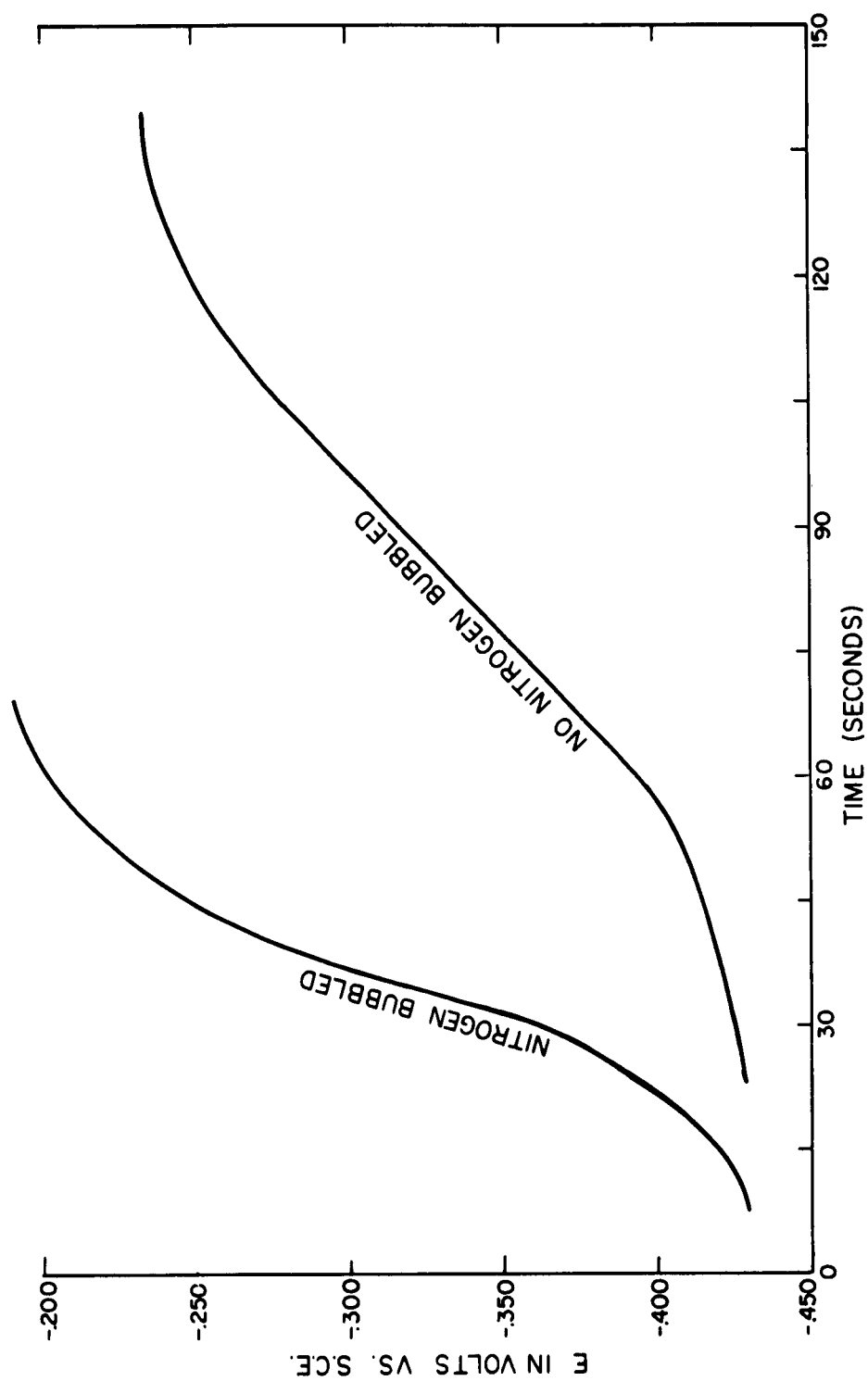
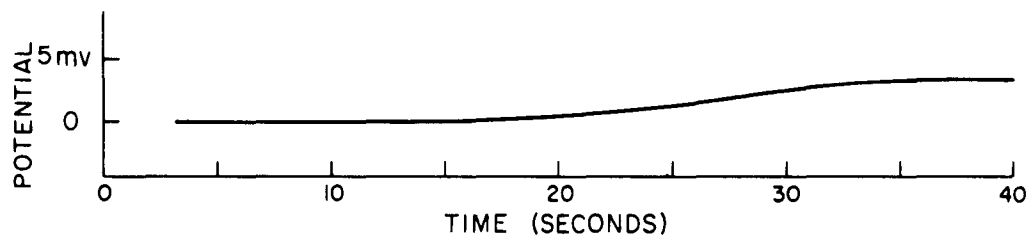
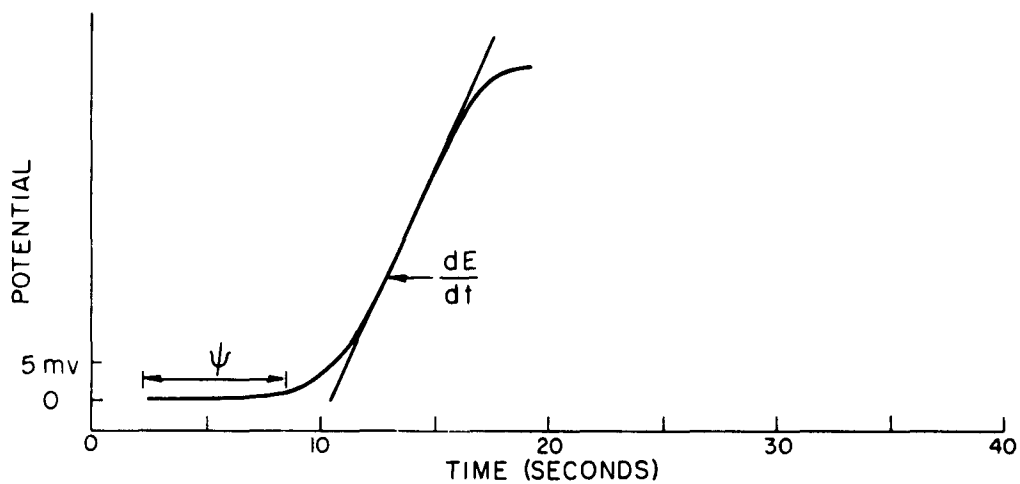


Fig. 19 Effect of Nitrogen Bubbling on the Rate of Rise of Potential from the Minimum at Open Circuit.



(a) EFFECT OF NITROGEN BUBBLING ON RISE OF POTENTIAL AFTER MINIMUM AT pH 5.72



(b) EFFECT OF CARBON MONOXIDE BUBBLING ON RISE OF POTENTIAL AFTER MINIMUM AT pH 5.72

Fig. 20 Effect of Carbon Monoxide Bubbling on the Rise of Potential from the Minimum at Open Circuit.

TABLE XIV

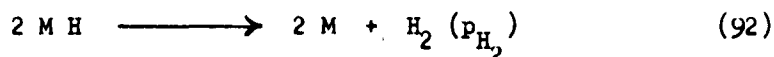
Effect of Carbon Monoxide on Rise of Potential After
Minimum at Open Circuit pH 5.72

$\% \text{ CO}^1$	φ sec.	$(dE/dt)^*{}^2$ mv/sec.
0	> 46	
	> 54	
25.8	7	38
	3	41
	2	33
	2	39
	2	31
	2	33
	2	34
	2	30
100	0	89
	0	78
	0	78
	0	91
	0	78
	0	68
	0	60
	0	73

¹ Total flow rate constant; other gas present was nitrogen.

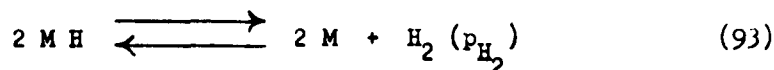
² This slope is the maximum rate of rise of potential occurring at the inflection point of the voltage-time curve (see Figure 6).

platinum surface to hydrogen and some organic species. The minimum potential at open circuit is due to the adsorbed hydrogen on the surface. The final steady state open circuit potential is a mixed potential involving residual hydrogen and at least one other species present on the electrode surface. The rate of rise of potential to the steady state open circuit potential is dependent on the rate of desorption of hydrogen.



The rate of diffusion of hydrogen from the electrode is enhanced by bubbling an inert gas past the electrode surface. Thus, when nitrogen is bubbled past the platinum electrode the potential rises faster at open circuit.

Since the steady state potential is a mixed potential of residual hydrogen and some other species, the steady state potential depends on the equilibrium



As equation (93) is shifted to the right due to a lower partial pressure of hydrogen, the number of adsorbed hydrogen sites must decrease and the steady state potential increases. This accounts for the higher steady state potential observed when nitrogen was bubbled past the electrode (see Figure 19) since the bubbling of an inert gas past the electrode will decrease the partial pressure of hydrogen near the electrode.

The effect of carbon monoxide cannot be explained as simply. The higher steady state open circuit potential observed when carbon monoxide is present in the system could be due to the adsorption of carbon monoxide itself. On the other hand, the carbon monoxide might be reacting with some organic species which already exists on the electrode surface.

Other unusual effects noted when carbon monoxide was present are discussed in Appendix A.

C. Double Layer Capacitance

1. Current Potential Curves: Effect of Pretreatment

Chronopotentiometric experiments showed that the transition time obtained in the oxidation of formic acid in acid or neutral solutions was markedly dependent on the pretreatment of the electrode. In particular, when platinum oxides were allowed to form in a 0.01M HCOOH and 0.10M HNa_2PO_4 solution, the transition time was a function of the time the electrode was left in solution after the oxides had been reduced. The longer that the electrode had been left in solution, the shorter the transition time would be. (Results and Discussion A4.). This was interpreted to be caused by some species formed chemically from the formic acid and strongly adsorbed on the electrode surface.

If this hypothesis were valid, then the effect of the adsorbed species should be magnified in more concentrated solutions of formic acid. In more concentrated solutions of formic acid, where diffusion of reactant to the electrode was not an important consideration, the current-potential relationship should be a strong function of electrode pretreatment.

According to this theory, if a current were placed on the plain platinum electrode sufficiently large to cause platinum oxides to form and then turned off, the subsequent current potential data would be a function of the time taken between oxide reduction and the start of the next run. When the oxide is just reduced, the electrode is thought to be "clean". However, as the electrode sits in the solution the formic acid is thought to decompose to hydrogen and an organic species which is not easily oxidized on plain platinum. Thus, current-potential data that are obtained by turning on the current immediately after platinum oxide reduction would be expected to exhibit low polarization and a relatively high double layer capacitance; whereas, the

current-potential data that are obtained a longer period after platinum oxide reduction would be expected to exhibit high polarization and a relatively low capacitance. An adsorbed organic species acting as a blocking agent would cause, (1) the higher polarization by decreasing the electrode activity and (2) lower double layer capacitance by causing greater charge separation.

In order to examine what would happen under these conditions a solution of 1.0M HCOOH and 1.33M HNa_2PO_4 was prepared. The apparatus was arranged as in Figure 12. The oscillator frequency was 1200 cps. and the square wave input current was 0.14 ma. This input caused a cell voltage response of less than 5 mv. The plain platinum electrode was 1.23 cm^2 in apparent area and the temperature was held at 26.1°C. The data are shown in Table XV.

The results from Table XV show quite clearly that electrode pretreatment has a considerable effect on the current-potential behavior of plain platinum. Perhaps most startling is the comparison of runs 61-C-9 and 61-C-27. By starting the current immediately after oxide reduction the electrode carries fifty times the current than it can when the electrode has been left in solution for thirty minutes before current application. Similarly, it is quite evident that at a given voltage the double layer is greatly reduced when the electrode is left in solution before current application.

Other observations regarding the current-potential curves of formic acid on plain platinum are given in Appendix A.

2. Double Layer Capacitance Measurements During Voltage Oscillations in Concentrated Formic Acid

a. Plain Platinum

In order to determine the condition of the metal surface during oscillations, double layer capacitance measurements were taken when galvanostatic voltage oscillations were induced on a plain platinum and platinized

TABLE XV

Current-Potential Data Showing the Effect of Pretreatment at26.1°C on Plain Platinum in 1.0M HCOOH and 1.33M Na₂HPO₄

Run	i ma	v. vs. S.C.E.	C $\frac{\mu f}{cm^2}$	comments
61-C-6	0	-.398	16	in solution 1/2 hour
61-C-7	0.0218	-.140	15	
61-C-8	0.0304	-.040	15	
61-C-9	0.0420	+.035	15	
61-C-10	0.0541	+.085	15	current increased in steps. readings every 1/2 minute.
61-C-11	0.0589	+.095	15	
61-C-12	0.0621	+.100	15	
61-C-13	0.0639	+.100	15	
61-C-14	0.0657	+.105	$14\frac{1}{2}$	
61-C-15	0.0678			oscillations started
61-C-26	2.50	+.060	$24\frac{1}{2}$	
61-C-27	2.23	+.030	26	
61-C-28	1.23	-.015	25	each run measured individually 15 seconds after oxide reduction
61-C-30	0.760	-.030	22	
61-C-31	0.565	-.040	22	
61-C-32	0	-.370	41	

All voltages $\neq$.005 volts

In Runs 61-C-26 through 61-C-33 current turned on less than one second after oxide reduction.

platinum electrode in a 1M NaOOCH and 90% HCOOH solution at 17.5°C. The conditions were chosen since Muller⁴¹ had reported previously that reproducible oscillations had been obtained on rhodenized platinum under similar conditions.

Oscillations were observed having a period of about 37 seconds and a minimum potential of +0.310 v. vs. S.C.E. and a peak potential of +0.800 v. vs. S.C.E. when a direct current of 0.180 $\pm$.002 ma was passed through the 2 cm² plain platinum electrode. Occasionally the voltage would rise a few hundredths of a volt higher than the peak voltage just before the voltage drop. A picture of the oscillations is shown in Figure 21. A small rise above the peak is shown in the second oscillation in Figure 21.

The double layer capacitance was measured by taking pictures of the cell voltage response on the C-12 camera and measuring the slope of the ramp portion of the response. The square wave current was 1.32 ma at a frequency of 1000 c.p.s. Pictures of the data obtained are shown in Figure 22. The abscissa in these pictures is 0.1 m sec. per cross-hatched division. The ordinate of the cell response trace is 5 m v. per cross-hatched division. The straight line trace is a d.c. voltage measured between the test electrode and the d.c. dummy at 100 mv/cm.

The magnitude of the a.c. voltage change in the cell response was necessary since, when a more sensitive voltage scale was used, clear pictures could not be obtained. This was due to the fact that the d.c. voltage changes in the oscillations caused the trace to move too rapidly in the vertical direction when greater sensitivity was used. In fact, capacitances could only be measured during the comparatively slow rise in potential and not during the rapid drop in potential. The large a.c. voltage change necessitated a relatively large square wave current to be used. Enough of the square wave current must have been spent in the faradic process to affect the d.c. process, because when the function generator was turned off, the d.c. voltage went through only one further oscillation and then came to rest at the oxide potential.

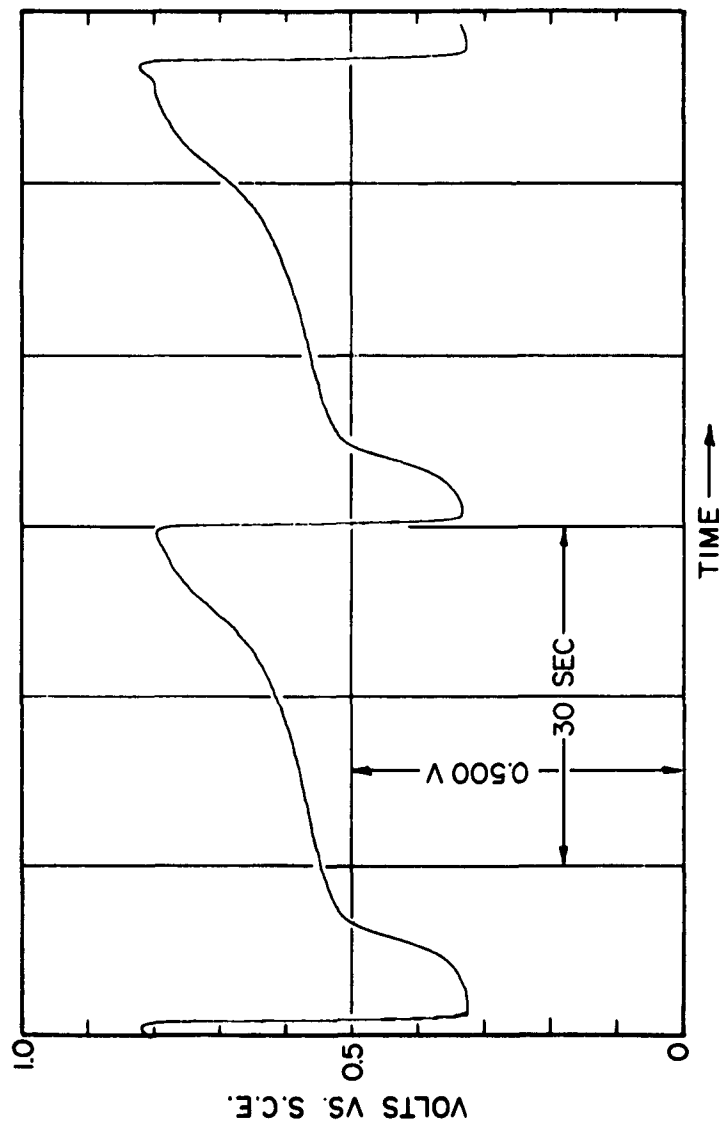
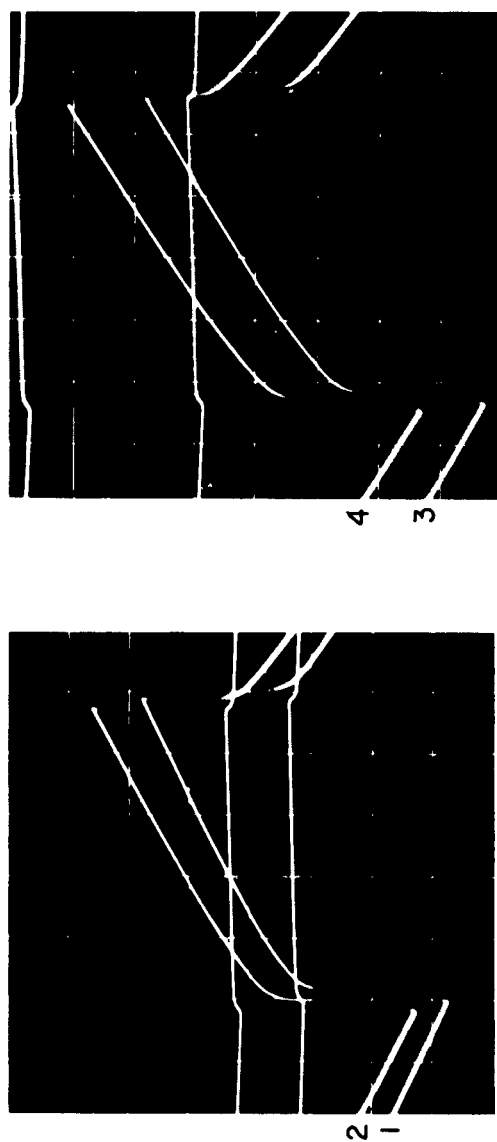


Fig. 21 Oscillations on Plain Platinum in 1M NaOOCH and 90 % HCOOH at 17°C.



UPPER TRACE: 69D2
LOWER TRACE: 69D1

69D4
69D3

Fig. 22 Pictures of Cell Voltage Response During Oscillations on Plain Platinum in 1M NaOOCH and 90% HCOOH at 17°C .

The data obtained during oscillations are shown in Table XVI. Run 69D4 was taken on a rise above the peak just before a drop to the minimum. The value of the capacitance at +.825 v is slightly higher than at 0.770 v vs. S.C.E., whereas in all other cases the capacitance decreased as the voltage increased. Thus, the current was raised so that the oscillations stopped and the potential rose to a point where oxides were definitely on the electrode. The capacitance was measured at this potential and the following result obtained.

<u>Run</u>	<u>v. vs. S.C.E.</u>	<u>C μf</u>
77D1	+1.03	54.0

The data from Table XVI and Run 77D1 are plotted in Figure 23. The sudden rise observed in Run 69D4 suggests the possibility that oxide formation on the electrode plays an important role in the oscillations. In order to investigate this possibility, it was decided that a study be undertaken in a more well-known system. In particular, a system where the regions of anion and oxygen adsorption were more clearly established. However, before this investigation was carried out, the capacitance and voltage relationships during galvanostatic voltage oscillations on platinized platinum electrodes was examined.

b. Platinized Platinum

Because of the large capacitance of the platinized platinum electrode a sine wave input at 1000 c/s was used and a series circuit was assumed. A square wave input at 1000 c/s showed no curvature but the voltage rise in the ramp was so small that much accuracy was lost.

The measurements were taken at 13°C in a 1M NaOOCCH and 90 HCOOH solution. The apparent area of the electrode was 1 cm². The alternating current was 1.60 ma. The oscillations had a length of about 10 seconds and exhibited

TABLE XVI

Data on Double Layer Capacitance and Voltage During Oscillations
on Plain Platinum in 1M NaOOCH and 90% HCOOH at 17.5°C

Run	v. vs. S.C.E.	C μf
	<u>+ .005</u>	<u>+ .5</u>
67D1	+ .770	36.6
67D2	.325	55.2
68D1	.330	50.0
68D2	.435	47.1
68D3	.530	43.1
69D1	.355	52.1
69D2	.465	44.5
69D3	.535	42.5
69D4	.825	38.8

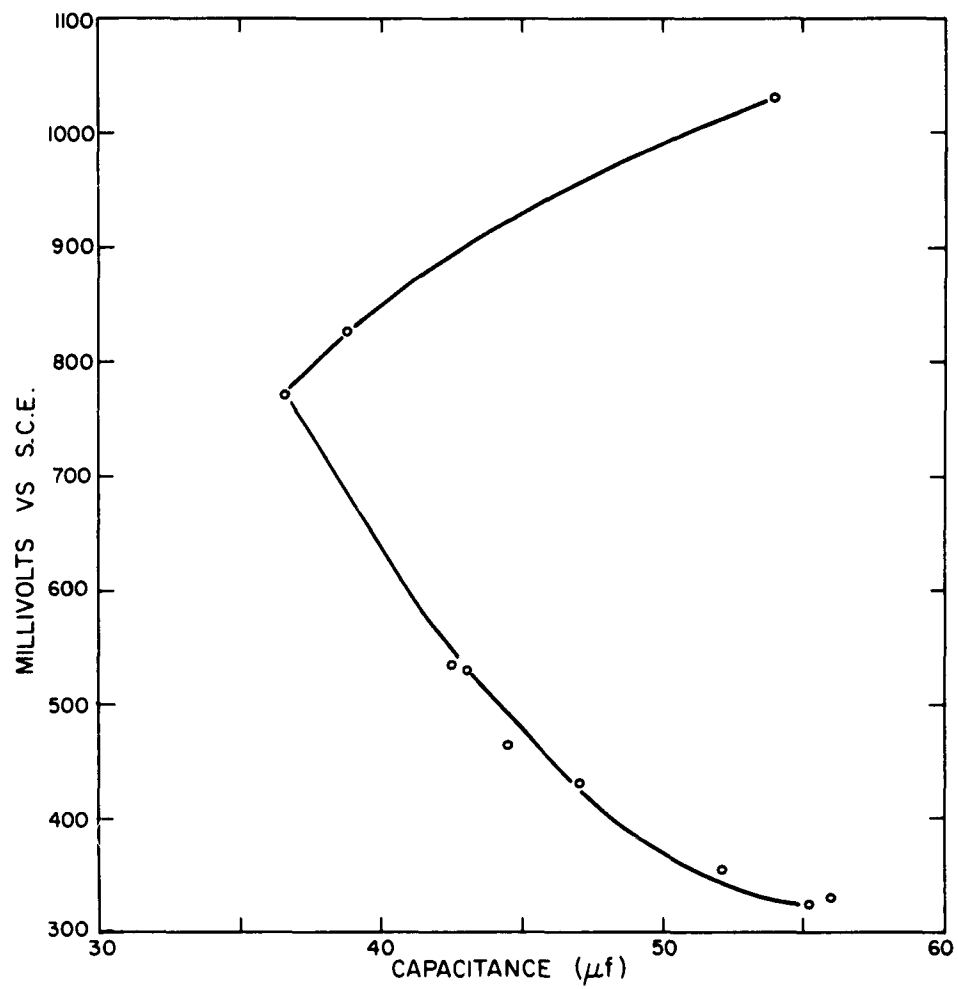


Fig. 23 Relation Between Capacitance and Voltage.

a well at +0.53 v. vs. S.C.E., an inflection point at +0.93 v. vs. S.C.E., and a peak at 1.30 v. vs. S.C.E. The direct current was 25.4 to 23.6 ma. The oscillations are shown in Figure 24.

The capacitance was seen to decrease up to 0.93 v. and then rise to the peak of 1.30 v. The sine wave input had no effect on the oscillations. When the generator was turned off, the oscillations continued unchanged in frequency or voltage. The data is summarized in Table XVII.

The constancy of R_g serves as a check on the assumption of the ideally polarized electrode.

The rise in capacitance after the inflection point indicates that either an organic species is desorbing or that an oxide is being formed simultaneously. Certainly, at +1.30 v. vs. S.C.E. oxides are present on the electrode surface.

3. Double Layer Capacitance on Plain Platinum in HCOOH and 1N H₂SO₄

In an effort to determine whether metal oxides played an important role in the galvanostatic voltage oscillations found in formic acid solutions, a number of constant potential experiments were performed in 1N H₂SO₄ on a platinum wire electrode at various concentrations of formic acid. It was the purpose of the constant potential experiments to establish data so that the equilibrium capacitance-potential relationships could be established. Then, using the same apparatus, but controlling the current, oscillations would be generated. From measurements of the capacitance-potential behavior during oscillations, an insight into the processes occurring on the electrode would be obtained.

The apparatus and experimental procedure has been presented in Apparatus and Experimental Procedure B3b.

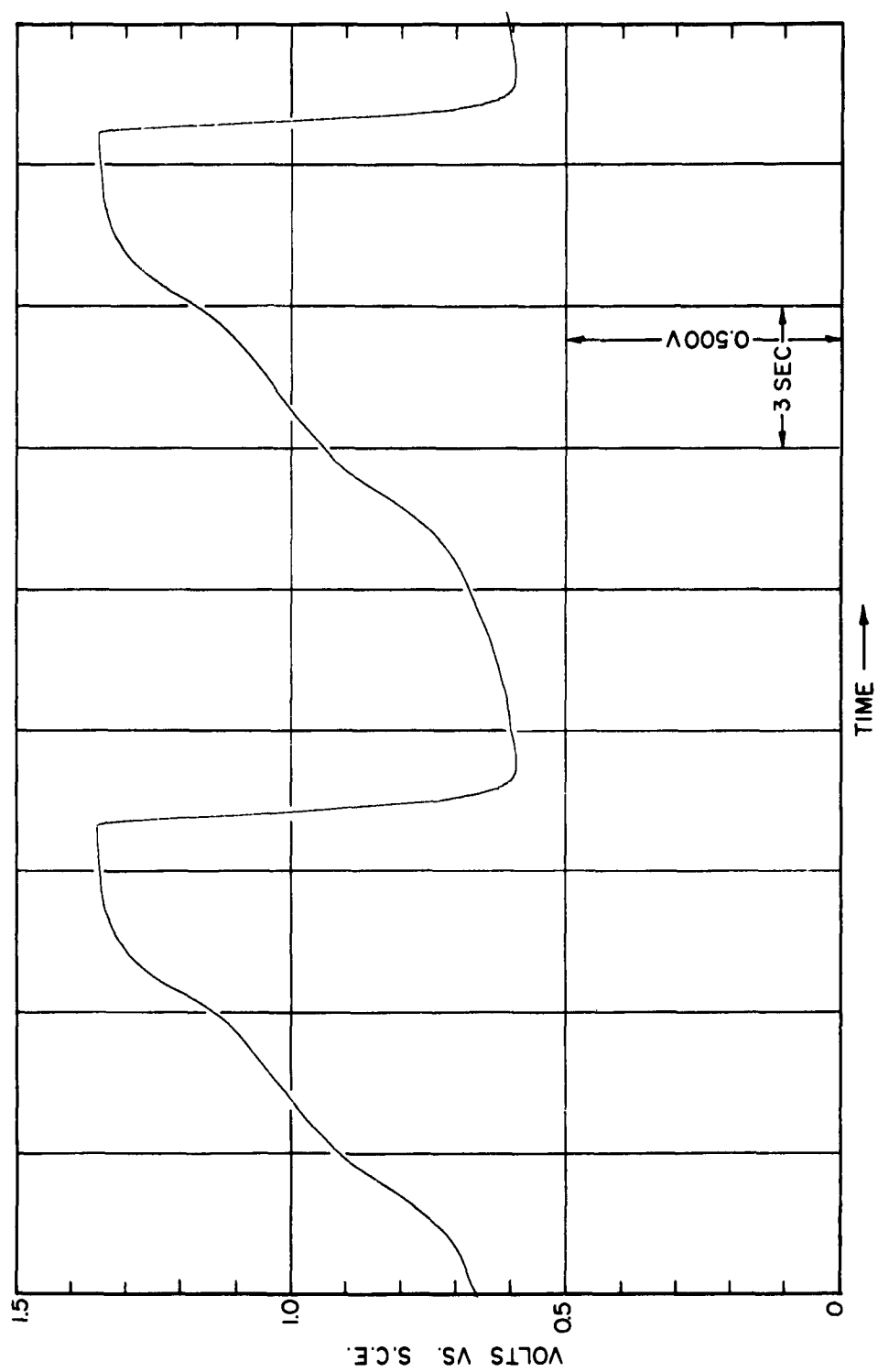


Fig. 24 Oscillations on Platinized Platinum in 1M NaOOCH and 90% HCOOH at 13°C.

TABLE XVII

Capacitance on Platinized Platinum During Oscillations

v. vs. S.C.E.	C μ f	R _s Ω
0.53	800	13.5
0.7	270	14.5
0.93	215	14
1.1	320	14
1.30	350	14

Four sets of experiments were performed in 1N H_2SO_4 at different concentrations of formic acid; 0 M, $1.56 \times 10^{-3}\text{M}$, $1.56 \times 10^{-4}\text{M}$, and 1.56M HCOOH . The data are presented in Figure 25; the detailed data are tabulated in Appendix D.

The shape of the capacitance-potential curve in 1N H_2SO_4 when no formic acid was present is similar to that obtained by Breiter⁴ on platinum in 1M HClO_4 . When no adsorbable species are present in solution, three distinct regions can be distinguished for a platinum electrode. As Breiter points out, in perchloric acid hydrogen is adsorbed between 0 and +0.4 v. vs. a hydrogen electrode in the same solution. Neither hydrogen nor oxygen is adsorbed between +0.4 and +0.8 v. where platinum behaves as an ideally polarizable electrode. The chemisorption of oxygen takes place between +0.8 and +1.6 v.⁴

It can be seen in Figure 25 that the capacitance decreases slowly until a potential of 0.8 v. vs. H_2 has been reached. At this point the capacitance rises sharply and shows a peak. This increase has been explained by Laitinen and Enke³¹ as being due to the formation of an oxide layer.

When formic acid is present in the system two changes in the capacitance-potential curve are apparent. It can be seen in Figure 25, that the double layer capacitance is decreased in the region where platinum acts as an ideally polarizable electrode. Also the potential at which the sharp rise in capacitance occurs is shifted to more anodic potentials. These phenomena were also observed on platinum by Breiter⁴ when amyl alcohol was added to perchloric acid.

The lowering of the capacitance in the region +.4 to +.8 vs. H_2 with increased formic acid concentration represents increased coverage of some species on the electrode. According to the parallel capacitor model (see Introduction B4c.). By assuming complete coverage at 1.56M HCOOH , an estimate of the degree of coverage in the intermediate concentrations can be made by equation (67).

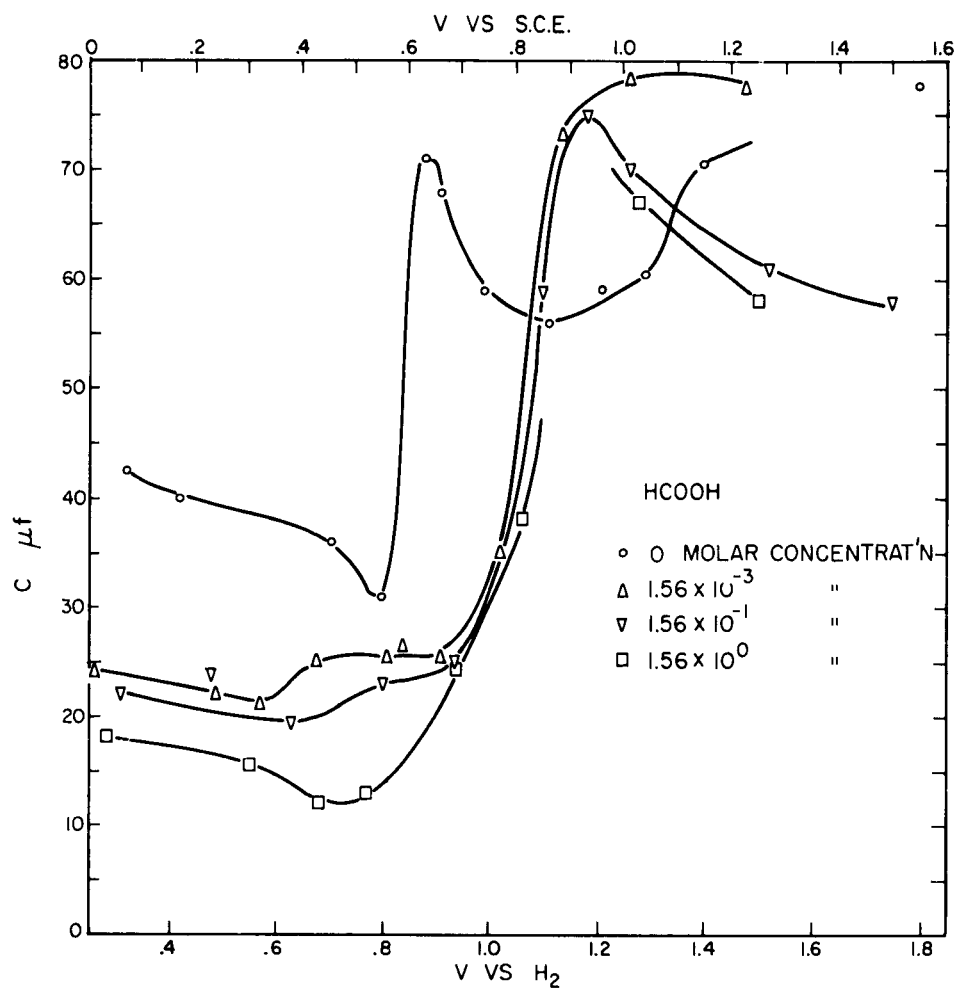


Fig. 25 Capacitance vs. Potential for Formic Acid in 1N H₂SO₄ on Plain Platinum.

TABLE XVIII

Capacitance and Voltage Data from Oscillations in 1.56M HCOOH
and 1.0N H₂SO₄ at 35°C on a Plain Platinum Electrode

<u>Run</u>	<u>v. vs. S.C.E.</u>	<u>C μf</u>
101D1	+0.51	18
101D2	+0.61	15 $\frac{1}{2}$
101D3	+0.66	15
101D4	+0.76	15
101D5	+0.87	15
101D6	+0.89	15 $\frac{1}{2}$
101D7	+0.90	15 $\frac{1}{2}$
101D8	+0.91	16
101D9	+0.92	16

in order to obtain galvanostatic voltage oscillations, the external circuitry was modified so that a constant current could be applied. At $1.56 \times 10^{-3} \text{M}$ HCOOH no oscillations could be obtained. At $1.56 \times 10^{-1} \text{M}$ HCOOH oscillations were observed at 0.222 ma. but they were irregular, having maxima ranging from +0.46 to +0.70 v. vs. S.C.E. and minima from +0.22 to +0.34 v. vs. S.C.E. Furthermore, these oscillations died out rapidly, the potential coming to rest in the region of potentials where oxides exist on the electrode. With a concentration of 1.56M HCOOH, however, fairly regular oscillations were observed at 0.138 ma. The potential and capacitance data from these oscillations is shown in Table XVIII. The oscillations obtained under these conditions were different in shape from those shown in Figure 21 or 24. In the oscillations observed here, the potential rose to a plateau near +0.90 v. vs. S.C.E. held at that point for a few seconds and then suddenly dropped to a minimum.

By comparing the data in Table XVIII, taken at constant current, with the data in Figure 25, taken at constant potential, a surprising observation is made. If the capacitance of the data taken at constant current is compared at the same voltage with the capacitance data taken at constant voltage, it is seen that only the point at +0.51 v. vs. S.C.E. lies above the constant voltage curve.

Since oxides can exist on the platinum electrode above 0.55 v. vs. S.C.E., and oxides on platinum increase the double layer capacitance, it appears that the constant voltage data above +.55 v. vs. S.C.E. represents a surface partly covered by oxide and partly covered by an uncharged organic species. Buck, et al,¹⁰ and Muller⁴⁰ have shown that when a platinum surface is covered with oxides the oxidation of formic acid is completely inhibited. Muller's³⁹ current-potential data, taken at constant potential, show a decrease in current with increasing potential in the region +.55 to +.90 v. vs. S.C.E. with 1N HCOOH and 1N H₂SO₄ (see Figure 7). Thus, this concept of a partially oxide-covered surface ties together the previous data with the present work.

Then the capacitance data of constant current could correspond to a build up of adsorbed species in the region +.55 to +.9 v. vs. S.C.E. No oxide is present under these conditions.

However, as the potential builds up, because of the formation of organic species, the driving force for oxide formation increases. Near 0.9 v. vs. S.C.E. the constant voltage capacitance data in Figure 25 indicates that the surface is covered with oxide and no organic species remains on the platinum surface. It seems likely then, that at constant current the oxides begin to form near that potential. However, if the adsorbed species can react with the oxides then both could be removed, and since the potential is dependent on what exists on the surface, the potential falls and a new oscillation begins.

The current peak near +1.1 v. vs. H_2 found by Buck, et al.,⁹ could possibly represent this oxidation of adsorbed species by or in the presence of platinum oxides. It is suggested that cyclic voltammetry be utilized to determine this hypothesis. The height of the current peak at +1.1 v. should be examined as a function of the pretreatment of the electrode and the speed of the voltage scan. If the peak is due to the oxidation of the adsorbed blocking agent, then the height of the peak should increase with increasing time between runs at open circuit.

D. Discussion of Results in Relation to the Work of Others

The important results about the electrochemical oxidation of formic acid on plain platinum that we have found here are summarized as follows: The minimum potential is due to the presence of hydrogen. Some uncharged organic species causes the rise in potential from the minimum potential at open circuit. Both the hydrogen and the organic species are formed from formic acid itself. The organic species is more difficult to oxidize than formic acid

and is strongly adsorbed on the surface of a plain platinum electrode. The organic species seems to be the cause of the galvanostatic voltage oscillations. Platinum oxide may also play an important role in the voltage oscillations.

Muller also felt that hydrogen was the cause of the minimum potentials. However, he did not believe that formic acid would decompose to hydrogen to any great extent on plain platinum.

Buck, et al, noted that pretreatment changed the shape of the voltage-time curves observed in chronopotentiometry of formic acid on platinized platinum foil electrodes. They saw evidence that a species more easily oxidized than formic acid formed on the electrode when only short times between experiments were taken. This "species" should be adsorbed hydrogen according to our results. At longer times, Buck, et al, observed a species formed that was more difficult to oxidize than formic acid. This latter "species", we suggest, corresponds to the "blocking agent" which we have observed on plain platinum. Buck, et al, observed no change in transition time between the two cases on platinized platinum. However, we believe that, if lower formic acid concentrations were investigated, so that the number of coulombs passed would be reduced, a plot of the $(i_0 \tau^{1/2}/C)$ product vs. $(1/\tau)$ would indicate the presence of an adsorbed species when short times are taken between runs. Also, if exceptionally long times are allowed to pass between runs, a dependence of transition time on time between runs will be noted due to the "blocking agent". This latter effect would not be expected to be as significant on platinized platinum as we have found on plain platinum because of the greatly increased true surface area of the plated electrode. In these chronopotentiometric experiments, shielded electrodes are recommended, as suggested by Bard,² to reduce errors due to local convection caused by the considerable change in density of the products compared to the reactants.

The leading candidate for the identity of the "blocking agent" is carbon monoxide. The blocking agent is formed from the chemical decomposition of formic acid and seems to be more rapidly formed in acid solutions. It is well known that carbon monoxide is a product of formic acid decomposition in acid solutions. Havel, et al, have shown that carbon monoxide caused polarization in a room temperature hydrogen fuel cell.

A possible key to the identification of carbon monoxide as the strongly adsorbed species might be found in the use of cyclic voltammetry. One should compare the potential of the current peaks obtained in the oxidation of carbon monoxide with the potentials of current peaks observed when formic acid in acid solution oxidized after the electrode was left in solution for thirty minutes. Then remove all organic species from the platinum electrode in formic acid by holding the potential at some value where organic species cannot exist. Immediately after breaking the circuit a voltage-time sweep should be made. If there is a current peak corresponding to carbon monoxide oxidation in the formic acid oxidation and it has been significantly reduced in relation to the other current peaks, by the latter pretreatment strong evidence for the identification of carbon monoxide as the "blocking agent" will have been established.

V. CONCLUSIONS

1. The minimum potential obtained at open circuit when platinum oxides are reduced by formic acid is due to the presence of hydrogen on the electrode.
2. The rise of the potential at open circuit after the minimum is obtained is caused by adsorption of an unknown uncharged organic species on the platinum electrode.
3. Both the hydrogen and uncharged organic species are formed from the chemical decomposition of formic acid.
4. The adsorbed organic species is more difficult to oxidize than formic acid. There are strong indications that this unknown species is carbon monoxide.
5. The organic species seems to be the cause of the galvanostatic voltage oscillations. Platinum oxide may also play an important role in the voltage oscillations.

VI. RECOMMENDATIONS

1. In order to determine whether carbon monoxide is the uncharged, strongly adsorbed organic species responsible for "blocking" the electrode the following experiment is recommended. A voltage-time sweep of an acid solution saturated with carbon monoxide should be made on a platinum electrode. Next, a voltage-time sweep of a solution of formic acid at the same pH should be carried out on the same electrode. The electrode should be left in the formic acid solution for thirty minutes at open circuit. The potential at which the voltage sweep is initiated should correspond to the final open circuit potential of the platinum electrode. The potentials at which the current peaks were obtained in these two experiments should be compared. If there is a carbon monoxide oxidation peak at a potential corresponding to a peak observed in the formic acid oxidation, one more experiment should be carried out.

All organic species should be removed from the platinum electrode by holding the potential of the electrode for sixty seconds at a potential where no organic species can exist. Next, break the circuit holding the potential and the potential will drop rapidly at open circuit to the minimum potential. Immediately after the minimum potential is established a voltage-time sweep should be started. The initial potential of the voltage sweep should correspond to the potential of the electrode at open circuit immediately before the sweep. If the current peak common to both the oxidation of formic acid and carbon monoxide is reduced relative to the other formic acid current peaks, strong evidence for the identification of carbon monoxide as the "blocking agent" will have been established.

2. Chronopotentiometric experiments on plated noble electrodes at low formic acid concentrations should be attempted to confirm the existence of adsorbed hydrogen on these electrodes. By examining the effect of time

between runs on the transition time one may be able to determine the interaction between the adsorbed hydrogen and the blocking agent. In these chronopotentiometric experiments, shielded electrodes are recommended, as suggested by Bard.²

VII. APPENDIX

A. Supplementary Results and Discussion1. Unusual Potential Behavior in the Presence of Carbon Monoxide

When a current pulse of 10 to 11 ma/cm^2 was applied to the plain platinum electrode in 1N HCOOH at a pH of 5.72 in the presence of carbon monoxide the potential was seen to rise with time for a period of about one to two seconds after the current was turned off. This effect was not observed when nitrogen was bubbled through the solution under the same conditions. The potential was seen to rise after current cut off and then sharply drop to a minimum value. These observations are tabulated in Table XIX.

It can be seen from Table XIX that the increase in polarization after current cut off, ΔV , was greatest when the current pulse was long, i.e., V_1 was high and when the pulse was started shortly after the previous minimum, i.e., V_0 was low. The former is seen by comparing ΔV values at the beginning of Table XIX with those at the end, since the data in Table XIX are arranged in order of increasing V_1 . The latter effect is shown clearly in the data at $V_1 = .000$ v. vs. S.C.E. Under this condition, two runs (75 x 8.7) were carried out where V_0 was close to the steady state value yielding values of ΔV equal to 165 and 175 mv., while two other runs (75 x 17, 13) were started much closer to the minimum potential and yielded values of ΔV equal to 205 and 210 mv.

The effect of increased polarization after current cut off was noted at other pH values when carbon monoxide was present but not investigated quantitatively. Further experiments are necessary in order to clarify this unusual phenomena.

2. Observations on Current-Potential Curves

When a plain platinum electrode was placed in a concentrated formic acid solution so that diffusion would not be important the following general trends were observed under galvanostatic conditions. If the electrode was

TABLE XIX

Unusual Behavior of Potential in Presence of Carbon Monoxide
and 1N Formic Acid: Rise of Potential after Current Cut Off
on Plain Platinum at 35°C and pH 5.72

Run	V. v. vs. S.C.E. ¹	V. ₁	ΔV mv
75X10	-.325	-.275	65
75X18	-.310	-.250	100
75X12	-.315	-.250	105
75X14	-.315	-.250	85
75X11	-.315	-.250	110
75X16	-.305	-.150	130
75X15	-.305	-.120	155
75X3	-.270	-.040	185
75X2	-.260	-.050	170
75X1	-.270	-.060	170
75X17	-.375 *	-.000	205
75X13	-.360 *	.000	210
75X8	-.315	.000	165
75X7	-.295	.000	175
75X9	-.305	+.050	155
75X5	-.320	+.100	180
75X4	-.315	+.100	180
75X6	-.315	+.165	180

TABLE XIX (Continued)

Rate of rise after current cut off about 130 mv/sec.

V_0 = potential at start of current pulse

V_1 = potential at end of current pulse

ΔV = change of potential after current cut off

All voltages $\pm .005$ v. or ± 5 mv

* indicates run was started during time of rapid rise of potential from minimum. All other runs were started close to steady state potential.

left in solution until a steady state open circuit potential was attained, over thirty minutes, and then current applied, the potential would rise sharply and then level off to a constant value (see Figure 26a.). If the current was decreased at this point, the potential dropped rapidly but then rose slowly to a steady value (see Figure 26b.). If the current was increased at this point, the potential would rise sharply, as before, and then decrease to a steady value (see Figure 26c.). When the current was increased still higher and the potential would rise, the onset of oscillations was observed.

Unfortunately, a given constant voltage did not correspond to a certain voltage on plain platinum so that a quantitative investigation of this strange behavior was not undertaken. However, a qualitative explanation is offered. It has been assumed before that some species forms chemically from the decomposition of formic acid. This species is adsorbed on the platinum electrode blocking the surface and inhibiting further reaction.

From this basis, let us now examine the qualitative phenomena in Figure 20. As the current is increased from 0 to some small value at point 1 in Figure 24a, the potential first rises then slowly drops. It has been shown that the blocking agent is oxidizable. Thus, it seems that the equilibrium coverage of this species decreases with increasing voltage. Immediately at point 1, the coverage is nearly the same as when no current was flowing. However, some of the species is slowly oxidized and the potential drops.

Similarly at point 2 when the current is decreased, the coverage of the "blocking agent" is at first low, then slowly builds up to a steady state value.

It must be noted that other simple explanations do not account for this "overshooting" effect. For example, if diffusion were important the effect would be exactly opposite. The potential would tend to rise slowly to a

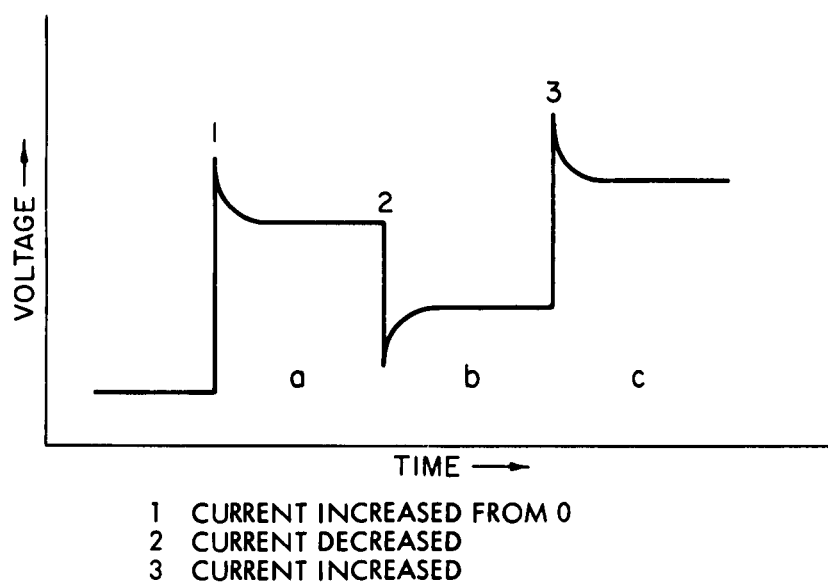


Fig. 26 Current-Potential Observations for Formic Acid under Galvanostatic Conditions in Low Potential Region.

steady state value when the current was increased and fall slowly to a constant value when the current was decreased. A large capacitance effect, hardly likely on a plain platinum electrode would have the same effect as diffusion.

A decrease in extent of coverage of the "blocking agent" with increased potential is not possible in the low potential region if the "blocking agent" were a negatively charged species, such as formate ion. But it is possible if this species is an uncharged molecule. The indication that high currents can be carried when the blocking agent is not allowed to form first gives further support to this theory.

B. Standardization of Equipment

1. The Sargeant MR Recorder

The Sargeant MR voltage recorder was standardized internally by mercury cells. Periodically this recorder was checked against the potential of a Weston cell and found to be perfectly accurate within the degree of accuracy of the reading of the potential (one to two parts per thousand).

2. The Weston 911 Ammeter

The Weston 911 ammeter was calibrated against the Sargeant MR recorder operating as a current measuring device. The accuracy of the ammeter was limited only by the degree precision at which the current could be read, about one part in one hundred.

3. The Tektronix 502 Oscilloscope

The Tektronix 502 Oscilloscope was standardized in two ways. The time sweep was checked with the Hewlett-Packard 202A function generator. The d.c. voltage displacement was checked with the Sargeant MR voltage recorder. The accuracy of the reading was limited by the precision at which the oscilloscope could be read, plus or minus two per cent of full scale reading.

4. The $10^4 \Omega$ Resistor

The $10^4 \Omega$ resistor was made one arm of a bridge circuit. The other resistors in the circuit were one per cent precision resistors. The resistance was measured as a function of frequency of a sine wave a.c. signal generated by the Hewlett-Packard function generator. The Tektronix 502A oscilloscope served as a balancing instrument. The resistances obtained and the wave length of the a.c. signal are tabulated below.

R	λ
$\times 10^4$	$\times 10^{-3}$ sec
1.016	5.3 x .1
1.016	6.1 x .5
1.016	6.1 x .5
1.018	6.1 x 0.05

5. Beckman Calomel Reference Electrodes

The Beckman Calomel reference electrode was periodically checked against a fresh Beckman Calomel reference electrode. The maximum disparity found was two millivolts.

C. Sample Calculations

In order to make sure that a number of chronopotentiometric runs in one solution did not change the concentration of the solution, the following calculation was performed.

For a diffusion controlled process with no kinetic effect,

$$i \tau^{1/2} = \frac{A C^{\circ} n F D_o^{1/2} \pi^{1/2}}{2} \quad (92)$$

where i is the current in amperes, τ is the transition time in seconds, A is the area for the diffusion front in square centimeters, C° is the concentration in moles per cubic centimeter, n is the number of electrons per mole, D is the diffusivity in square centimeters per second, and has its usual significance. The number of moles used up if all the coulombs passed went to the decomposition of formic acid is,

$$i \tau = n F M \quad (93)$$

where M is the number of moles decomposed. Since the anode compartment of the cell had a capacity of 100 cubic centimeters, the number of moles, M , is,

$$C^\circ \times 100 = M \quad (94)$$

If we restrict the change in M to two per cent, then

$$M = C^\circ \times 2 \quad (95)$$

and combining equations (92) through (95),

$$\frac{i \tau^{1/2}}{i \tau} = \frac{A C^\circ n F D^{1/2} \pi^{1/2}}{4 n F C^\circ} \quad (96)$$

or, after rearranging and canceling terms,

$$A \tau^{1/2} = 4 D^{1/2} \pi^{1/2} \quad (97)$$

For a diffusivity of 10^{-5} cm²/sec

$$A \tau^{1/2} = 7.13 \times 10^2$$

Since A never exceeded 7 cm², the sum of the transition times in one solution should not exceed 10.000 seconds. In our work no transition time longer than two minutes was carried out and no more than twenty runs were made in the same solution, so that the chronopotentiometric runs did not appreciably change the concentration of the solution.

D. Summary of Data

TABLE XX

Summary of Data Showing Influence of Pretreatment on
Chronopotentiometric Transition Time on Plain Platinum
in 0.01M HCOOH and 0.1M Na₂HPO₄ at 35°C

Run	T sec	i ma	θ sec	$i \tau^{1/2} / C$ ma. sec. ^{1/2} l./m.
32X2	180	.620	13-1/2	402
32X3	180	.620	14	375
32X4	180	.620	14	369
32X5	180	.620	14-1/2	342
32X6	180	.620	14	356
32X7	180	.620	14-1/2	377
32X8	180	.620	14-1/2	345
32X9	180	.620	14-1/2	313
32X10	180	.620	14-1/2	284
32X11	180	.620	14-1/2	274
32X12	180	.620	14-1/2	260
32X13	180	.620	14	277
32X14	180	.620	15	262
32X16	90	.622	15	332
32X17	90	.622	14-1/2	298
32X18	90	.622	17-1/2	326
32X19	90	.622	15	328
32X20	90	.622	14-1/2	346

TABLE XX (Continued)

Run	T sec	i ma	o sec	$i \tau^{1/2}/C$ ma. sec. $^{1/2}$ l./m.
32X21	90	.622	15	340
32X22	90	.622	14-1/2	354
32X23	90	.622	14-1/2	362
32X24	90	.622	14	335
32X25	90	.622	15	362
32X26	90	.622	15	343
32X27	90	.622	15	357
32X28	360	.615	14-1/2	185
32X29	360	.615	15	135
32X30	360	.615	15	106
32X31	360	.605	15-1/2	100
32X32	360	.605	15	98
32X33	90	.622	15-1/2	236
32X34	90	.622	15	271
32X35	90	.622	15	281
32X36	90	.622	14	295
32X37	90	.622	14-1/2	302
32X38	90	.622	15	317
33X1	90	.622	14-1/2	323
33X2	90	.622	14	317
33X3	90	.622	14-1/2	331
33X4	90	.622	15	349
33X5	90	.622	14-1/2	332

TABLE XX (Continued)

Run	T sec	i ma	θ sec	$i \tau^{1/2} / C$ ma. sec. ^{1/2} l./m.
33X6	90	.622	14-1/2	332
33X7	90	.622	15	357
33X8	90	.622	14-1/2	354
33X9	180	.620	49-1/2	340
33X10	180	.620	50	364
33X11	180	.620	49-1/2	364
33X12	180	.620	50	364
33X13	180	.620	50	367
33X14	180	.620	50	352
33X15	180	.620	50	367
33X16	90	.620	50	395
33X17	90	.620	50	397
33X18	90	.620	50	407
33X19	90	.620	50	390
33X20	90	.620	50-1/2	384
33X21	90	.620	50-1/2	392
33X22	90	.620	50-1/2	395
33X23	360	.615	51	190
33X24	360	.615	50-1/2	162
33X25	360	.615	50-1/2	139
33X26	360	.610	50-1/2	121
33X27	360	.610	50-1/2	116
33X28	360	.610	50	129

TABLE XX (Continued)

Run	T sec	i ma	θ sec	$i \tau^{1/2}/C$ ma. sec. ^{1/2} l./mi.
33X29	90	.622	50-1/2	298
33X30	90	.622	50-1/2	314
33X31	90	.622	50	349
33X32	90	.622	50-1/2	346
33X33	90	.622	50-1/2	351
33X34	90	.622	50	341
33X35	90	.622	50	341
33X36	90	.622	50-1/2	332
33X37	90	.622	50	327
33X38	90	.622	50-1/2	346

TABLE XXI

Summary of Data on Minimum Open Circuit Potentials

58-X Runs

1M HCOOH	pH 4.39	i = 10.5 - 11.5 ma.
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No nitrogen bubbled during minimum 35°C

-.376	-.353	-.366 v. vs. S.C.E.
-.377	-.358	-.342
-.377	-.341	-.334
-.345	-.348	-.372
-.361	-.352	-.348
-.352	-.340	-.347
-.367	-.350	

Nitrogen bubbled

i = 67-1/2 - 72-1/2 ma.

-.468	-.471
-.477	-.472
-.479	-.470
-.473	-.471
-.477	-.472

TABLE XXI (Continued)

59-X Runs

1M HCOOH

35°C

pH 5.72

No nitrogen bubbled

i = 40 - 45 ma.

-.348

-.340 v. vs. S.C.E.

No nitrogen bubbled

i = 70 - 75 ma.

-.346

-.353

-.350

Nitrogen bubbled

i = 70 - 80 ma.

-.527

-.543

-.538

-.549

-.537

-.547

-.538

-.550

-.545

-.547

-.546

-.550

-.547

TABLE XXI (Continued)

60-X Runs

1M HCOOH	35°C	pH 2.61
Nitrogen bubbled		i = 44 - 49 ma.
-.331	-.350	-.355
-.340	-.354	-.352
-.350	-.363	-.356
-.343	-.355	-.359
-.341	-.355	-.358
Carbon dioxide bubbled		
-.343	-.315	-.353
-.330	-.324	-.342
-.346	-.350	-.350
-.350	-.349	-.335
-.334	-.340	-.348
-.352		

TABLE XXI (Continued)

61-X Runs

1M HCOOH	35°C	pH 11.32
No nitrogen bubbled		i = 80 - 90 ma.
-.696	-.679	-.703
-.700	-.698	-.690
Nitrogen bubbled		i = 75 - 85 ma.
-.750	-.750	-.750
-.750	-.750	
Carbon dioxide bubbled		i = 75 - 85 ma.
-.736	-.745	-.735
-.740	-.735	-.750
-.736	-.735	

TABLE XXI (Continued)

62-X Runs

1M HCOOH

35°C

pH 3.50

No nitrogen bubbled

1 = 65 - 70 ma.

-.289	-.278	-.292
-.283	-.307	-.292
-.288	-.296	-.292
-.288	-.284	

Nitrogen bubbled

1 = 62 - 67 ma.

-.410	-.420	-.420
-.412	-.434	-.414
-.416	-.432	-.416
-.418	-.444	-.409
-.416	-.423	-.412
-.419	-.430	

Carbon dioxide bubbled

1 = 62 - 67 ma.

-.417	-.411	-.412
-.418	-.420	
-.412	-.410	

TABLE XXI (Continued)

63-X Runs

1M HCOOH	35°C	pH 3.03
No nitrogen bubbled		i = 40 - 45 ma.
-.282	-.284	-.321
-.296	-.296	-.315
-.287	-.314	-.309
-.291	-.300	-.314
-.276	-.321	-.320
-.299	-.304	-.310
-.304	-.303	
Nitrogen bubbled		i = 40 - 45 ma.
-.379	-.384	-.387
-.377	-.379	-.385
-.377	-.387	-.386
-.383	-.390	
-.386	-.382	
Carbon dioxide bubbled		i = 40 - 45 ma.
-.383	-.380	-.388
-.384	-.378	-.388
-.386	-.392	-.385
-.383	-.389	
-.388	-.388	

TABLE XXI (Continued)

64-X Runs

1M HCOOH	35°C	pH 0.68
No nitrogen bubbled		i = 28 - 30 ma.
-.110	-.132	-.130
-.103	-.124	-.160
-.138	-.133	-.132
-.138	-.104	-.138
-.135	-.129	
Nitrogen bubbled		i = 28 - 30 ma.
-.150	-.162	-.163
-.164	-.164	-.165
Carbon dioxide bubbled		i = 28 - 30 ma.
-.152	-.160	-.162

TABLE XXI (Continued)

65-X Runs

1M HCOOH

35°C

5M H₂SO₄

Nitrogen bubbled

i = 45 - 50 ma.

+.35

+.31

+.30

+.38

+.30

+.35

+.39

+.21

+.45

TABLE XXI (Continued)

66-X Runs

1M HCOOH	60°C	pH = 0.68
No nitrogen bubbled		i = 40 - 50 ma.
-.123	-.142	-.147
-.130	-.143	-.136
-.120	-.142	
-.160	-.138	
Nitrogen bubbled		i = 40 - 50 ma.
-.191	-.190	-.190
-.190	-.187	-.194
-.187	-.187	
Carbon dioxide		i = 40 - 50 ma.
-.196	-.193	-.194
-.195	-.192	-.195

TABLE XXI (Continued)

68-X Runs

1M HCOOH	35°C	pH 0.68
Nitrogen bubbled		
		i = 11 ma.
-.160	-.160	-.160
-.165	-.188	-.150
-.153	-.193	
25.6% CO bubbled		
		i = 11 ma.
-.241	-.250	-.251
-.250		
61.5% CO bubbled		
-.259	-.260	-.261
-.260	-.264	-.270
-.260	-.264	
100% CO bubbled		
		i = 11 ma.
-.282	-.281	-.285
-.281	-.281	-.284

TABLE XXI (Continued)

69-X Runs

1M HCOOH

35°C

pH 2.61

Nitrogen bubbled

i = 10 ma.

-.334	-.333	-.345
-.330	-.337	-.345
-.335	-.343	-.350

Nitrogen bubbled

i = 20 ma.

-.350	-.365	-.362
-.355	-.355	-.362
-.355	-.355	-.362
-.355	-.358	-.364

37.5% CO bubbled

i = 20 ma.

-.360	-.369	-.360
-.367	-.364	-.363
-.365	-.355	

52.4% CO bubbled

i = 20 ma.

-.365	-.368	-.376
-.374	-.374	
-.371	-.370	

TABLE XXI (Continued)

69-X Runs

1M HCOOH	35°C	pH 2.61
68.7% CO bubbled		
		i = 20 ma.
-.378	-.380	-.381
-.375	-.379	-.377
100% CO bubbled		
		i = 20 ma.
-.377	-.389	-.388
-.384	-.392	-.392
-.390	-.380	-.393
-.384	-.394	
Nitrogen bubbled		
2 to 3 minutes after CO off		i = 20 ma.
-.376		-.390
-.382		-.385
Nitrogen bubbled		
45 minutes after CO off		i = 20 ma.
-.314	-.348	-.345
-.327	-.350	-.357
-.342	-.360	-.359
-.337	-.340	-.346
-.342	-.351	-.359

TABLE XXI (Continued)

69-X Runs

1M HCOOH	35°C	pH 2.61
55% CO immediately after last runs		i = 20 ma.
-.352	-.356	-.366
-.352	-.370	-.372
78% CO		i = 20 ma.
-.374	-.377	-.376
-.375	-.375	-.385
-.370	-.380	-.385
-.370	-.383	-.380

TABLE XXI (Continued)

71-X Runs

1M HCOOH

35°C

pH 5.72

Nitrogen bubbled

i = 11 ma.

-.528	-.530	-.538
-.525	-.535	-.540
-.525	-.538	
-.525	-.535	

19% CO bubbled

i = 11 ma.

-.561	-.561	-.565
-.558	-.570	-.563
-.564	-.570	-.574
-.571	-.561	-.560
-.571	-.570	-.574
-.565	-.560	

100% CO bubbled

i = 11 ma.

-.542	-.625	-.545
-.566	-.570	-.578
-.575	-.570	-.547
-.610	-.575	-.560
-.572	-.579	-.550
-.584	-.582	-.573

TABLE XXI (Continued)

87-D Runs

1M HCOOH 35°C pH 4.39

Nitrogen bubbled

i = 10 ma.

-.464	-.468	-.466
-.467	-.470	

CO₂ bubbled

i = 10 ma.

-.442	-.475	-.467
-.462	-.475	

CO bubbled

i = 10 ma.

-.480	-.497	-.505
-.491	-.500	-.505
-.497	-.500	
-.491	-.505	

Nitrogen bubbled
60 minutes after CO off

i = 10 ma.

-.454	-.468	-.472
-.480		

TABLE XXII

Double Layer Capacitance Measurements on Plain Platinumin 1M H₂SO₄ at 35°C at Constant Potential

95-D Runs

no HCOOH

Run	v. vs. S.C.E.	x axis x 50 μ /sec.	y axis x 1 mv.	i _{ac} x 10 ⁻⁴ amps.	C μ f
1	1.15-1/2	5.7	5.0	6.2x2	70-1/2
2	.86	6.6	5.0	8.5x1	56
3	1.55	5.1	5.0	7.6x2	77-1/2
4	1.04	6.6	5.0	9.2x1	60-1/2
5	.74	6.4	5.0	9.2x1	59
6	.17	6.4	5.0	6.3x1	40
7	.45-1/2	5.7	5.0	6.3x1	36
8	.07	5.0	5.0	8.5x1	42-1/2
9	.63	5.7	5.0	6.2x2	71
10	.55	5.3	5.0	5.9x1	31
11	.66	7.1	5.0	4.8x2	68
12	.96	6.7	5.0	8.8x1	59

TABLE XXII (Continued)

97-D Runs

 $1.56 \times 10^{-3} \text{M HCOOH}$

Run	v. vs..S.C.E.	x axis x 50 μ sec.	y axis x 1 mv.	i _{ac} x 10 ⁻⁴ amps.	C μ f
1	.24	5.0	5.0	8.7x.5	22
2	.88-1/2	7.3	5.0	10.0x1	73
3	.32	6.4	5.0	6.6x.5	21
4	1.01	6.0	5.0	6.5x.2	78
5	.77	7.0	5.0	10.0x.5	35
6	.66	5.1	5.0	10.0x.5	25-1/2
7	.59	5.3	5.0	10.0x.1	26-1/2
8	1.23	7.7	5.0	10.0x.5	77
9	.56	5.1	5.0	10.0x.5	25-1/2
10	.01	4.8	5.0	10.0x.5	24
11	.42-1/2	5.0	5.0	10.0x.5	25

TABLE XXII (Continued)

98-D Runs

 $1.56 \times 10^{-1} \text{ M HCOOH}$

Run	v. vs. S.C.E.	x axis x 50 μ /sec.	y axis x 1 mv.	i_{ac} x 10^{-4} amps.	C μ f
1	0.55	6.2	5.0	7.5x.5	23
2	0.38	5.2	5.0	7.5x.5	19-1/2
3	1.27	6.1	5.0	10.0x.1	61
4	1.01	7.0	5.0	10.0x.1	70
5	.93	7.5	5.0	10.0x.1	75
6	.85	5.9	5.0	10.0x.1	59
7	.69	5.0	5.0	10.0x.5	25
8	.23	4.8	5.0	10.0x.5	24
9	1.50	5.8	5.0	10.0x1.0	58
10	.06	4.4	5.0	10.0x.5	22

TABLE XXII (Continued)

100-D Runs

1.56M HCOOH

Run	v. vs. S.C.E.	x axis x 50 μ sec.	y axis x 1 mv.	i _{ac} x 10 ⁻⁴ amps.	C μ f
6	1.03	6.7	5.0	10.0x1	67
7	.52	6.4	5.0	10.0x.2	13
8	.43	6.6	5.0	10.0x.2	12
9	1.25	5.8	5.0	10.0x1	58
10	.30	7.8	5.0	10.0x.2	15-1/2
11	.81	7.6	5.0	10.0x.5	38
12	.69	5.0	5.0	10.0x.5	25
13	.03	8.9	5.0	10.0x.2	18

E. Nomenclature

C	concentration, capacitance
C^0	initial concentration
$\bar{C}_1$	average double layer capacitance
D	diffusivity
E	potential
e^-	electron
F	Faraday's number
f	farad
G	free energy
G^*	free energy of activation
h	atoms of hydrogen per cm^2
I^0	exchange current
i	current
i_0	current density
i^0	amplitude of alternating current
K	constant
KWH	kilowatt hour
k	rate constant
NCE	normal calomel electrode
n	number of electrons
P	pressure
Q	charge
R	gas constant, resistance
SCE	saturated calomel electrode
T	temperature
τ	time, see Figure 16
t	time
V	voltage
$\bar{V}$	rate
v	volt
x	distance
Z	charge per ion, impedance

α	transfer coefficient
Γ	moles per unit area adsorbed
γ	see equation (47)
η	overpotential
θ	time, see Figure 14
λ	see equation (45)
μ	chemical potential
μ	electrochemical potential
ρ	number of particles
τ	transition time
ψ	inner electrical potential
ϕ	phase angle
R	resistance, ohms

Subscripts

e	equilibrium value, electrochemical reaction
t	total
l	double layer
s	solution, series circuit

F. Location of Original Data

The original data are located in three notebooks which are in the possession of Professor Charles N. Satterfield, M.I.T., Department of Chemical Engineering.

G. Limits of Literature Survey

The literature survey covered the period from about 1920 to December, 1962. Any references cited for work prior to 1920 were for the primary purpose of developing historical background.

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I. Biographical Note

The author, Robert Slett, was born in Chicago, Illinois on September 14, 1936. He attended elementary school and high school (Senn) in the Chicago Public School System.

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