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STUDY OF THE DIRECT METHODS FOR THE MEASUREMENT OF POLARIZATION

by
Robert Stephen Karpiuk

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A review of polarization data shows an exceedingly wide divergence in the values for polarization or overvoltage obtained by different investigators. Since the commutator method has been shown to be definitely inferior to the direct method of measurement, a study of the four common modifications of the direct method and of some of the variables affecting the measured potentials was made, both potentiometrically and oscillographically, in an attempt to clarify this situation.

The methods studied were (a) the Haring cell arrangement, (b) the front method, i.e., with the tip of the probe in firm contact with the front face of the electrode, (c) the back method, i.e., with the probe placed anywhere behind the electrode, and (d) the hole method, in which the tip of the probe was brought from the back, through a hole in the electrode and placed flush with the front face.

Both static values and polarization data were obtained with large copper electrodes in acid copper sulfate solution and with bright platinum in molar sulfuric acid. By following certain precautions previously found necessary in this laboratory, an accuracy of 1 mv. or better was attained.

It was found, in a study of both large and small electrodes, that a uniform current density was absolutely necessary for significant results by any method. A non-uniform current density creates regions of different concentration resulting in corrosion currents. This may add to or oppose the potential difference being measured and appears as an IR drop between the two half-cells used in the measurement. To obtain the above ideal condition, the back of the electrode must be insulated in order to limit the apparent surface area to the cross-sectional area of the cell. With smaller electrodes, the position of the probe has a pronounced influence on measured potentials, and correct polarization values can not be obtained by such an arrangement.

In all cases in which measurements were made by the various methods, and the back of the electrode was properly insulated, the Haring cell method gave consistently lower values (by about 10%) for polarization than the front method. The results are highly reproducible and if deviations of the above magnitude are permissible, the method provides a simple convenient tool.

Measurements by the front method must involve both an IR drop and a shielding effect which, however, tend to counteract each other. Results of this research indicate that the corrections for IR drop between the probe and the electrode, by using the bulk conductivity of the solution, may be in error. It has been shown also that the extrapolation technique

used to correct for IR drop exaggerates the error due to the shielding effect. Thus, no exact value of polarization can be obtained by the front method even when the commonly used methods for corrections are used.

On the basis of this research, it is concluded that the back method gives precise and reproducible values to 1 mv., provided precautions are taken to ensure uniform current distribution and to insulate properly the electrode. If a uniform current distribution can not be obtained, the hole method will give the best results provided suitable precautions and design are employed.

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INTRODUCTION

From the beginning of quantitative electrochemistry, approximately 100 years ago, potential measurements have been a major consideration both in theory and practice. For many years, because of lack of equipment, measurements were limited to total cell potentials. It was soon appreciated that the cell potential is a combination of at least two separate parts: the sum of the two single electrode potentials and the IR drop through the solution. Since the potential of a single electrode can be determined only with respect to a second electrode, preferably one which theoretically has zero potential, these separate portions of the total potential could only be determined after a suitable standard had been adopted.

The first such standard was ultimately developed by Lippman[1] in 1873 in the form of the capillary electrometer, which was considered on the basis of fundamental theory, at that time, to have zero potential. Later, other electrodes were developed which on other theoretical grounds should also have had zero potential. However, when these were intercompared they were found to show differences of potential. This led eventually to the adoption of the normal reversible hydrogen electrode as an arbitrary standard, and it was assigned the value zero at all temperatures. Due to the limitations in the construction of the hydrogen electrode, other secondary reversible standards have been constructed for practical use.

Under actual working conditions, current flows between electrode and solution. It was early noted that the potential of an electrode was always ~~greater~~ different when current was flowing than when it was not. Observation of this phenomenon, later known as polarization, has recently been recognized as the best means for studying the mechanism of electrode processes, which is today the major unsolved problem in electrochemistry. The accurate measurement of electrode potentials, under current flow, is therefore of the greatest importance.

Reversible electrodes in equilibrium with their ions in solution can be treated thermodynamically but irreversible electrode reactions may not be so treated, i.e., reactions which require more than an infinitesimal change in electrode potential to reverse the direction of the current through the electrode.

The potential of an electrode in a solution depends upon several factors. If no current is flowing through the electrode, the potential difference between it and the solution may be determined easily with reference to the assumed standard. However, if current is allowed to flow through the electrodes, both concentration and electrochemical changes are produced. The difference between the electrode potentials with and without current flowing is in general called polarization.

The various methods used for the study of polarization and electrode processes may be grouped under three general headings: (1) through the measurement of electrode potential

changes with changes in current density; (2) through the measurement of potential changes with time and, (3) through observations of film formation, dissolution or other changes at the electrode surface.

Method (1) has been most generally used. The data for this method are obtained either by (a) measurement of the potential at a series of constant current values or (b) measurement of the current at a series of definite potentials. Both methods will give the same numerical values if sufficient time is allowed to reach a steady state. A typical curve, such as shown in Figure 1, consists of two linear sections connected by a transition interval. The so-called "decomposition potential" is located somewhere within this transition interval. If the electrode in the system is highly reversible, then the decomposition voltage will be the same as the single potential of the electrode in the system. In most instances, however, the electrode reaction is not electrochemically reversible so the measured decomposition potential is greater than the single electrode potential measured in the solution, or the theoretical value; the difference, i.e., one type of polarization, is called "overvoltage".

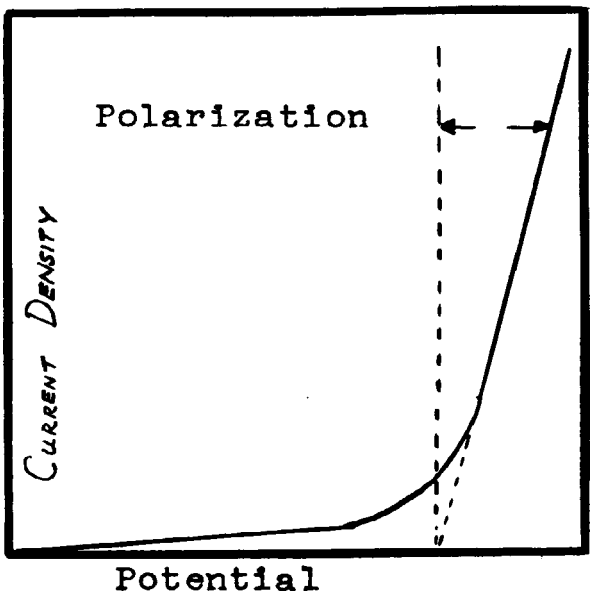


Fig. 1. Typical Current Density vs. Potential Curve.

The inflection of the current-density-electrode potential curve is never sharp, and various methods have been suggested for selecting the proper value. This inconsistency accounts partially for the lack of agreement by various authors. Several ways for the determination of the decomposition potential have been described in the literature: (1) some authors project the second linear portion of the curve till it crosses the electrode potential axis as in Figure 1; (2) others project the two linear portions to their point of intersection; (3) in the older literature the appearance of the first bubble on increase of current density, or the disappearance of the last bubble on decrease of current density beyond the decomposition potential; and (4) the appearance of a certain number of bubbles in a specified time, e.g., one bubble per minute, was considered as representing the decomposition potential.

The second method for studying polarization consists in observation of the variation of potential with time. Early studies were made with the commutator in which the potential was mechanically interrupted for varying lengths of time and the potential measured during these intervals. Between then and the present, many types of experimental arrangements have been used as a commutator culminating in the cathode ray oscillograph. Both charge and discharge curves have been studied. The results have led to several theories of the mechanism of polarization and overvoltage.

In the third method the nature of the materials formed as the result of current passage may be conveniently studied through their influence as depolarizers when the current is reversed, as shown by potential-time curves. From a study of these curves, the specific nature of the electrode reactions that took place during the forward passage of current can be deduced.

In all cases, the changing potentials have been measured by reference to some type of standard electrode. However, there has been wide divergence in opinion as to the technique, manner and method of carrying out these measurements. The major developments during the present century have been extensive testing, detection and elimination of sources of error. The result has been the discarding of several methods and improvement of the remainder, so that now fairly reproducible polarization and overvoltage values may be obtained.

All methods for the measurement of polarization may be grouped under two headings: the direct method and the indirect or commutator method. The direct method includes all variations of technique and apparatus in which measurements are taken while the polarizing current is passing through the cell. In the commutator method, the actual measurement is taken in a more or less short interval during the periods of interruption of the polarizing current.

In all cases, until recently, when both methods were used to make measurements under otherwise identical conditions, the direct method gave larger values than the commutator

method. Those who supported the commutator method accounted for this by contending that measurements by the direct method contained an IR drop through the solution in addition to the desired electrode potential. On the other hand, those who supported the direct method pointed out that a polarization potential drops off exceedingly rapidly so that a portion is lost between the time of opening the polarizing circuit and the time of making the potential measurement. After many years of study it was shown in this laboratory[2,3,4,5] that both methods give identical values if measurements are properly made.

In the great number of papers which have appeared in the literature on the subject of polarization and overvoltage since Gautherot's[6] detection of the phenomenon, the striking fact is the pronounced disagreement in the experimental values obtained by supposedly similar methods and equipment. In the introduction to overvoltage in the International Critical Tables, Knobel states that "the actual magnitude of any overvoltage cannot be specified precisely because of uncontrollable variability". Farther on he says: "The hydrogen overvoltages are most reliable and by careful duplication of conditions are reproducible to 0.1 volt", and concludes with, "It is impracticable to attempt to average the results of different investigators on accounts of the sensitivity of the many conditions of measurement". That progress is being made in this very important phase of electrochemistry is

indicated by the fact that modern workers often set the limit of reproducibility at 0.01 volt. However, even in the work of modern investigators employing refined techniques, there are still considerable variations. For instance, mercury is possibly the metal most investigated and the one for which the overvoltage is claimed to be known most accurately; yet, a comparison of the values of Bethune and Kimball[7], Iofa and Mikulin[8] and Bockris and Parsons[9] shows a deviation of 20% or more.

Among the major factors which contributed to these variations are: lack of standardization of technique and of method for selecting the decomposition potential, differences in surface condition, the presence of trace impurities, and of course the type of method employed.

Thus the choice of method of actually measuring the magnitude of polarization is still a matter of opinion. Several different ways are being employed, and, unfortunately, no standardization had been attempted. Each modification is championed almost fanatically. An enumeration and discussion of the methods are given in the Theoretical Section of this dissertation. A study of one phase of this problem was suggested by Dr. A. L. Ferguson as the subject of this investigation.

Extensive studies in this laboratory have dealt with the comparison of the commutator and direct methods for measuring polarization. The results of this work have demonstrated the superiority of the direct method. The chief objection which

has been raised to the direct method is that the potential measured must invariably include a potential due to an IR drop between the tip or "Luggin capillary" of the reference electrode and the active electrode. Various investigators using the direct method have adopted different means of reducing this effect to a minimum, each maintaining that his own method is the only correct one. In order to attempt to settle this controversy the present work involves the simultaneous measurement of the potential by the various methods both potentiometrically and oscillographically.

HISTORICAL AND THEORETICAL

Introduction.

The history of polarization, and hence its detection and measurement, is almost as old as electrochemistry itself. Some claim that the original detection was by Gautherot[6] in 1801, just nine months after Volta's historic announcement of his "pile". As suitable measuring devices were then unknown and unavailable, Gautherot detected this phenomenon by differentiating the taste while the current was passing and the taste after the current had stopped flowing. He recognized that the sensation in the second case was that of reversed polarity to the first case. His apparatus consisted of a voltaic pile, two platinum wires and dilute sulfuric acid. Almost simultaneously, Johann Ritter of Jena duplicated Gautherot's work using gold wires.

Since that early beginning, the literature of polarization consisting of facts, data and theories, became more profuse. The present literature is too extensive for a complete survey, and errors and contradictions appear frequently. This voluminous literature has only added to the general confusion relative to correct values and theories. As the quantity of published material is enormous and complex, only that pertinent to this investigation will be considered.

Many excellent reviews which cover the field of polarization, hydrogen overvoltage, kinetics of irreversible electrode processes and theories, have been published within the

last twenty years[10-19]. A comprehensive review of the present state of the hydrogen overvoltage theories has been given by Bockris[17], and the General Discussion of the Faraday Society on Electrode Processes[18] has brought together a wealth of informative material by the active workers in electrochemistry. The latest review on cathodic hydrogen evolution is given by Bockris and Potter[19].

Definitions.

There are numerous definitions of polarization and overvoltage, as well as many names for the same phenomenon. Names such as metal overvoltage, true overvoltage, false overvoltage, total overvoltage, polarization overvoltage, type A overvoltage, type B overvoltage, negative overvoltage, and electrolytic overvoltage only added to the existing confusion. The phenomenon was first given a name (Ueberspannung) by Caspari[20] in 1899, and later translated as overvoltage. Caspari considered hydrogen overvoltage as the difference between the potential of the hydrogen electrode and the potential of the electrode in question under the same conditions when hydrogen is being evolved upon it during electrolysis. Tafel[21,22] associated the idea of overvoltage with the difference of potential between the electrode concerned at which gas is evolved during electrolysis at a definite current density and the reversible electrode in the same electrolyte. Foerster[23] considered overvoltage as the excess potential necessary above the thermodynamic reversible value required

to set gas free at the electrode. Other definitions might be listed, but the definition of polarization which is generally accepted and the one used in this dissertation is that of Blum and Vinal[24]. They define polarization as "Any change in the static or equilibrium potential in a given electrolyte produced by the flow of current, regardless of the mechanism". It is applied to any electrolysis, whether the products are solid or gaseous. The term overvoltage is restricted to the excess of potential over the equilibrium value required to reverse the normal direction of current through an electrode.

Polarization.

In the application of thermodynamics to electrochemistry, the same tacit assumptions of reversibility and thermodynamic equilibrium are retained. Thus, for the reversible electrode potential, E_r, of copper in a solution of cupric ions, the process occurs reversibly or infinitely slowly. Experimentally, the reversible potential must be measured in such a manner that no net current is passing through the circuit, i.e., at a static condition.

If the potential, E_p, of the copper electrode is measured when current is flowing at a current density, i, then invariably E_p differs from E_r and this difference from reversibility may be defined as polarization, η, at the current density i. Thus,

$$E_p - E_r = \eta \qquad (1)$$

It is possible to distinguish at least three main causes

of irreversibility in electrode reactions due to passage of current:

(1) Concentration polarization in which positive ions, such as cupric ions, in the immediate vicinity of the electrode-solution interface, may become depleted due to the deposition of the positive ions and diluted due to the water of ionic hydration, and hence, the cathode potential which depends upon the concentration of ions in the solution in immediate contact with the cathode according to Nernst's equation, is made less positive. Since, in the method used by most investigators, the reference electrode is situated outside the region affected by the concentration changes near the electrode at which the reaction is taking place, the measured potential difference between the two electrodes may include a term due to the concentration difference. Thus, if C_e is the concentration or activity of the ions at the electrode interface, and C_o the concentration or activity of the ions in the bulk of the solution, and assuming small departures from equilibrium so that thermodynamic equations are applicable, the overvoltage caused by these concentration changes is:

$$\eta = \frac{RT}{nF} \ln \frac{C_e}{C_o} \qquad (2)$$

where R is the gas constant, T temperature in degrees absolute, n the valency of the ions in question and F the faraday.

This kind of polarization, as defined above and which

is unavoidably present in every electrode process occurring at an appreciable rate, is termed concentration polarization (or concentration overvoltage), η_c. It cannot be avoided, but may be greatly reduced by rapid agitation or other devices which increase diffusion so that $C_e \cong C_o$.

(2) Activation polarization is a term used to signify a considerable polarization which appears to have its origin in some slow process among the reactions involved at an electrode. Relating this slow process to kinetics and the concept of high energy of activation, this polarization (or overvoltage) is termed activation overvoltage, η_a.

(3) When the probe or Luggin capillary leading from the reference standard is placed in front of the electrode in question, and if the measurements are made while the polarizing current is flowing, or if a film (usually oxide) is present on the electrode surface that sets up an appreciable resistance to the passage of current, the measured value will include a potential of an IR nature between the tip of the reference electrode and the electrode under investigation. This measured potential, often called ohmic overvoltage, η_r, is then given by IR where I is the current strength and R the resistance between the electrode and an equipotential surface in the capillary tip. Since η_r is not a true active potential, most of those working in the field agree that it should not be considered as a part of overvoltage. As frequently measured, the value is the sum of the three components, thus

$$\eta_m = \eta_c + \eta_a + \eta_r \qquad (3)$$

Theoretically, it should be possible to distinguish between true overvoltage and an IR drop, since, when the circuit is opened, the latter should decay instantly while true or active overvoltage decays more or less slowly. Though there is this distinction between the two types and it might, therefore, be concluded that they could be distinguished easily, yet all efforts to devise equipment which will provide an unquestionable distinction have failed since overvoltage measurements were first made.

Resistance Polarization

In the direct method for measuring overvoltage, the tip of the Luggin capillary of the reference electrode is generally placed as close as possible to the front face of the working electrode. Thus the electrode potential measured while the current is flowing will include a potential drop due to the resistance of the solution between the tip and the electrode. The magnitude of this resistive potential drop depends upon the experimental set-up and the conductivity of the solution. The resistance due to oxide or other poorly conducting films on the electrode surface provides another problem since it cannot be measured by ordinary means.

If the total concentration of the electrolytes near the electrode remains constant, this resistive potential drop, or resistance polarization must be given by

$$\eta_r = \text{constant} \times I \qquad (4)$$

Such an equation should hold at each current density for

electrolytic systems which contain a large excess of some foreign electrolyte which takes no part in the electrode reaction, so that the concentration throughout the solution is constant. In this case, it is possible to apply a correction for the resistance polarization, or in many instances, to neglect it entirely in comparison with the other types of polarization.

In other cases, such as the deposition of a metal from a solution containing one of its salts, this is no longer true. Owing to concentration changes with current density, the resistance of the solution near the electrode is not constant, and may attain very large values if the diffusion layer becomes seriously depleted of ions. Another factor which has received some consideration and the effect of which is often many times that due to the removal of the ions is the dilution at the electrode interface caused by the dehydration of the liberated ion and the migration of water with the ion involved. The uncertainty is due to the unknown degree of hydration of ions even under ideal experimental conditions, without the complexities caused by electrolysis. One factor which has not received any consideration so far is the orientation of solvent molecules at the electrode-solution interface and its accompanying salting-out effect.

For the study of convection and diffusion processes, semi-empirical and approximate methods utilizing the concept of the "diffusion layer" of Noyes and Whitney (1897) and

developed by Nernst (1904) and Brünner (1904) have been employed. The results of such calculations are dependent upon so many doubtful assumptions that their validity is highly questionable. It is sufficient for the present purpose to indicate that due to diffusion and electrolytic transport, concentration changes are produced in the electrolyte which will give rise to a potential difference as a result of current flow. This potential difference could be calculated by the well-known Nernst equation if the concentration ratio could be accurately calculated. However, this has not been successful for practical systems.

The theoretical consideration of this resistance has received only scant attention. Hickling and Salt[25] consider the calculation of the IR drop as inherently inaccurate owing to the existence of an unknown specific conductance in the diffusion layer, whereas Frumkin[26] considers it permissible to use the bulk specific conductance. This latter view is undoubtedly incorrect, although Bockris, et al.[27] in their experiments on the screening effect of the Luggin capillary on the current lines used the ~~specific~~ conductivity of the bulk electrolyte in the calculation of the ohmic drop.

Methods of Measurements of Polarization.

As has been previously stated, there are two distinct classifications of methods for measuring polarization; the direct method and the indirect or commutator method and in all work until recently these methods gave different results.

This has been one of the major reasons for the disagreement of the values reported for polarization.

Commutator Method

The general principle behind all commutator methods is that the electrolyzing current is interrupted momentarily during the measurement of electrode potential. The period of interruption is made as small as possible and then gradually increased. The decay curve is then plotted and extrapolated to zero time. Various devices have been used to interrupt the current such as tuning forks, mechanical relays, rotating commutators, and the latest, electronic interrupters. With the electronic interrupter used by Hickling[28] and by Yeager and co-workers[29] at Western Reserve, the shortest time interval is of the order of 10 microseconds. This materially decreases the loss of potential due to the decay immediately following the current interruption, but it still has many of the inherent errors of all commutator methods. The comparative work done by Bockris using the direct method with that of Hickling in similar solutions indicates that results by both methods may be reproduced to 0.01 volt.

Schuldiner and White[30] used a D.C. interrupter method for oscillographic studies of time - potential changes at an electrode surface for corrosion studies. The time interval was one to 120 microseconds. The phenomena which occurred at the electrode such as potential changes, double layer capacity effects and resistive potential during interruption

were measured. These phenomena were discussed in terms of an equivalent electrical circuit.

Apparently the first instrument making use of the commutator principle was that devised by de la Rive in the 1840's using a Saxton's machine; he had the same purpose in mind of eliminating the IR drop. Similar commutators were also built about the same time by Poggendorff and Vorsellmann de Heer. Later Raoult and then Helmholtz employed it, but it was not until the work of Le Blanc in 1910 that the method became extensively used. More recently, many others such as Rothe, Pring, Glasstone, Hickling and, particularly, Newbery championed the commutator method.

Work by Dunnil[31], Tartar and Keyes[32], Bowden[33], Baars[34], MacInnes[35], Knobel[36] and many others, especially Ferguson and co-workers[2,3,4,5] have convincingly proven that the commutator method does not give true polarization values and they favor the direct method.

Direct Methods

A group of experimental methods generally classified as the "direct method" has one thing in common: the polarizing current is flowing while measurements are being taken. The techniques involved are basically the same with the exception of the position of the Luggin capillary. One group of investigators prefer the tip in front of the working electrode, another group logically claims the proper position is behind the electrode whereas a third group disagrees with the two

above and insists that the only correct method is to insert the probe of the search electrode into a hole drilled in the active electrode. As will be seen each method has its advantages and thus its adherents.

Slightly different in the experimental arrangement is the method devised by Haring[37], in which no search electrode is employed, but a three compartment electrolysing cell is used. Another method is that based on using a metal electrode as a standard at a definite distance from the active electrode and correcting for any IR drop involved. The other methods described below are outmoded and are only of historical interest.

PROBE IN FRONT OF ELECTRODE

Some of the modern workers in the field of polarization and overvoltage place the tip of the Luggin capillary of the salt bridge connecting the half cell in front of the electrode under consideration. Although it had been used in the past frequently, its more or less universal acceptance was not until the work of Knobel, Caplan and Eiseman[38] reported unfavorably on the technique of positioning the probe of the reference half cell behind the working electrode.

It might be pointed out here, however, that they presented no experimental evidence for their conclusion and, from a careful analysis of their arguments, their statements appear open to question. In the description of their apparatus they state that they used electrodes the backs of which were insulated (a very necessary precaution in all such work); however, in their arguments against the use of the electrode

in back they state, "This is obviously in error for the current density is indefinite and much smaller on the back face of the cathode and the potential so measured bears no relation to the potential difference between the electrode and the solution in contact with the front face. While the electric potential of the whole electrode is the same, the solutions in front of and behind the electrode by no means have the same electric potential, and therefore, the potential difference between the electrode and electrolyte will be different on the two sides. While seemingly unnecessary, we have tested this point experimentally and confirmed the statement made". The above statements would appear to imply that the back of the electrode was not completely insulated.

Well known older investigators such as Haber[39], Foerster and Muller[40], and Fisher[41], all used the tip in fron of the electrode at one time or another. Of the later workers, Holler[42], Lloyd[43], Butler[44] and practically all the workers using the commutator method, with the possible exception of Newbery[45], placed the exploring tip in fron of the electrode. Tartar and Keyes[32] compared simultaneously the commutator with the direct method, using the tip in front for the latter method.

PROBE IN HOLE IN ELECTRODE

The method of inserting the tip of the exploring standard electrode in a hole through and flush with the front face of the electrode under investigation was used by Haber[47] as

one of the early modifications of the direct method. He gave a detailed account of the electrode construction, as did Foerster and Müller[40] and Müller and Soller[48]. Later investigators from 1926 on who also used this method were Fürth[49], Grant[50], and Lloyd[51] and recently (1948), it has been championed by Piontelli and Poli[52].

Grant used the method of drilling a small hole in the cathode so that the end of the capillary tube was flush with the electrode at the point where it emerged. He bubbled hydrogen across the tip so as to keep it clear from minute bubbles. He found that this had a marked effect on stabilizing the overvoltage so that consistent and reproducible results were obtained. Piontelli and Poli recommended this method to overcome some of the difficulties encountered in the measurement of polarization.

PROBE IN BACK OF THE ELECTRODE

The original direct method was devised by Fuchs[53] in 1875. His experimental arrangement may be described as follows: The metal being examined was made the cathode, the anode was platinum and the electrolyte was dilute sulfuric acid. By connecting the electrolyte behind the cathode by means of a siphon tube to a normal reference electrode, the voltage of the combination could be obtained, and hence that of the cathode by simple subtraction. It is to be noted that the connecting tube was originally placed behind the cathode in Fuch's original method. The distinct advantage of this

method was recognized by the early researchers and in the discussion of Sand's[54] paper on "Measurement of the Potential of the Electrodes in Stationary Liquids", (1905) J. K-H. Inglis asked Dr. Sand "whether he had tried the plan (advocated by Luther) of placing the capillary connection to the normal electrode just behind the electrode. In this way, since the capillary would not cut the lines of force between the anode and cathode, no fall of potential due to Ohm's law would come into consideration and therefore the calculation would become easier".

A comprehensive list of the investigators who used this method would be very lengthy, but it is interesting to note that many of the more authoritative and more often quoted results were obtained by this method. Such workers as Roszkowski[55], Haber[47], Müller[48], Nutton and Law[56], Pring and Curzon[57], Thiel and Breuning[58], MacInnes[35], Baars[34] and Ferguson and co-workers[2-5,59], authored many important articles and all utilized the method originated by Fuchs. Odd as it may seem, Newbery[45], for forty years the most active advocate for the cummutator method, placed the capillary tip behind the electrode. In 1919, he stated, "A standard mercurous sulfate or calomel electrode dipping in the liquid behind either electrode showed the same potential difference with respect to that electrode in any position . . ."

Lately, Petrocelli[60], who studied the overvoltage at oxidation-reduction electrodes with indications that both

activation and concentration polarization were present, employed the tip "behind" method. Turner[61], who studied the anodic polarization effects on nickel in sulfuric acid also positioned the capillary tip behind the working electrode.

Comparative Analysis of the Above Methods

There are three general disadvantages of the direct method with the capillary probe in front of the electrode in question: (1) part of the electrode surface is shielded from its share of current lines which results in a decreased current density directly in front of the tip and an increased value outside, (2) at high current densities, the ohmic potential difference between the end of the tip and the electrode may become significant in the total measured potential, and (3) local differences of potential over the electrode may affect the working electrode. It should be understood that the potential actually measured by this method is that at the spot on the electrode directly in front of the capillary.

Using the modification of positioning the half cell in a hole in the cathode, the disadvantages enumerated above are only partially removed. Thus, instead of (1) we have an area of higher current density around the metallic edge of the hole due to the distortion of the lines of force to the periphery of the hole and it is the potential at this periphery that is actually measured. There is no assurance that (2) is eliminated and consideration would show that this is dependent upon the width of the glass in the capillary tip and this ohmic drop is then the product of the distance from the

solution of the tip to the metal serving as the electrode and the increased current density at the periphery of the hole. The change in (3) is probably magnified, because of the higher energy area at the edge of the hole due to the drilling process.

However, if the tip is placed behind the electrode under investigation, all these disadvantages are greatly reduced or completely removed. No shielding of the current lines occurs and no IR drop is measured since the current lines do not go beyond the working electrode if the back is insulated and the working electrode is properly placed. This fact has been demonstrated experimentally on many occasions. Another indication of the merit of this location is the experimental fact that the same value is obtained irrespective of the location of the tips at the back of the insulated electrode. In regard to criticism (3), this arrangement gives only a single value for the potential for the electrode.

Horsford Method[62]:

This is one of the oldest methods (1847) for the quantitative determination of polarization. A current was passed between two electrodes in a rectangular trough and the current and voltage measured. The electrodes were brought closer together and the current increased, but by inserting a resistance wire in series with the cell, the current could be restored to the original value. Horsford assumed that the effect of polarization was the same in both positions of the plates and that the resistance of the wire then gave the

value for a column of liquid equal in length to the distance through which the plates were moved together. Knowing the resistivity of the solution and the original distance between the electrodes, the total polarization can be calculated. This method is dependent upon the accuracy of the linear measurement and has the disadvantage that it does not give anodic or cathodic polarization, but only total polarization. This method, with slight modifications, is still used for semi-quantitative results.

Haring Method[37]:

This method of measuring polarization and resistivity was devised in 1926, improving the Horsford method. In the experimental arrangement, the electrodes which serve as anode and cathode, respectively, have each an area equal to the cross-section of the solution. This condition is assumed to produce a uniform current distribution throughout the cell and on the electrodes, an essential requirement for significant measurements of polarization and resistivity. The intermediate electrodes consist of gauze which are assumed to have no polarization because of continuous mixing from the two sides. In short, these gauze electrodes are supposed to constitute non-polarised electrodes. To be effective the holes must be large enough (20 to 8 mesh) to facilitate convection and mixing of the solution and the metal area large enough to prevent appreciable polarization by any small amount of current that may be drawn from the gauze during potential measurements, either with a high resistance voltmeter, or a

potentiometer for greater accuracy.

This method does not claim to be accurate, but only approximate and convenient. For these reasons it has been widely used in industrial practice, as well as for semi-quantitative research. There is a difficulty in measuring accurately the lengths of the various compartments, especially since they change in length with plating time. It is difficult to prove that the gauze electrodes are completely non-polarizable. The results give a single value of polarization for the entire cathode surface. Different areas of the electrode are at different potentials as the processes taking place vary from locality to locality in the electrode surface, particularly the cathode during a plating process.

The Haring cell is divided into three compartments; the center compartment is assumed to have no polarization and the measured potential between the two gauze electrodes is all resistive potential. As the three compartments are equal in length and area, the difference in potential of the anode or cathode compartments from the middle compartment is assumed to be due only to polarization for the respective electrode.

The question of accuracy of the Haring cell method for measuring polarization was the subject of some discussion based on the article by Petrocelli[64]. The author states, "Our experience with the cell shows that there probably is some polarization at the gauze electrodes; however, we do not believe that our values differ from the true values by more than 5%".

Taft and Messmore[65] studied the influence of gelatin upon the polarization at the cathode during the deposition of copper using the Haring cell. They record, "The method of Haring, while doubtless not as precise as other methods, is admirably adapted for our present needs . . . this method gives the average polarization over the entire surface of the electrode and not that due to any particular area". They undoubtedly mean not "average" value, but a single value.

A modified Haring cell was used by Stareck and Taft[66] for the study of irreversible processes involved during the electrolysis of silver from silver nitrate and from cyanide solutions on platinum electrodes. They concluded from their experiments that the voltmeter method using the Haring cell is not satisfactory for irreversible reactions. They found that it was impossible to find gauze electrodes at which polarization never occurred and at high current densities they frequently had sufficient polarization to cause an electrode reaction to occur on the gauze surfaces.

Dorrance and Gardiner[67] employed the Haring cell for polarization and resistivity measurements on nickel plating solutions using the inaccurate voltmeter method. Gauvin and Winkler[68] have studied this method to obtain reproducibility in determining the gelatin concentration in copper refining baths by changes in polarization. They studied the effect of acid concentration, temperature, addition agents, surface condition and time. The greatest single contributing cause for

the lack of reproducibility was claimed to be the absence of a "steady state" surface on the copper cathode which may take 50 to 90 minutes to acquire. Lately, Schrier and Smith[69] used the Haring cell along with the standard half cell technique in an attempt to obtain reproducible results in a study of acid copper sulfate solutions. They found that the gauzes were polarized to some extent owing to the concentration changes produced in the electrolyte during electrolysis, when the lower layers of the solution became richer in copper than the upper layer.

Kern and Rowen[90] compared the Haring method with the direct method using the Graham type of reference cell and copper electrodes in a $CuSO_4$ solution and concluded from his measurements that the Haring cell gave higher anodic and cathodic polarization potentials than the calomel electrode as a reference electrode. Differences amounting from 0.006 v. by the direct method to 0.022 v. by the Haring method at 55 degrees for the anode and 0.016 by the direct method to 0.029 by the Haring method at 55 degrees for the cathode values are recorded. Variations illustrated here deviate by more than 50%.

Small Wire Electrode as Reference

Another approximate method, which is not entirely new, was used by Fink and Philippi[72] in their studies on copper refining cells. Their exploratory electrode was made of 1.5 mm. diameter copper wire which was immersed in the solution to the same depth as the anode and cathode. By means

of a high resistance voltmeter, the voltage readings were taken between the anode and exploring electrode when the latter was located at the distance 5, 10, and 15 cm. from the anode. In addition, the overall voltages between the anode and cathode were taken immediately after each of the above readings. By plotting these values, it is possible by extrapolation to determine the anode and cathode polarization as well as the IR drop through the solution.

The above technique may be criticized on possibly three points: (a) a single 1.5 mm. diameter wire as a reference search electrode may have some polarization at the time the measurement is made. Haring strongly recommends as large area as possible to give accurate results and this large area is the purpose of a gauze electrode; (b) it is difficult to measure exact distances with the exploratory electrode and a difference of 0.01 inch will make an appreciable error in the determination of anode and cathode polarization; and (c) in view of the discussion on resistance polarization, there is extreme doubt as to the validity of the extrapolation of the IR drop at the electrode-solution interface. The use of a high resistance voltmeter does drain some current from the cell being measured and decreases the polarization.

A similar method was used by Carmody and Rohan[73] in their study of polarization at oxidation-reduction electrodes. They used an ordinary platinum wire sealed-into-glass electrode which was brought up to within 1 mm. of the face of the investigated electrode. The wire was covered with paraffin

to the tip where only the cross-section was left exposed. They criticized the ordinary search electrode when high current densities and high concentration polarization are present, claiming that in all probability the presence of the tip close to the electrode interferes with the normal convection processes by which the ion involved is brought up to or removed from the electrode surface. Due to this interference, abnormal concentrations prevail at this point which result in abnormal measured voltages. They also claimed that the use of an inert electrode as reference avoids junction potential. The voltages between the several electrodes were read on a Leeds and Northrup student potentiometer.

The positioning of the reference electrode at a measurable distance from the experimental electrode always introduces the necessity of estimating the IR drop in the solution and particularly that portion between the search and working electrodes. These authors used the bulk conductivity in their estimation and they claimed that the element of uncertainty was insignificant. There seems to be little doubt that this method of determining IR drop is erroneous. There is still sufficient shielding to cause disturbances in the current path. They give no experimental evidence to support their contention that the "inert" electrode is really unaffected by the experimental conditions.

Additional Observations Relative to the Difficulties of Measurements

Piontelli and Poli[52], in an excellent review have

discussed some of the difficulties encountered in the measurement of activation polarization such as (1) the superposition of concentration polarization on the barrier effects (activation polarization); (2) the difficulty of measuring polarization directly without including chemical effects; (3) the difficulty in obtaining uniform current distribution on the electrode; (4) the possibility that measurements cause local displacements in the uniform distribution of current density; (5) the uncertainty of the values of the actual effective area on the electrode surface which is always greater than the apparent surface area and causes the value of the current density to be uncertain; (6) the effects of the methods of preparing the electrode, the treatments to which the electrodes have been subjected and the condition of the surface; and (7) the fact that current density and polarization vary generally with time. They recommended the following precautions to attempt to insure reproducibility: (a) the use of electrodes prepared under standard conditions, preferably by electrodeposition; (b) use of cylindrical cells with electrodes occupying the entire cross-section so as to insure uniform current distribution; (c) use of the direct method with the Luggin capillary behind the electrode and the tip in a small hole through the electrode; (d) energetic stirring of the solution with oxygen-free nitrogen to insure constant concentration and (e) taking an ample series of individual measurements at any current density and waiting till the

potential becomes stabilized. It should be pointed out that in this recommendation, no evidence was cited to show that the proposed position for the tip of the reference electrode is actually the best for minimizing the difficulties pointed out above, some of which obviously must still remain.

The difficulties in obtaining reproducible results were brought out by Smith and Breckenridge[74] who used a cathode plate, 3" x 2", and measured the polarization at nine different positions and averaged them. They used the direct method with the tip of the probe in front of the active electrode. Part of their difficulties was due to local differences in concentration, as stirring tended to decrease the differences of potential. Fink and Hogaboom[75] also stressed the difficulty in obtaining reproducible results in their study of electrode potentials of silver in cyanide solutions. They claim that the differences are due to a solution film at the electrodes, a descending film at the anode and an ascending film at the cathode because of density variations. They used the direct method with a saturated calomel exploring electrode of the Graham type. They also found that the dynamic potential of an electrode is not the same at all points on its surface. A comparison was made of the polarization potentials obtained by the calomel electrode and the Haring method and found that the greatest discrepancy was in the values for anode potentials in a silver cyanide plating solution and that this discrepancy increased with time. The greatest difference was in the anodic polarization of

25 mv., or about 50% difference based on the calomel potentials. Cathodic values had a maximum variation of 10%. Recently Schrier and Smith[69] also described experiments in an attempt to evolve a technique for reproducible polarization measurements in $CuSO_4$ solutions.

Oscillographic Method

GENERAL REMARKS

A comprehensive study of the change of potential with time after the cessation of the electrolysing current should give at least three bits of information. It should give conclusive evidence for the occurrence of any resistance at the electrode-solution interface; various names for this effect have been used by different authors, such as transfer resistance, boundary resistance, surface resistance, film resistance, ohmic resistance, etc. This information is desirable in the clarification of the method of measurement, since any potential being measured as IR drop cannot, according to consensus, be called a component of polarization. As previous workers claimed to have found a vertical drop in some cases (Newbery and Holler) and others (Baars, Bowden, Ferguson *et al.*), claimed no IR drop, this point is of fundamental concern, both in its relation to the magnitude of the measured potential, and in the elucidation of the theories of polarization and overvoltage.

A decay curve study should give some information on the type of active polarization, whether it be activation, concentration or both. From theory, it might be expected that

activation polarization would decay exponentially. Experimentally some decay curves actually appear to have an exponential character. Since, on the other hand, concentration polarization depends in part upon diffusion, its decay curve would be expected to be slow and somewhat complex. If the active polarization is predominantly one or the other, it may be possible to differentiate on an oscillographic trace the portion due to activation from that due to concentration polarization. If both occur simultaneously, some workers have employed mathematical calculation in an attempt to determine the portion due to each. Thus, if the separation of the components of polarization could be effected a further insight into the mechanism of polarization would be gained. Evidently, unless polarization potentials can be accurately measured, no such procedure would be justified. Other criteria have been employed in attempts to distinguish between activation and concentration polarization; these include (1) effect of agitation, (2) nature of electrode surface, (3) temperature coefficient of polarization potential, (4) form of the charge-time curve and (5) the effect of current density on potential.

PREVIOUS WORK WITH OSCILLOGRAPHS

Reichenstein[76] (1910) was one of the most important early investigators who attempted to interpret the potential decay of both anodically and cathodically polarized electrodes by a combination of the laws of reaction kinetics and Nernst's theory of concentration cells. To record the extremely rapid

fall of potential, he used a Siemens and Halske oscillograph (electromagnetic). Since the most sensitive scale of this type of oscillograph required a current of a few milliamperes for a full scale deflection and vacuum tubes for amplifying purposes were then unknown, the results of Reichenstein were deceiving and worthless since he polarized the polarization potential which was being studied.

About the same time as Reichenstein reported his work, LeBlanc[77] was carrying out very extensive oscillograph measurements on polarization potential and overvoltage. The results which he obtained, also, were later discarded when it was realized that the considerable current which was required to operate the oscillograph was supplied by the cell under investigation, thus affecting the desired potential difference.

Holler[42] in 1925 was the first to overcome the objection to the application of the oscillograph as used by LeBlanc and Reichenstein in the study of the potential decay curve. He used a Duddell oscillograph with an amplifier (made possible due to the recent development of the vacuum tube) to minimize the current drain from the cell to be measured. According to his films and interpretation, in some of the systems which he studied, he found an appreciable resistance which he termed "boundary resistance". He used a standard mercurous sulfate half cell (density of H_2SO_4 = 1.25) the tip of which was kept in contact with the front surface of the working electrode in order to reduce to a minimum the resistance of the electrolyte

between the tip of the half cell and the active electrode. His results seem to indicate that the resistance between the tip of the half cell and the terminal of the electrode under investigation was of a readily measurable magnitude in some cases. His films for platinized platinum showed an instantaneous drop of potential when the current was interrupted which he attributed to an IR drop. For bright platinum, he concluded from the oscillographic record that the potential difference due to resistance was much greater than in the case of platinized platinum. In general, his conclusions support the assertions of Newbery that there is an IR drop of some kind at the electrode-electrolyte interface. Although his films showed a sudden drop, this was later demonstrated to be due to insufficient resolution with time and the fact that his oscillograph had to overcome a certain amount of inertia.

Newbery[78] (1925) was the first investigator to use the cathode ray oscillograph with a vacuum tube amplifier in an attempt to prove more convincingly his theory of transfer resistance. In all cases which were investigated, he found a more or less large sudden drop in potential at the instant the current was interrupted, followed by a more gradual decay. The results he obtained for transfer resistance differ by a factor of ten from those obtained by Holler. In a following report[79] he admitted that his measurements were somewhat erroneous since he did not avoid sufficiently the potential drop in the electrolyte. He used a standard mercurous sulfate half cell the tip of which was placed behind the cathode. The

films in general are poor and ill-defined. The potential lines are too wide and do not line up properly in the vertical plane, probably due to the multiple exposures required for the cathode ray oscillograph to energize the film (poor photographic efficiency and screen). Since the oscillograph at that time had many defects as compared to the modern tube, it was necessary that he make approximately 400 exposures for each curve (the current was made and broken for equal intervals of 0.075 second and a total exposure of thirty seconds). Part of the poor reproducibility may have been due to inferior electronic components, but another to the mechanical commutator which might have not broken the current at exactly the same spot consistently. However, he says, "The results prove conclusively that transfer resistance is a real quantity of anything but negligible dimensions, rising at least to 100 ohms/cm.^{2} under certain conditions". In his later work[80], he also says, "The obvious conclusion from this work is that if a metal only is being deposited, there is no overvoltage or transfer resistance, in other words, metal overvoltage does not exist".

The most recent contributions by Newbery[81,82] are two papers, one of which described a cathode ray oscillograph suitable for measurements on electrolytic cells and the other which described overvoltage measurements with the above oscillograph on various metals. Although he states that his previous work had certain errors, he still advocates the idea of transfer resistance and the commutator method,

changing his theoretical views to suit the information from his latest work. Even with his improved apparatus, the quality of his films is inferior and the lines are indistinct.

In 1928, Baars[34] published a report on an intensive careful experimental work on polarization. He used the direct method, tip in back of the electrode under study, in completely deoxygenated solutions and an electromagnetic oscillograph which at that time was superior to the cathode ray oscillograph. He concluded, "In none of the cases studied was there a purely ohmic resistance of more than a few ohms (for this is the limit of error) at current densities of the order of 10^{-3} amperes per cm.^{2}. Therefore, any error in the direct method of overvoltage caused by a purely ohmic resistance can be at most, a few millivolts; and this is certainly not larger than the usual inherent indeterminacy of overvoltage".

Baars also states, "it thus becomes certain that the contrary results of Newbery are in error - - - this error is to be ascribed to Newbery's insufficient resolution of the process in time".

There has accumulated much indisputable evidence during a twenty year period of intensive investigation in this laboratory that the direct method is distinctly superior to the commutator method. Dr. Ferguson[2-5] and his co-workers in this project, Van Zyl[3], Chen[4] and Kleinheksel[83], have compared the direct and commutator methods independently,

simultaneously and in conjunction with a moving-cell oscillograph. Based upon the experimental results from their detailed studies, they have arrived at several inescapable conclusions, (i) that the commutator method gives only average values which are misleading and result in erroneous conclusions, (ii) that the commutator method has inherent sources of error and is thus undesirable for polarization measurements, (iii) that there is no transfer resistance or any other type of resistance at the electrode interface for the materials used and under their experimental conditions, and (iv) that the direct method for measuring polarization can be relied upon, within the current density used, to give true polarization values. In all their work, they used Fuch's original method of placing the tip of the reference half cell behind the working electrode. However, before adopting it, they made an extensive study to demonstrate its reliability. They used a supersensitive moving coil oscillograph made to order by Westinghouse and a suitable amplifier in conjunction with the oscillograph so as not to affect the potential being measured. With their equipment it was possible to detect a change of one millivolt in one ten thousandth of a second and to reproduce their data to approximately one millivolt.

The measurements obtained with their final apparatus are doubtless the best available with an electromagnetic oscillograph. However, in view of modern technological advances, their measurements may be open to criticism on only two

points: (1) the electromagnetic oscillograph is not totally free from inertia and (2) their resolution against time might be considered insufficient. The present work may be classified as an extension of the previous measurements, with the two objections eliminated.

In a recent report on the topic of the direct observations of electrode potentials by means of a cathode ray oscillograph, Lebbink and co-workers[84] describe their electronic apparatus and a few preliminary experiments using platinum electrodes in 0.1 N H_2SO_4 solutions. The authors studied the self-depolarization caused by the natural processes such as diffusion, etc. They suggest that the polarizing layer behaves more or less as a charging (or discharging) condenser. They conclude that their photographs seem to suggest the conception of Baars[34] and Ferguson (see above) that the actual hydrogen overvoltage does not contain a contribution due to true ohmic resistance and support the conclusion of Baars[34], Ferguson and co-workers[2-5,83] and Bockris[85] that measurements by the direct method for current densities of the order of 0.001 to 0.1 amps./cm.^{2} give reliable results.

RECENT WORK ON EVALUATION OF METHODS

The importance of the method of measuring electrochemical polarization has been further discussed and evaluated in four recent articles. Mattson[86] concluded that the correct polarization values cannot be obtained when the Luggin capillary is pressed against the front or back side of the active electrode,

but believes that approximately correct results will be obtained if the Luggin capillary is bored through the working electrode from the back side. He also considers that the reliability of the Haring method is questionable based on the proposal by Reed and Schriever[87] that a macroscopic space charge exists in an electrolyte which is subject to electrolysis (i.e., Ohm's law does not hold for solutions). Mattson used a 1 M $CuSO_4$ solution, a mercurous sulfate reference electrode, the three direct methods as discussed previously and a simple potentiometric circuit. His experiments were elementary and not studied in detail so as to be able to distinguish the cause of any variation in potential.

At the May, 1952, National Meeting of the Electrochemical Society, two papers pertinent to the measurement of polarization were presented. Eisenberg and co-workers[88] studied the "back" Luggin capillary method of electrode potential in relation to its adaptability to polarization measurements. The interpretation of polarization values measured over surfaces of non-uniform current distribution was considered. Oscillograph measurements indicated that in certain cases, concentration polarization could be measured after the current has been interrupted. While the chemical polarization decays rapidly, the decay of concentration polarization is slower, and can be extrapolated to its value prior to current interruption.

At the same meeting, Barnartt[89] discussed the primary current distribution around capillary tips used in the measurement of electrolytic polarization. He mapped out

the equipotential lines between the electrode and the tip of the Luggin capillary for the following arrangements, (a) capillary in front of the electrode, (b) capillary behind a finite electrode having an insulated back, and (c) capillary through the back of the electrode and having its tip at the front surface. He concluded that arrangement (a) can be used for accurate measurements if the distance between the electrode and the capillary tip of radius r is 4r or more, and any appreciable IR drop subtracted. Arrangement (b) is claimed to be unsatisfactory because the current density varies over the surface of the electrode. With arrangement (c), the current density is increased at the area nearest the capillary, hence the polarization measurements tend to be too high.

Piontelli and Bianchi[95], using a D.C. source, non-polarizable probes and a magnified model, have applied the technique of mapping the primary current distribution to the study of the position of the capillary of a search electrode in the direct method. They conclude from their study that in the front method with the capillary close to the active electrode, a shielding error, negative relative to the potential to be measured, is introduced, which may over-balance the positive error due to the ohmic fall which is included in the measured potential.

Barnartt[89] has criticized Piontelli's method on the grounds that the model is incorrect, being an infinitely long sheet of electrolyte between insulating plates, but

in general the conclusions from his work of the front method support Piontelli. However, Barnartt's own method may likewise be criticized on the basis that his arrangement is not a true model. The insulator which he substitutes for a probe is actually a wall and is large in comparison with his electrode. From his figures, it may be concluded that the larger the probe the greater the compression of the current lines at the face of the electrode. His cell was purposely devised to be non-polarizable; completely different conditions are present with polarization.

The conclusion deduced from the "back" method is particularly misleading. The impression is given that a potential exists behind the back of the insulated electrode, whereas the potential lines must either return to the exposed front face and thus negate any of their effects or the back of the electrode is not properly insulated and is conducting. A further objection is the use of an electrode smaller than the anode; consequently uniform current distribution is not obtained, and the top edge has a higher current density. A lower potential would probably be obtained in the area behind the electrode if an electrode occupying the total cross-sectional area was used.

Barnartt arrives at a dubious conclusion when he states: "This arrangement (back method) is basically unsatisfactory because the current density varies continuously over the surface of the electrode". Since there is no disturbing influence

at the face of the electrode, i.e., it is similar to the arrangement with the probe in front and relatively far from the electrode, the current density should be the same all over the electrode, not "vary continuously".

The problem of an IR correction, so essential for his recommended procedure, is still present since a high degree of uncertainty exists in the value of the conductivity of the solution between the tip and the electrode.

It thus becomes evident that there is still no agreement among the modern workers in the field of polarization regarding the method of evaluating the magnitude of polarization. This research is concerned with the measurement of polarization by the direct method, using (a) the capillary tip in front, (b) the capillary tip in back, (c) the capillary tip in a hole through the active electrode, and (d) the Haring method. By a comparison of the values obtained potentiometrically, and later, by an oscillographic study, a critical evaluation of the various procedures should aid in deciding which is the preferred method.

APPARATUS

Introduction:

The measurement of polarization involves the accurate determination of electrode potential. The problem of measuring the electrode potential relative to some standard or reference electrode falls in two classifications: (1) static or reversible, i.e., with no polarizing current flowing between the electrode in question and the ions in the solution, or a small current of such magnitude that it sensibly does not affect the equilibrium, and (2) dynamic or irreversible, i.e., with an appreciable current flowing which disturbs the equilibrium. Some static potentials may be accurately measured with a simple potentiometric circuit. However, the measurement of dynamic potentials and the change of this potential with time may involve considerable instrumentation, depending upon the method of measurement.

Ferguson and his co-workers[2-5,83] in an extensive series of investigations in this laboratory on the experimental procedures available for the study of polarization have demonstrated in a very convincing fashion that the so-called direct method can be relied on to give correct values if properly carried out. With the advent of electron tubes and suitable electronic circuits, Hickling[25,28] has adapted his modern version of the commutator, the electronic interrupter, in obtaining polarization data which Bockris[85] has confirmed

using the direct method. Lately, Yeager[29] and others[30] utilized electronic interrupters in their electrochemical studies.

Since the electronic interrupter has certain of the adverse characteristics of the old commutator method, since the instrumentation is accordingly much more complex and since the direct method has been proven to be satisfactory, a study of the modifications of the direct method was the objective of this research.

A study of the decay of the dynamic electrode potential with time may permit separation into the various components which make up the total measured potential. The best solution to the differentiation of the components of polarization is to follow the decay curve from the exact point of cessation of the polarizing current to the final static potential. If the sequence of events is slow, the decay curve can be followed with a potentiometer and stop watch. However, as the time period which yields the greatest information is probably the first few hundredths of a second, the instrumentation must be as automatic as possible, perfectly synchronized and must supply a permanent trace of events. The recording apparatus met these specifications: (a) it provided a continuous record of potential changes without distortion of the time axis, (b) it possessed a recording speed in which a change of potential within 26 microseconds was detectable, (c) it had a sensitivity of a milli-volt or better, (d) the apparatus did not draw any appreciable current from the system being measured,

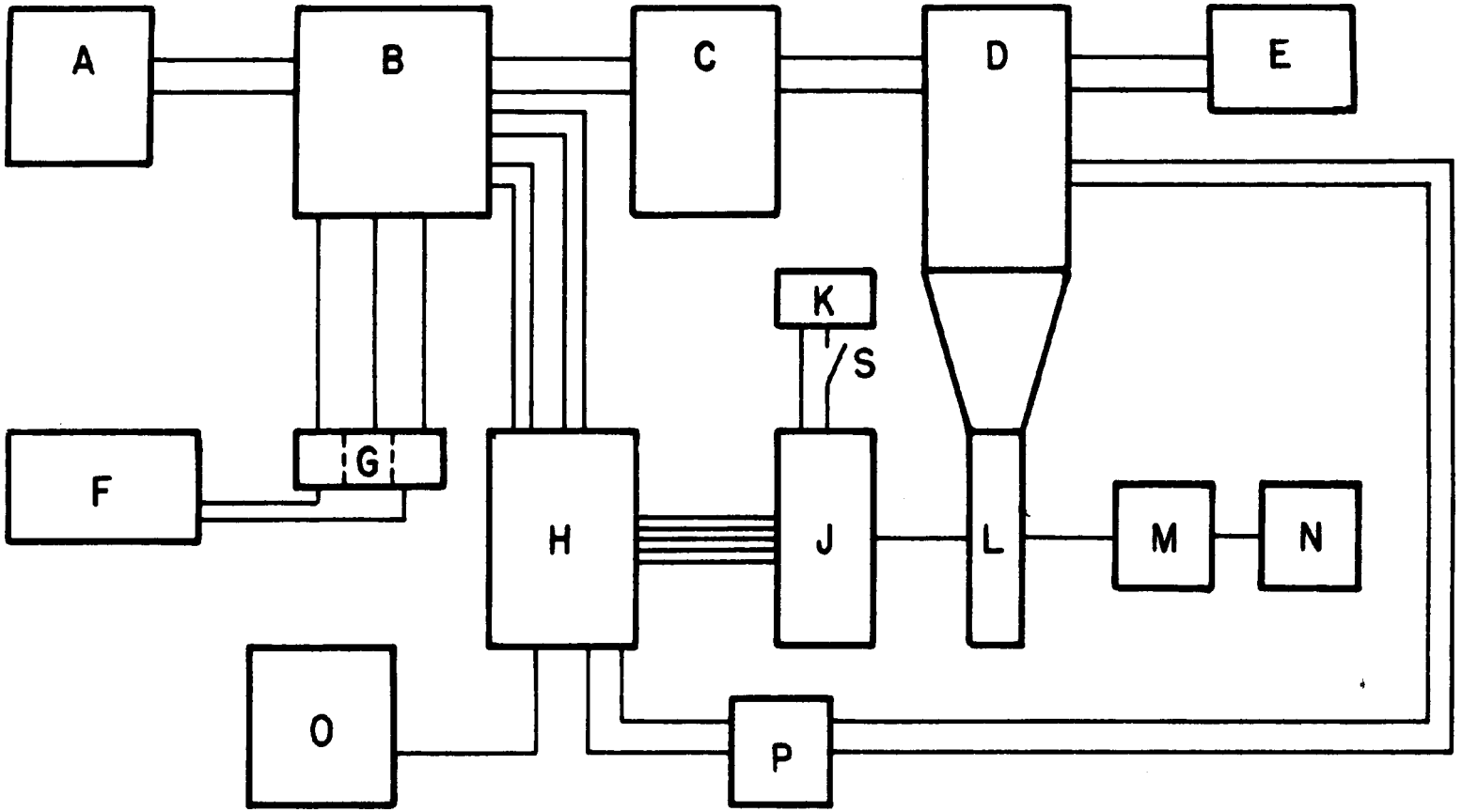
and (e) only a single exposure was necessary to make a permanent record on the film. The apparatus used for this phase of the investigation was primarily the cathode ray oscillograph and auxiliary apparatus built by Dr. D. R. Turner in this laboratory for the study of electrode reactions, with certain modifications in order to meet the above specifications and requirements for this research.

General:

The apparatus used in this research was of two types, (1) for the preliminary work a simple potentiometric circuit in conjunction with a modified Haring cell, and (2) for the second phase of the investigation which involved the identification and magnitude of the components of polarization, a cathode ray oscillograph with the necessary electronic units for the photographing of short-lived transients.

No discussion is necessary for the potentiometer circuit used. For the second portion of the work, the apparatus was essentially that built by Turner and will be only briefly described here since complete details are available in his dissertation. Any changes made in the apparatus will be treated in greater detail. A block diagram is given in Figure 2, which shows the individual components of the apparatus.

The ultimate aim of this apparatus is to produce a permanent trace of the potential-time curve for a short



A - POTENTIOMETER CIRCUIT
B - BUCKING VOLTAGE & SWITCHING UNIT
C - D.C. AMPLIFIER
D - OSCILLOSCOPE
E - HIGH VOLTAGE POWER SUPPLY
F - D.C. SOURCE FOR ELECTROLYZING CURRENT
G - ELECTROLYTIC CELL
H - PHOTO-SWITCH
J - PHOTO-CELLS
K - D.C. SOURCE FOR LIGHT
L - ROTATING CAMERA
M GEAR BOX
N - SYNCHRONOUS MOTOR
O - POWER SUPPLY FOR PHOTO SWITCH
P - SINGLE SHOT VIBRATOR
S - SWITCH FOR LIGHT IN PHOTO-CELL UNIT

FIG. 2 · BLOCK DIAGRAM OF RECORDING APPARATUS

interval before the electrolyzing current is switched off to a few hundredths of a second afterward. The potential changes are recorded by photographing on a strip of film the movements of a fluorescent spot across the screen of a cathode ray tube. The spot moves horizontally a distance proportional to the change in potential. The time axis is provided by the movement of the film perpendicular to the potential axis. This movement of the film is produced by a synchronous motor, N, through the gear speed reducer, M, to the drum camera, L; a rotating disc in the photocell box, J, which acts as a light shutter, is phased with the movement of the film in order to correspond to the potential changes under study.

The potential difference of whatever kind which is to be measured is transmitted to the switching box, B. By the proper manipulation of the switches in B, the potential may be measured on the potentiometer, A, or relayed to the oscillographic unit, D, through the amplifier, C. The potential changes produced in the cell are usually very small in comparison with that required to deflect the cathode ray spot so the high-gain amplifier, C, is required. This amplifier produces the necessary 150 volts for full screen deflection. An auxiliary balancing voltage, also located in unit B, is in series with the potential changes to be measured on the scope, and adjustment of this balancing voltage and of the amplification makes it possible to position the cathode ray spot on the screen so that the potential changes which follow will cover the entire width of the film.

To make a recording, all the electronic components in the various units are warmed up and the potential difference to be recorded is measured by the potentiometer, A. The potential is then switched to the amplifier, C, and oscillograph, D. The synchronous motor, N, is started and after it has been running a minute or so, the manual switch, S, in the photocell box, J, is closed. This starts a series of automatic switching operations. At the proper time, determined by the exposure of a photocell by a slit in a rotating disc, the first photocell is energized by the light beam which, through an amplifier, closes a relay in the photoswitch box, H. This relay acts to turn on the other two remaining lights in the photocell box, and the remaining switching is thus synchronized in the proper consecutive manner. The next photocell which is energized is connected to the single shot vibrator, P, which gives a positive pulse of about twenty volts to the oscilloscope which illuminates the screen with sufficient intensity so as to activate the film. At this point, the recording camera is synchronized to begin the actual recording of the events taking place.

After a definite and pre-determined time, which depends upon the event to be recorded, and the portion of the trace to be studied, which determine the position of the next slit in the disc, the third photocell is energized which operates two relays in the photoswitch box, J. The contacts of these relays open both sides of the circuit that supplies the electrolyzing current. This cessation of the electrolyzing

current instantaneously eliminates all IR drop in the solution, and the depolarizing cycle begins. By photographing the path of the cathode ray spot, a permanent trace is obtained for a period of about 0.03 second after the polarizing current is interrupted. The duration of the positive pulse from the vibrator determines the period of time that the cathode ray spot is illuminated sufficiently to activate the film and this duration is controlled by the resistance and capacitance of the vibrator time circuit.

Since the camera, L, is of the drum type, it is possible to make several exposures on one strip of film, but for the sake of clarity, usually only one trace was recorded. This also permitted the application of potential calibration lines on the film. These lines are necessary to provide the accurate potential measurement from the film. Since the events being recorded are of the duration of 0.04 seconds for about six inches of film, mechanically imposed timing dots proved unsatisfactory. After some experimentation it was decided to use the r.p.m. of the synchronous motor, N, as the time basis.

The potential calibration lines are recorded on the film by setting the potentiometer at the desired voltages and applying these potentials through the switch box with the same amplification as was used for the experiment. For each calibration line, the procedure is repeated as for the recording of the polarized potential. The only difference is

the re-setting of the time constant on the vibrator in order to shorten the length of the pulse, and hence the time of the fluorescent spot. The purpose of this shorter duration is to keep the calibration lines on one side of the film so that they will not interfere and possibly cause confusion in the identification of the stages in the decay curve.

Detailed Discussion of Apparatus:

Electrolytic Cell:

The electrolytic cell used throughout this research was a modified Haring cell made completely from 3/8" Plexiglass (see Figure 3). It had the internal dimensions of 6-1/32" long x 3" high x 2" wide, so that it could easily hold 500 ml. of solution. The required slots for the flat electrodes were accurately machined out so that the four necessary slots were all parallel to each other and perpendicular to the edge. Maximum possible deviation in these dimensions was ±0.010". The three compartments were 2" from the center of one electrode to the center of the next electrode. At each end of the Haring cell, a 1/8" hole was drilled vertically downward in the middle of the end-plate and another 1/8" hole was drilled horizontally from the inside face of the end-plate to meet the perpendicular hole. A well was thus provided into which it was possible to insert the capillary tip of a salt bridge which led to a standard mercurous sulfate electrode.

The advantage of using such a cell is that it can be

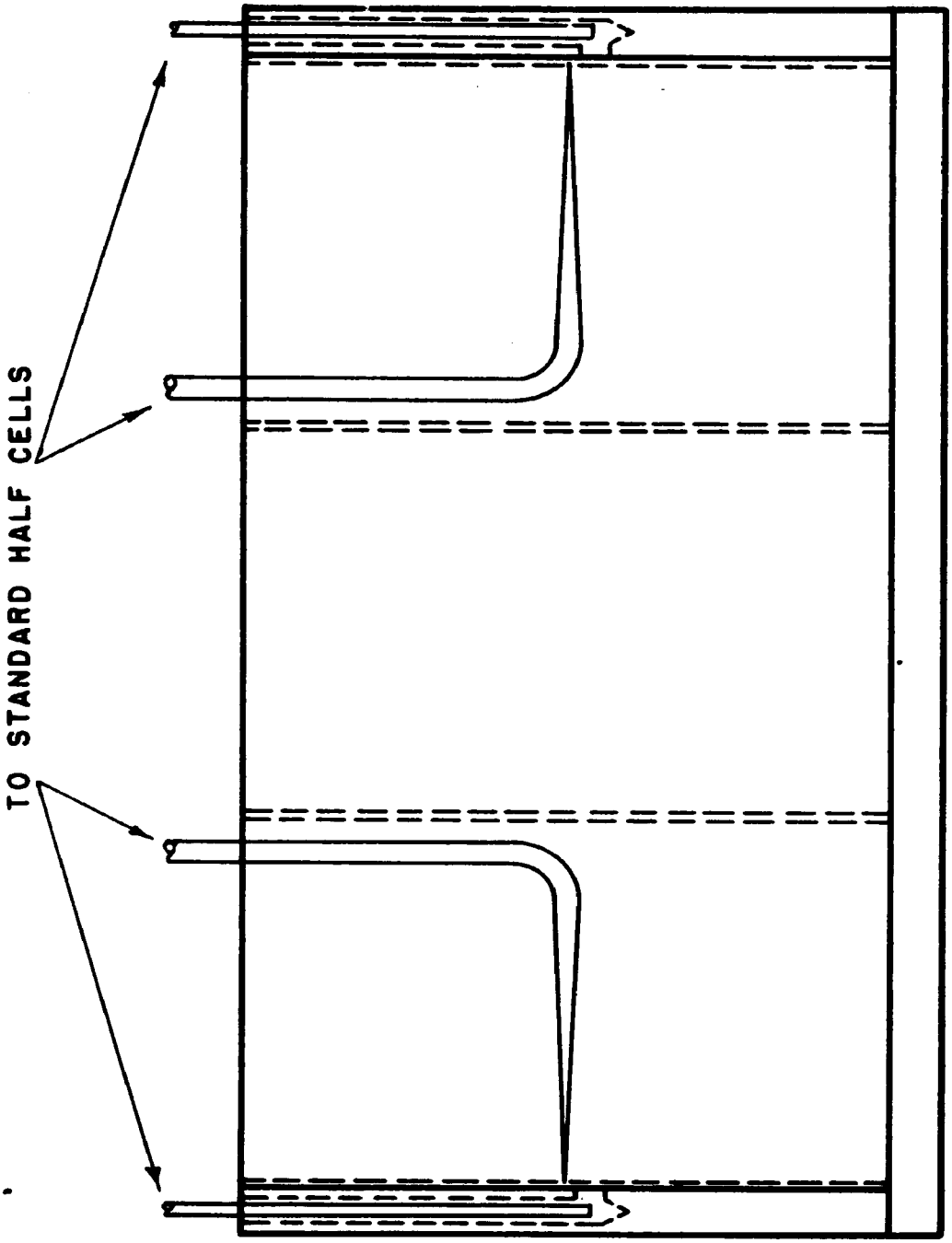


FIG. 3 ELECTROLYTIC CELL

utilized and adapted to any variation of the direct method. Using it as originally designed by Haring, potential measurements give both resistivity and polarization. By using a standard mercurous sulfate reference electrode in such a manner that the capillary tip is bent at right angles, and in close contact with the face of the electrode under investigation, the potentials measured are those obtained conventionally. By inserting a straight tip of the reference electrode in the well behind the electrode, another modification of the direct method is obtained. In the other variation of the direct method the reference tip is inserted in a hole through the back of the working electrode; this may be done in the present modification by removing a gauze electrode and replacing it with a solid electrode with the necessary hole.

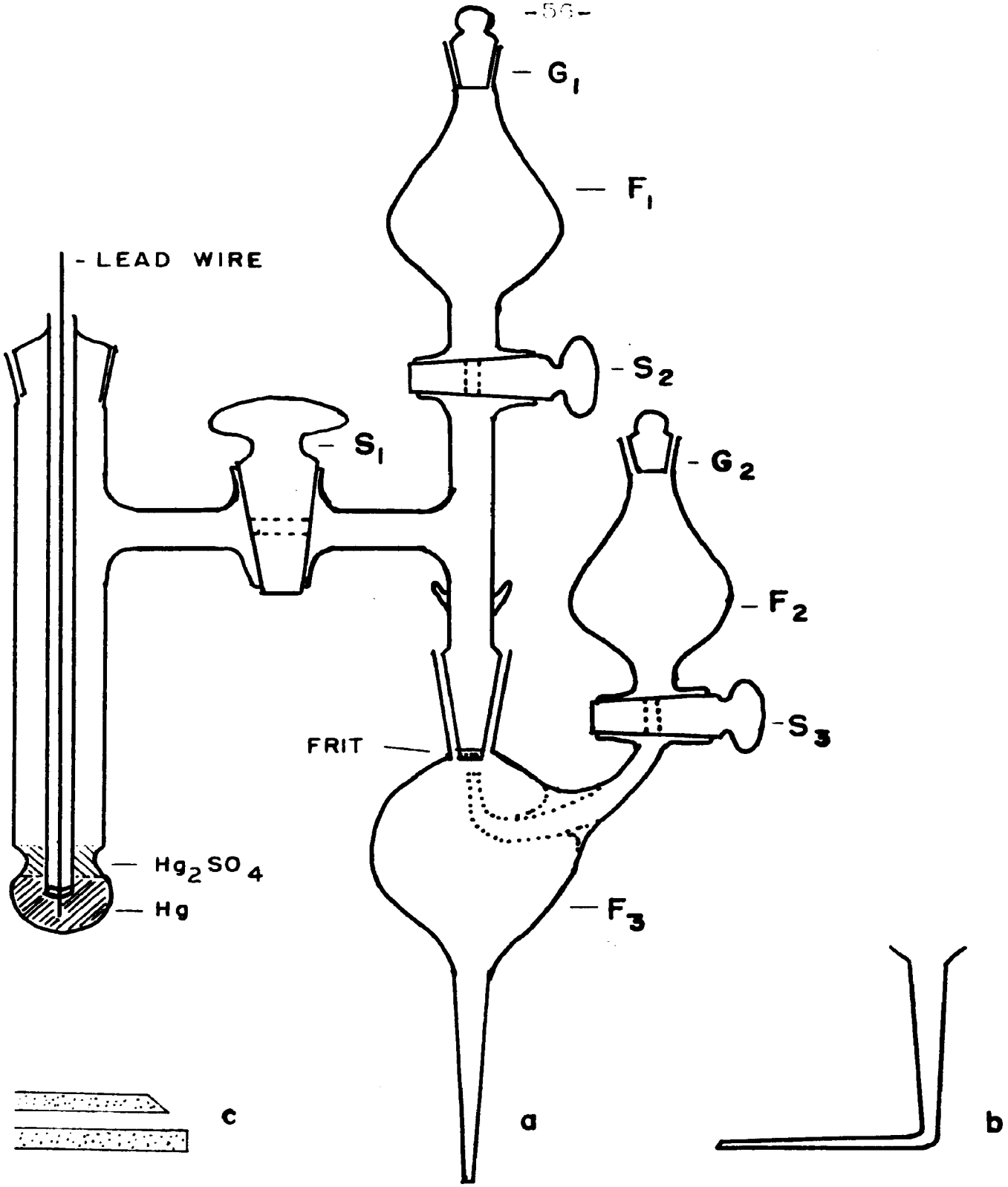
Standard Reference Electrode:

Since the solutions contemplated for this research were sulfuric acid mixtures, the standard reference electrodes throughout were mercury mercurous sulfate half cells, in order to minimize the liquid junction potential and avoid the introduction of foreign ions between the solutions in the reference electrode and in the Haring cell. The mercury was Mallinckrodt's analytical reagent grade and the mercurous sulfate was Baker and Adamson quality reagent; both were used without further purification. Six half-cells were made at one time, using the same reagents, and, after a

period of ageing, were found to agree among themselves with a maximum variation of ±0.3 millivolts. They were checked daily before and after a run. After a long period of use, larger deviations were sometimes observed; if these exceeded 3 mv. new standards were prepared. Since differences in potential were the essential objective in this work, extreme purity of reagents and absolute values of potential were not deemed necessary.

The potential of a mercurous sulfate reference half cell measured against a platinized platinum electrode in 2 N H_2SO_4 saturated with hydrogen at 25°C is 0.673 volt. Any value on the mercurous sulfate scale may be transposed to the hydrogen scale by utilizing the above figure.

The standard half cell shown in Figure 4 is a modification of the Graham type cell. The mercury and the layer of mercurous sulfate fill the oval end of the half cell. The constriction in the tube is to prevent the mercury from shifting and mixing the mercurous sulfate layer should the electrode be jarred or agitated while being moved or carried. Electrical contact was made to the mercury with a platinum wire sealed through the end of a glass tube which was in the center of the cell and fused to the ground glass stopper. The glass stopcock, S_1, in the connecting tube was usually kept closed until a measurement was being taken. In order to eliminate any metallic contamination of the standard electrode by the solution in the electrolytic cell, the



S_1 – 2mm. GLASS GROUND STOPCOCK

$S_{2,3}$ – 1mm. GLASS GROUND STOPCOCKS

F_1 – 50ml. FLASK FOR SULFURIC ACID

F_2 – 50ml. FLASK FOR ELECTROLYTE

F_3 – 50ml. FLASK FOR ELECTROLYTE, JUNCTION WITH H_2SO_4 & TIP

G_1, G_2 – GLASS GROUND STOPPERS FOR F_1 AND F_2

FIG. 4 STANDARD CELL

50 cc. bulb, F_1, which contained 2 N H_2SO_4 was used whenever necessary to flush the half cell by turning stopcock S_2 and removing the glass stopper G_1. However, since the standard half cell would be in contact with strong metallic ion solutions over a prolonged period of time in this work, it was necessary to reduce as far as possible the diffusion of the metallic ions into the standard electrode. To accomplish this, several methods previously employed for this purpose were used. A simple paper plug was tried, but was unsatisfactory for any length of time due to the acid digestion of the paper. The gelatin bridge type of plug was next attempted but the strong acid solutions hydrolyzed the gel within one or two days. With the same object, a silica gel made in acid solution was also tried but results similar to those with gelatin were obtained.

After trying, with poor results, several other methods to prevent diffusion, such as silica powder and parallel capillary tubes, it was decided to use a fine glass frit at the point of contact between the sulfuric acid of the standard half cell and the electrolyte of the solution. At first, results were not completely satisfactory, but more promising. By careful heating of the glass frit until most of the pores were fused and sealed, as indicated by testing with acetone and air pressure, the control of the diffusion of cupric ions into the half cell was such that not more than a very slight blue coloration was visible inside the tip after exposure of

the glass frit to the acid copper sulfate solution for a month at a time.

The unit attached to the stem of the standard cell was arranged in such a manner that the junction at the frit surface between the 2 N H_2SO_4 and the acid copper sulfate could be renewed by merely turning the stopcock, S_3, of the 50 cc. acid copper sulfate reservoir F_2 and removing the stopper G_2 to allow free flow. The exploring tip which formed the lower end of this unit was drawn to a fine capillary (less than 1 mm.) and turned at the proper angle according to the method used in the measurement. Thus, in the "back" method, the tip is straight and perpendicular (Figure 4a) since it is not necessary to bring it up to the back face of the electrode, whereas in the "front" method it is turned at right angles (Figure 4b) in order to come into close contact with the front face of the electrode.

The tip of the capillary of the searching standard electrode has received some study in the past since it was originally suggested by Luggin to Haber in 1905[39]. Knobel and associates[38] concluded that, if a tip is one millimeter or less in diameter, essentially correct values would be obtained. The tips were pressed directly but lightly against the active electrode surface during measurement. Boulach[91] studied the effect of the shape of the electrode tip on polarization data and recommended an oblique cut tip which permits regulation of the position of the tip in relation to the cathode and decreases the shielding effect.

In this work satisfactory results could be obtained if the tip was ground to a 45° bevel, the lower edge then ground flat (Figure 4c) and brought into firm contact with the electrode. In this way, a definite reproducible distance from the working electrode is insured and the shielding of the current lines from the area involved is greatly reduced. The possibility of entrapment of gas bubbles which would cause increased resistance is also minimized. The attached unit with the capillary tube is filled with the same electrolyte as in the Haring cell, and periodically flushed out in order to reduce variation of concentration due to diffusion at the frit junction. This unit is held by rubber bands attached to the glass prongs on the standard cell proper.

Solutions:

The ~~exploratory~~ primary work was done on a copper sulfate sulfuric acid solution of a suitable concentration for copper plating according to Blum and Hogaboom[92]. The acid copper sulfate solution which was used practically throughout the course of this work contained 150 grams of copper sulfate and one mole of sulfuric acid per liter. The copper sulfate was reagent quality grade used without further purification. The sulfuric acid was C.P. grade. The solution was boiled to expel dissolved gases and cooled under an atmosphere of tank nitrogen, with nitrogen gas bubbling through it. The volume contraction due to the cooling of the solution to 20°C and due to the removal of water by the nitrogen was

compensated for by performing the cooling in a volumetric flask after which the solution was again brought to the specified concentration with similarly treated distilled water. The molar sulfuric acid solutions used with the platinum electrodes was Baker's Analytical grade, made up with the same precautions as the copper sulfate solution.

It was found advisable to make up the acid copper sulfate solution with some pure copper in contact with the solution in order to establish the equilibria $Cu \leftrightarrows Cu^{+}$, $Cu \leftrightarrows Cu^{++}$ and $Cu^{+} \leftrightarrows Cu^{++}$ before the solution was placed in the electrolytic cell. This minimized the time required to establish an equilibrium static potential between the copper electrodes and the standard half cells.

Electrodes:

The working electrodes were copper and platinum. The copper electrodes were electroplated on a copper base sheet from a cyanide copper plating solution of the following composition:

Copper metal	42 g./l.
Free KCN	3.7 g./l.
NaOH	42 g./l.
DuPont Brightener No. 556	2 cc./l.
Temperature	60°
Plating Current Density	20 M'amps./cm.^{2}

For heavy deposits this was followed, after a rinse and

wash, by plating from an acid copper bath as recommended by Hogaboom and Blum[92].

The electrodes were made from 1/32" sheet copper 2-1/4" wide and 3-1/4" high fitting snugly in the slots provided in the Haring cell (see Figure 3). Before plating, the electrodes were cleaned in hot alkali solution, rinsed, acid dipped and rinsed again.

The platinum electrodes were sheet platinum obtained from the Baker Company and before use were given the same alkaline and acid cleaning treatments. For some of the experiments, these electrodes were platinized in the usual manner from chloroplatinic acid solution.

The gauze electrodes required in the Haring method were first made of copper gauze (18 mesh) on a copper frame, then electroplated from a copper cyanide bath. However, due to preferential corrosion at the solution level, after standing in the electrolyte for a prolonged period of time, in later work, it was found necessary to make the mesh and framework of platinum, fabricated by the Baker Company and then heavily plated with copper. It was found necessary to re-plate the gauze occasionally. The dimensions of the gauze electrodes were the same as those of the solid sheet electrodes.

Originally, the back surfaces of the active electrodes were not coated with any insulating material but later United Chromium Stop-Off Compound No. 311 (a high melting wax), General Electric's Glyptal and paraffin were tried. It was found that Glyptal performed most satisfactorily, being

harder and more resistant to chipping, scaling and chemical action. The application and use of this material on the electrodes will be described later.

The problem of approximating the true area of an electrode in relation to the apparent or measured area has been recognized for some time. It is universally agreed that the true area is often many times the apparent area which may account for some of the lack of agreement in measured values. An attempt at finding the ratio of real to apparent area was first made by Bowden and Rideal[93]. On the assumption that the electrical capacity of an electrode is a direct measure of its area, they concluded from their measurements that the real area of bright platinum was 2 to 4 times its apparent area. Because of the disagreement in the value of the capacity and the assumption that all metals have the same capacity for the same area, it was considered better to record merely the apparent area.

The shape of the cathode is important because of the desirability of a uniform distribution of current density over the entire surface of the working electrode. A method which insures uniform current distribution is to use large electrodes which occupy the total area of the cell in order to limit the current path to the area of the electrodes. Such a cell adequately conforming to the above specification is the type described by Haring and used throughout this work. Although circular electrodes in a cylindrical cell would be preferable from the theoretical distribution

viewpoint, the rectangular Haring cell is simpler from experimental considerations.

If electrodes small in comparison with the cell dimensions are used, the resistance of the cell is always less than the value calculated on the assumption that only the liquid between the electrode conducts. This is a consequence of the path of the current which is not straight but curved so that not only the electrolyte between the two electrodes, but also the electrolyte above, beneath and at the sides, takes part in the conduction. Therefore, using a small electrode a uniform current density is not obtained; this is due to non-linear current conduction resulting in an increased current density at the edge of the electrode. An example of greater current density at the edges is frequently seen in the deposition of metals where growths occur at such edges. For this reason, it is not advisable to use electrodes which are too small since then an appreciable fraction of the electrolysis may occur at higher current densities than the calculated one.

Arrangement for Maintenance of Nitrogen Atmosphere:

Since it is known that oxygen depolarization is operative in oxygen contaminated solutions at low current densities, it was originally proposed to do most of the work in an atmosphere of nitrogen. The effect, however, becomes practically insignificant above about 10^{-3} amps. cm.$^{-2}$. Consequently, in experiments at higher current densities and in the second part of the experimentation with the oscillographic apparatus,

the nitrogen atmosphere was not used.

The assembled apparatus of the Haring cell and four standard electrodes on suitable stands occupied an appreciable area and volume. No appropriate air-tight apparatus was easily available so a rectangular Lucite case was made which fitted a rectangular groove in a 1" plywood board. This groove was filled with sufficient mercury to provide a mercury seal. Electrical connections were made to the Haring cell by means of a sealed conduit to one banana jack panel in the case and one outside of the case. Inlet and outlet tubes were provided for the nitrogen. The nitrogen was not further purified. Tank nitrogen was bubbled through an acid copper sulfate saturator bottle and into the case. The outlet tube was connected to another saturator bottle containing six inches of water to provide a slight excess pressure in the container. On the top of the rectangular Lucite case were four mercury seals of the stirrer type positioned directly over the four reference electrodes. By a key which fitted snugly over the stopcock in the bridge arm of the standard cell, it was possible to turn the stopcock whenever necessary for a good electrical connection.

Constant Current and Auxiliary Voltage Circuits:

A constant current power supply was used which delivered up to 60 volts from a bank of storage batteries with a high resistance in series with the cell. The batteries were trickle-charged overnight whenever necessary. During any

experiment, any small changes in cell resistance were negligible as compared to the higher resistance in the circuit and thus a constant current was maintained. In some experiments where the current drain was high, the current was checked and adjusted if necessary immediately preceding any measurements.

Constant Current Regulator:

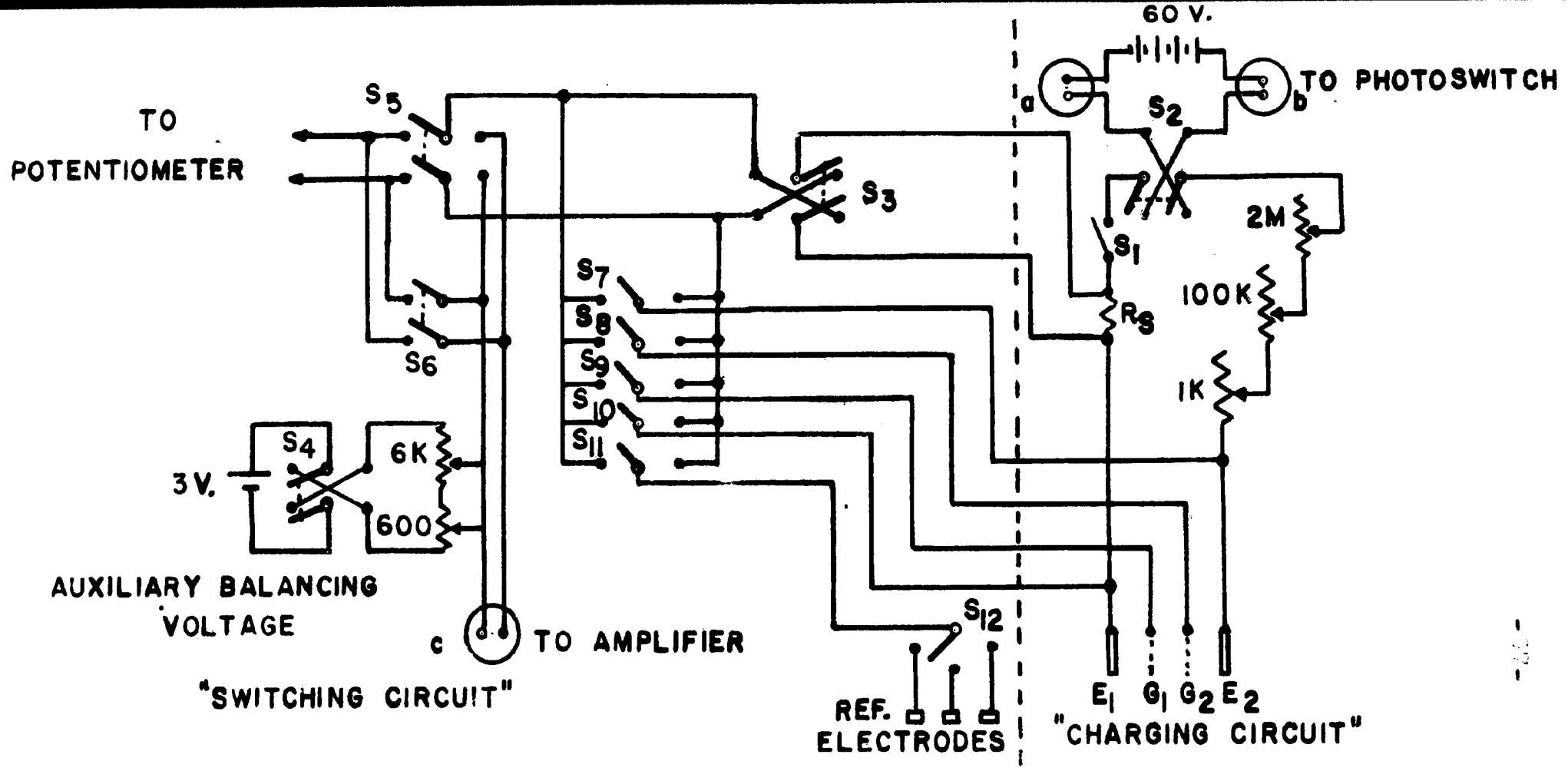
After a few exploratory experiments indicated that better current regulation was necessary, an apparatus formerly used for other work in this laboratory was modified to be applicable to the control of the current density and change in resistance in the present electrolytic cell. The current regulator was a modification of that developed by MacInnes[98]. The arrangement of parts is somewhat similar to that used in the present set-up. The electrolytic cell is in series with the power supply, a rheostat of the proper size depending on the current density, a potential divider and a standard resistance. Any change in the current through this standard resistance produces a change in the IR drop and this unbalances a Type K potentiometer which is continuously in the circuit. This results in a deflection of the mirror in a box-type galvanometer from its balanced position. The galvanometer deviation focuses a beam of light on one or the other of the light sensitive plates of a 930 twin photocell. The photoelectric current produced in this manner is amplified by a 6J5 tube which causes a relay to open if the light is in one direction or close if it is in the other direction. These relays cause

a motor geared to a potential divider to rotate in such a direction as to compensate for the change in the electrolyzing current. The potential divider was wound on a 12 inch porcelain tube with copper wire so that the total resistance was 1.2 ohms. The electrolytic cell resistance was in the neighborhood of 2.5 ohms. Thus, a fine control over the current was available.

The sensitivity of the apparatus is shown by the fact that 0.1 millivolt difference in the potential drop across the standard resistance (1 or 10 ohm, according to current density) would actuate the motor. With a current of 0.3 amperes and a standard resistance of 1 ohm, a 0.1 mv. sensitivity indicates about 0.03% variation.

Switching Circuit:

Figure 5 is a schematic drawing of the charging and switching circuits. Connections "a" and "b" lead to the photoswitches which are normally in the closed position and which open both sides of the power supply simultaneously in order to minimize switching transients from appearing on the film. Switch S_2 is a double pole double throw switch for reversing the polarity of the charging circuit. Switch S_1 closes the charging circuit causing current to flow through the variable rheostats and the electrolytic cell. For high current densities, a smaller slide wire rheostat was used. The cell current was measured with a suitable ammeter in the electrolyzing circuit and still more accurately by measuring



S_1 TURNS ON CHARGING CIRCUIT

S_2 D.P.D.T. SWITCH FOR REVERSING POLARITY OF CHARGING CIRCUIT

S_3 " " " " " " IR DROP ACROSS R_S

S_4 " " " " " " BUCKING VOLTAGE

S_5 " " " SWITCHING TO POTENTIOMETER OR RECORDING UNIT

S_6 D.P.S.T. " " CALIBRATING AMPLIFIER WITH POTENTIOMETER

S_7, S_8, S_9, S_{10} SWITCHES FOR ELECTRODE MEASUREMENT

S_{11} S.P.D.T. SWITCH FOR SWITCHING STANDARD ELECTRODE

S_{12} MULTISWITCH FOR SELECTING STANDARD ELECTRODE

FIG. 5 CHARGING AND SWITCHING CIRCUITS

with a potentiometer the potential drop across a standard resistance, R_s, of proper magnitude.

The polarization potential of the electrode is measured with reference to one of the standard mercurous sulfate electrodes, selected by switch S_{12}. This potential is applied in such a way that the polarity of the potential to be measured is transmitted with the proper sign to the D.C. amplifier, through the connection at "c". By the combination of S_{11} and S_{12} with either S_7, S_8, S_9 or S_{10} any potential may be obtained with respect to the standard electrodes. By using only S_7, S_8, S_9 and S_{10}, in the proper sequence and polarity, any of the potentials required by the Haring method are likewise obtained. The desired potential is then connected by means of switch S_5 to the potentiometer for the direct measurement or to the amplifier and oscilloscope for recording on the film. In order to obtain calibration lines on the film, S_5 is left open and S_6 is closed and a known potential is applied from the potentiometer through the amplifier to the film. By means of the polarity reversing switch, S_4, an auxiliary balancing voltage is connected in series with the potential under investigation so as to position suitably the spot on the cathode ray tube screen.

All switches were enclosed in a grounded metal box to prevent pick-up which would be amplified by the sensitive high gain amplifier. All the connections were microphone cable connectors with shielded and grounded leads. All

units were separately boxed in grounded metal shields. Despite these shielding and grounding precautions, a small extraneous A.C. potential was picked up which limited the D.C. amplifier to an amplification of 80,000.

Oscillographs:

After preliminary experiments indicated rather conclusively that the various methods of measuring polarization by the direct method do not agree with each other, it was necessary to prove which method of those tried gives the more nearly true polarization potential, i.e., with the minimum IR drop. In order to indicate what parts of the total measured potential are due to IR drop and to the different kinds of true polarization, it is necessary to study the decay curve in detail from the exact period of the interruption of the electrolyzing current and to follow the change of potential from the dynamic to the static value. That portion due to IR drop should appear as a vertical displacement. The remaining portion of the decay curve, which is the true polarization, consists of a rapid decay followed by a much slower change. To study the initial rapid changes, a photographic record of the time-potential curve as shown by a properly used oscillograph can provide the necessary information.

Comparison of Electromagnetic and Electrostatic Oscillographs:

(a) Electromagnetic Oscillograph.

As pointed out in the Historical Section, the application

of an oscillograph to electrochemical phenomena and particularly to polarization studies was made first by Rothé, then by Reichenstein and LeBlanc in 1910. They used the string, or mirror, oscillograph which operates on the principle of the permanent magnet galvanometer. This type of oscillograph as used by the early investigators gave results which were soon shown to be incorrect because the oscillograph drew so much current from the system that it polarized the cell being measured. The recognition of this error led to the discarding of the method until the advent of vacuum tube amplifiers. Holler[42] was the first to use such an amplifier to photograph time-potential curves on charge and discharge without drawing appreciable current. An instrument of this type was employed by Ferguson and co-workers in this laboratory[2-5,83], applying the supersensitive two element Westinghouse Osiso which was capable of detecting a change of one millivolt in 10^{-4} second, which brought the technique of measurement with electromagnetic oscillographs to its highest perfection and limit of attainment.

The major disadvantage of this type of oscillograph is its inability due to inertia of the moving element to record with fidelity phenomena that occur at high frequencies or rates. The upper frequency limit of the best oscillograph of this type is hardly more than 10,000 c.p.s.

(b) Cathode Ray Oscillograph.

The cathode ray oscillograph (hereafter indicated as C.R.O.) was first used for polarization studies by Newbery

in 1925[78]. His curves were very inferior according to modern standards. Since that time many electronic improvements, particularly during and after the war, make this method the best for photographing rapid transients. The C.R.O. was used by Butler and co-workers[94], Hickling[25,28], Newbery[78,81,82], Yeager et al.[29], Turner[61], Schuldiner[30] and many others.

The principal advantage of the C.R.O. over all other indicating devices lies in the fact that the electron beam has no appreciable inertia. Thus the beam of the ordinary C.R.O. will respond to each cycle of a very high frequency signal and will reproduce these signals without distortion. The mechanical devices are limited by at least one moving part which must possess some inertia and which is also affected by friction. The beam of the C.R. tube moves in a high vacuum and has no mechanically moving parts which may be hindered by friction.

The C.R.O. does, however, possess two disadvantages. The C.R. tube is insensitive - that is, it requires rather high voltages to deflect the beam in an electrostatic tube. However, it is possible to amplify the low voltage and then apply it to the deflection plates thus overcoming this disadvantage. The other disadvantage is its relatively poor photographic efficiency. The best photographic results are obtained with a blue fluorescing C.R. tube screen, high intensifier voltage, best camera lens available and the fastest photographic film. In order to overcome persistence of the image, the P-11 screen, which has the least persistence of

any made, was used. The limitations of the C.R.O. will be considered in the Discussion.

Oscillograph and Power Supply.

The apparatus used in the rapid recording was that built by Dr. D. R. Turner in this laboratory. The C.R. tube was a DuMont Type 5 SP11, using only one electron gun with intensifier electrodes. It had the usual intensity, focus and vertical positioning control of the electron beam. Horizontal positioning control was not used, as the spot was located by means of an auxiliary potential in the amplifier input circuit.

The high voltage power supply furnished 6000 volts and utilized a high voltage transformer, two 2X2 voltage rectifier tubes and an RC filtering network for smoother voltages. A variable input transformer to the high voltage transformer was used to slowly increase the voltages on the cathode tube when fast recordings were made.

Camera and Photographic Process:

In order to photograph single sweep transients the camera shutter was opened manually and the C.R. beam turned on automatically only for the duration of the transient. The camera consists simply of a cylindrical drum, eight inches in diameter mounted on ball bearings, on the circumference of which is attached a strip of film. With this method, recordings at high speeds are possible with a minimum consumption of film.

The camera uses 35 mm. film and the five inch maximum

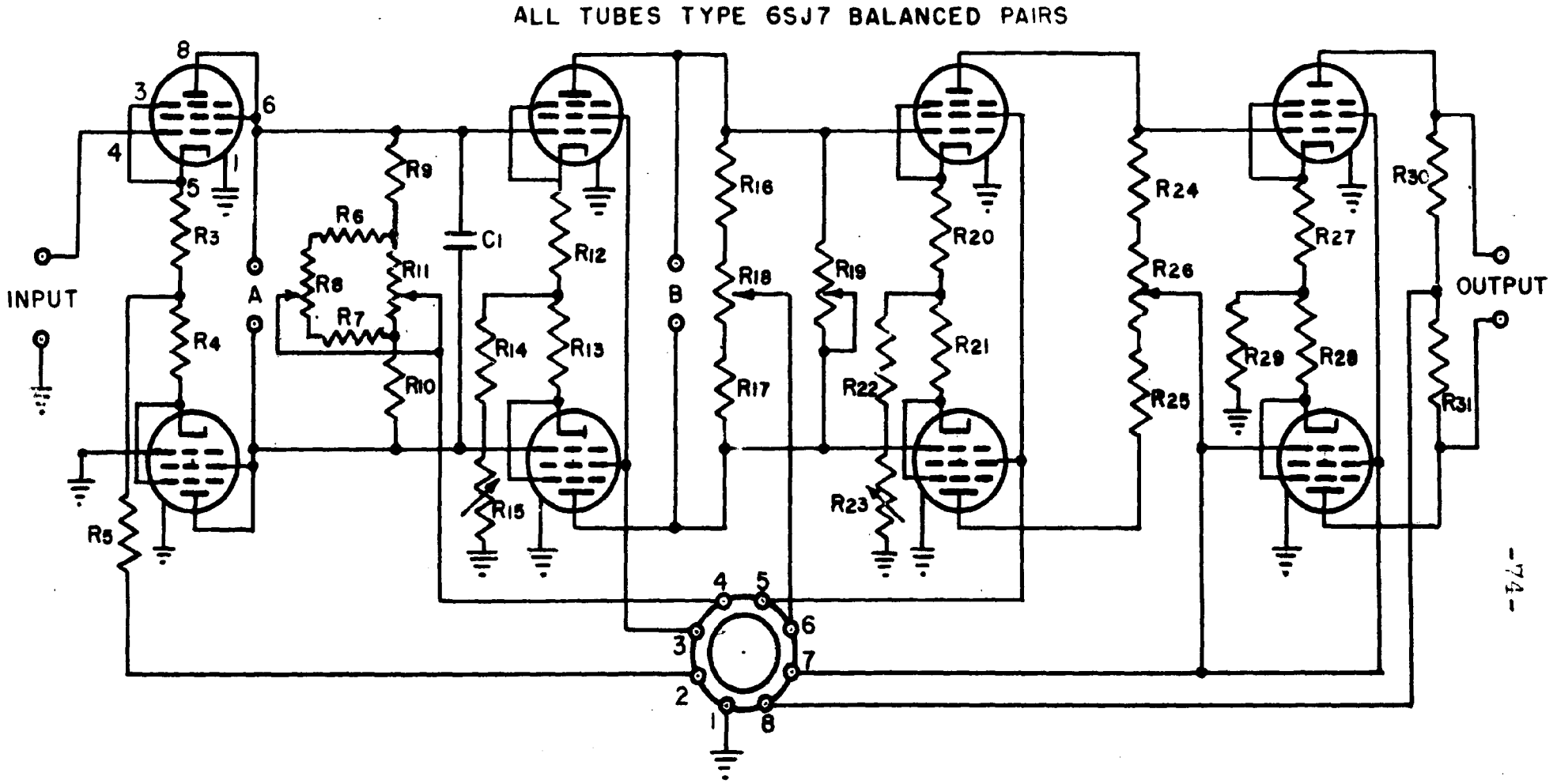
deflection on the C.R.O. screen is reduced to 35 mm. which results in a large ratio of object to image with the production of high photographic efficiency. The camera lens after being stationed in its fixed focus position had a rating of f:2.3.

To maintain a constant film speed the camera drum was rotated by an 1800 r.p.m. synchronous Bodine motor through a 5:1 Boston gear speed reducer. This gave a speed of 150 inches per second (0.26 milliseconds per millimeter). Thus for a film of about 6 inches, the time interval from start to finish was 0.04 second. Owing to the smallness of the time interval electronic rather than mechanical switching was employed. The synchronization was effected by a direct connection between the shaft of the Bodine motor, the film drum and switching device (see Figure 2).

The 35 mm. film used was Eastman Kodak Linograph Pan, emulsion No. 5244. The film was processed according to the procedure recommended by the manufacturer. This is as follows: Develop 9 minutes in Kodak D-19 at 20°C, wash with water, fix in Kodak F-5 for 10 minutes at 20°C, wash one-half hour in running water then air dry on a rapidly rotating cylinder.

D.C. Amplifier:

The high gain D.C. amplifier, Figure 6 was designed by Dr. Orr, of the Electrical Engineering Department of the University, and built by Dr. Turner for use with a C.R.O. It is a bridge balance amplifier utilizing such precautions



POWER PLUG	C1 - 100 MMf CONDENSER	R12,R13	- 2K	WIRE WOUND	R22	- 75 K
2 - -45 VOLTS	A,B - SHORTING PLUGS	R9,R10,R16,R17	- 250K	" "	R24,R25	- 240K
3 - +90 "	R3,R4 - 5K WIRE WOUND	R14	- 30K	" "	R27,R28	- 500 OHM
4 - +112 "	R5 - 100K " "	R15 (BIAS ADJ)	- 25K	" "	R29	- 40K
5 - +157 "	R11 - 25K " "	R18	- 50K	" "	R30,R31	- 50K
6 - +180 "	R26 - 50K " "	R23(BIAS ADJ.)	- 50K	" "		
7 - +270 "	R6,R7 - 1 MEG	R19(GAIN CONTROL)	- 1 MEG			
8 - +400 "	R8 - 500K	R20,R21	- 1K			

FIG. 6 - HIGH GAIN DIRECT COUPLED AMPLIFIER

for good stability as (a) constant B voltage supply, (b) constant cathode heater voltage, (c) a parallel balanced circuit with matched tubes and (d) large cathode resistors.

Since the amplifier is a voltage amplifier, the current drain on the B supply is small (about 7 mamps.) and a series of 45 volt dry cell batteries form a convenient power supply with a stabilized voltage. A constant cathode heater voltage is necessary if the tube temperatures are to remain constant. Except at the higher amplifications, a battery charger was floated across a lead storage battery which kept it fully charged. The voltage applied to the heaters was adjusted to exactly 6.0 volts with a series rheostat. The tubes were matched for static and dynamic characteristics and noise value.

The cathode resistor in the first stage is common to both carefully matched tubes; its resistance of 100,000 ohms is considerably larger than the plate resistance of a 6SJ7 tube operated as a triode.

To attain maximum amplification, extreme precautions as to component and construction details are necessary. The first stage was tested for microphonics, mounted on cushioned sockets and enclosed in a heavy felt-lined steel box which was also mounted on rubber to the chassis. All resistors passing appreciable current were precision wire-wound.

The amplifier was designed to obtain an amplification of 10^6 but the maximum amplification experimentally attained with D.C. only and no superimposed frequencies was only 80,000.,

i.e., 0.002 volt to 160 volts for a full screen deflection on the C.R.O. With pure D.C. amplification, a perfectly spherical spot could be focused on the C.R.O. screen. With superimposed A.C. or other frequencies a horizontal line was obtained, increasing in length with increasing amplification, i.e., amplifying the wave length. A photograph of the line along with a frequency study with a DuMont C.R.O. showed that the disturbing frequency was about 15,000 cycles.

To eliminate this extraneous signal component, an attempt was made to find the source of the "noise" which generated this frequency. This disturbance may be introduced from (1) the "hum" in the power supply, (2) microphonic noise, (3) pick-up from external sources as a result of imperfect shielding, (4) noise arising from defective components and (5) inherent tube and resistor noise.

As recommended by Elmore and Sands[96], hum pick-up from an A.C. operated heater with appreciable gain may be eliminated by using a D.C. heater supply and utilization of shock mountings against mechanical vibrations. According to Turner's directions, the tubes in the first stage were selected carefully for low microphonics and matched characteristics. All wires were in grounded shielded cables and the sheet metal box of the amplifier was enclosed in a 1/4" thick steel housing which was lined with 1/2" felt. However, the signal pick-up was still present at the higher gains whence it was concluded that the difficulty was due either to defective components or inherent tube and resistor noise. Replacement of these elements in the first

two critical stages reduced but did not completely eliminate the difficulty.

Because of normal ageing, the tubes were carefully tested periodically for differential and dynamic output with a tube matcher developed by Turner.

The linearity of output of the amplifier in respect to input was frequently checked at various amplifications. The procedure was to use the potentiometer as the source of accurately measured potential which was amplified and the output measured with a vacuum tube voltmeter. Figure 7 shows the linearity of amplification in several ranges.

Photocell Activated Switching Circuits:

The photocell activated switching circuit was a modification of the one used by Turner. With rapid switching such as that required to record practically instantaneous potential changes with time, mechanical switches, which have been used with slower oscillographs, are not suitable for several reasons. Among these reasons are (a) the time lag after contact has been made, (b) the failure to reproduce the make or break at exactly the same position and (c) the appearance on the film of certain transient phenomena which possibly may arise from capacitive and inductive effects in the electrolyzing circuit.

Whatever type of high speed switching is utilized, the following problems may be listed: (1) synchronization of the desired sequence of events on the strip of film, (2) limita-

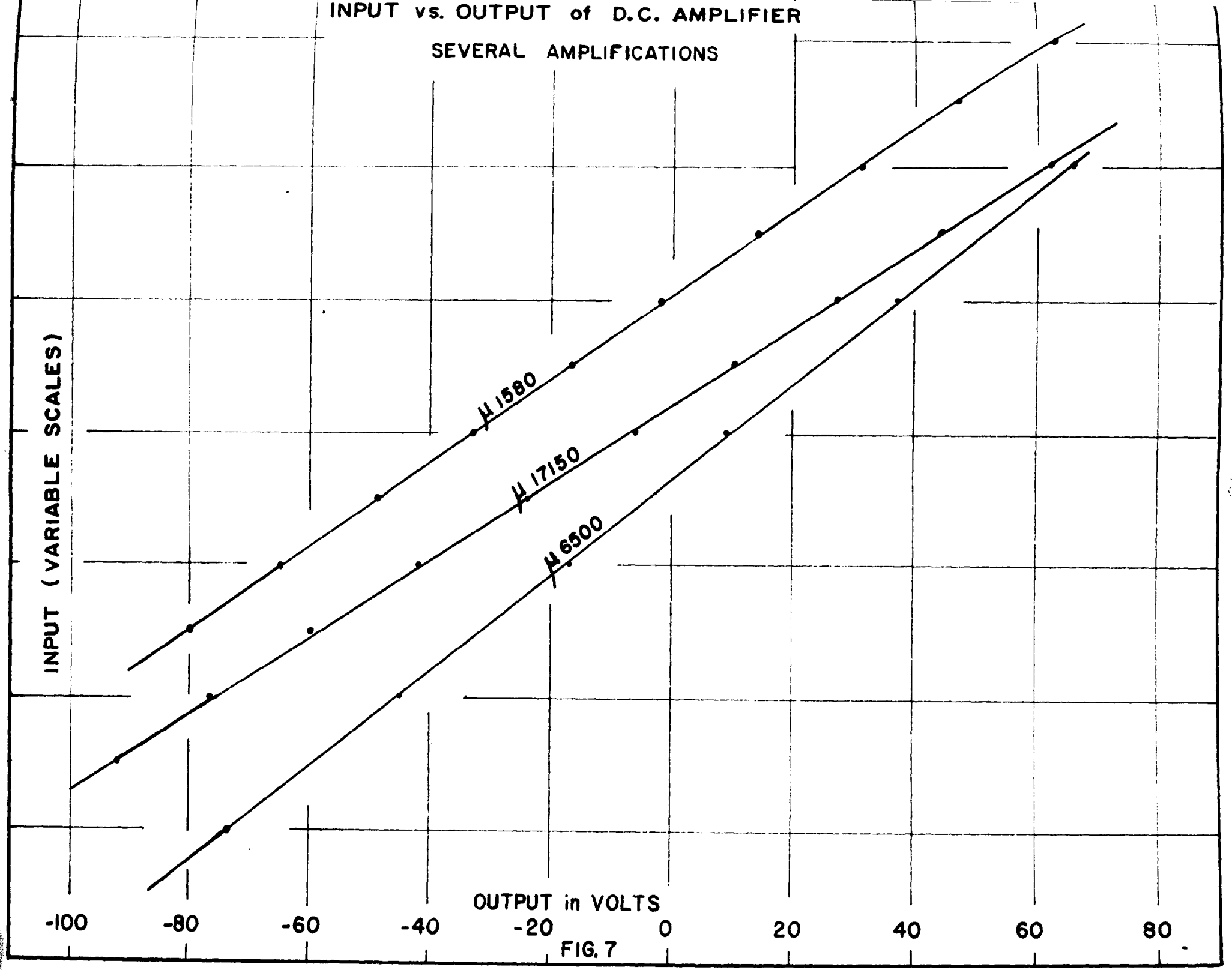

INPUT vs. OUTPUT of D.C. AMPLIFIER
SEVERAL AMPLIFICATIONS
INPUT (VARIABLE SCALES)
μ 1580
μ 17150
μ 6500
OUTPUT in VOLTS
-100
-80
-60
-40
-20
0
20
40
60
80

FIG. 7

tions of relay operating speed and (3) elimination of switching transients. The solution to the first problem was accomplished by a rotating disc which was coupled directly to the camera shaft. The disc was located between three small flashlight bulbs and three corresponding photocells with each pair on a different radius from the center. By cutting one-eighth inch wide slots of a suitable arc length at these radii, it was possible to expose the individual photocells to the energizing light beam in the proper sequence. The details of the operation will be described later.

Electromagnetic relays, once energized, require a definite time to operate and one may think that this would be a determining factor. In fact, however, the deciding factor in this connection is not the lag time required to energize the relays but the time required for the relay to break the contacts. This and other major factors involved will be discussed later in connection with the films. In this work, sequence and reproducibility of the breaking of the electrolyzing current were satisfactorily accomplished through the use of Stevens-Arnold type 172 relays, the best available for the purpose, which respond with a guaranteed operating time of one millisecond or less. The switching transients were partially eliminated by following Turner's suggestion of opening both sides of the charging circuit simultaneously.

The basic phototube circuit was the one used by Turner adapted from the one developed by Bull and Lafferty[46] and shown in Figures 8 and 9. The operation is fundamentally as

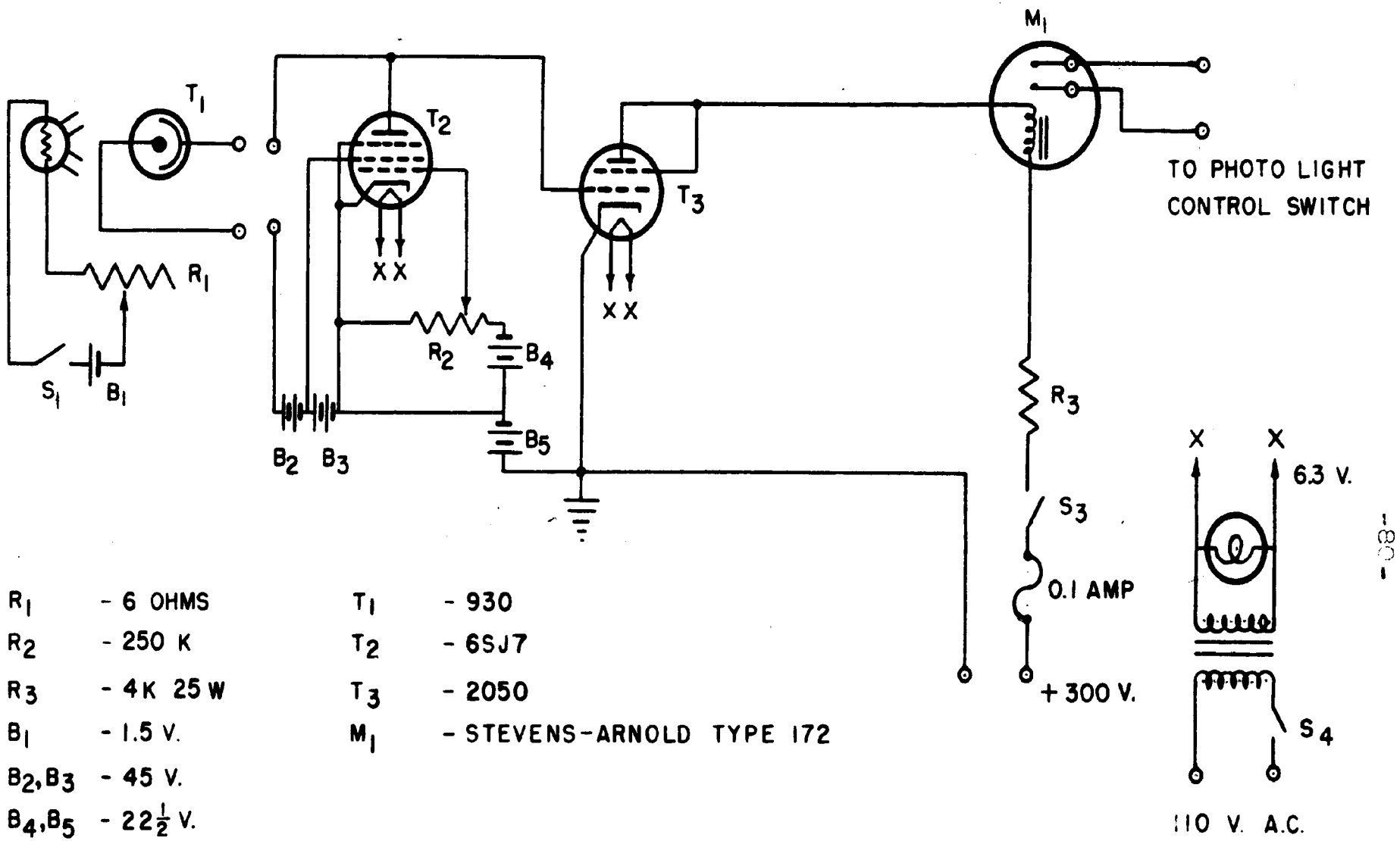
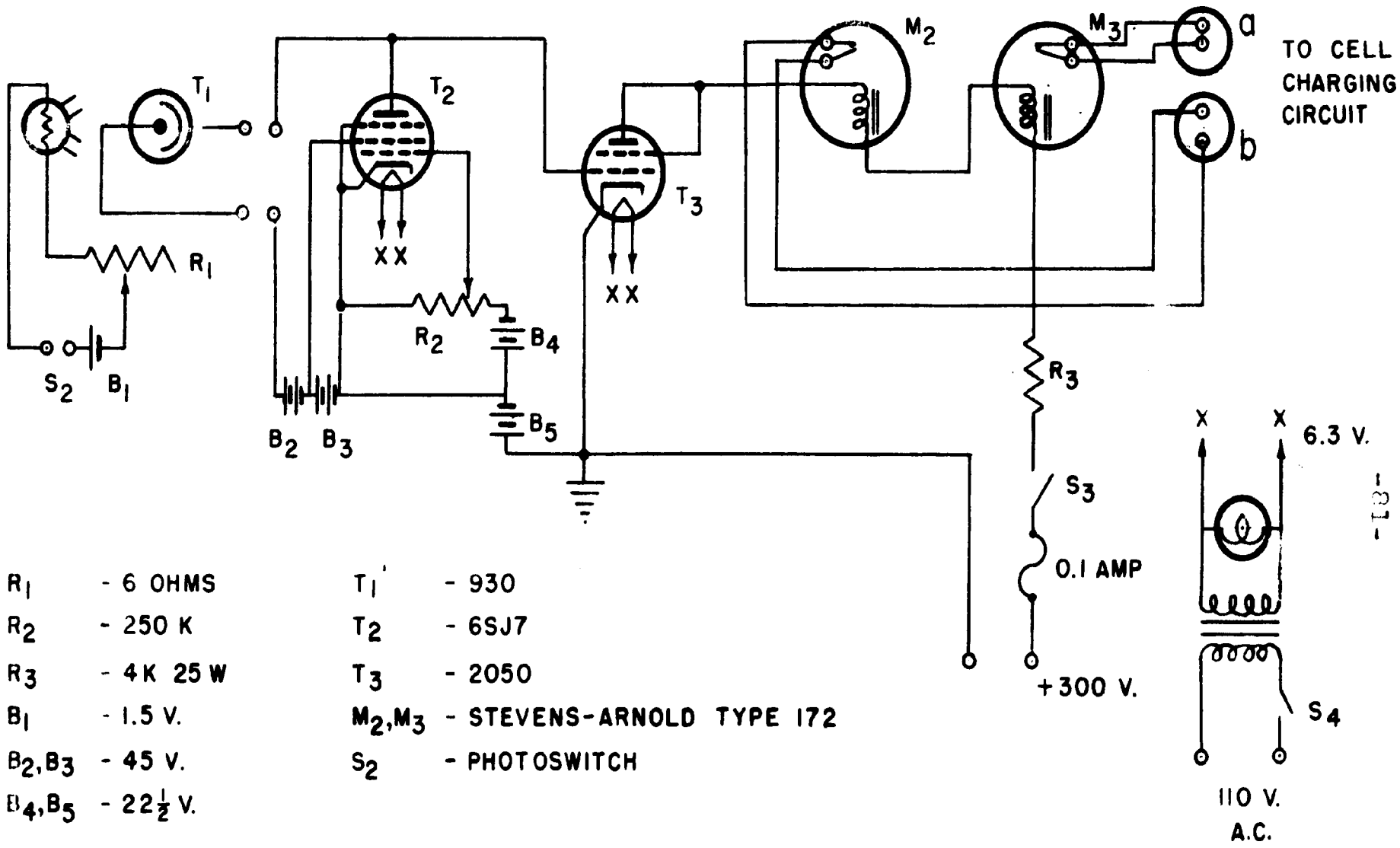


FIG. 8 - SCHEMATIC FOR AUTOMATIC PHOTOLIGHT CONTROL SWITCH



R_1	- 6 OHMS	T_1	- 930
R_2	- 250 K	T_2	- 6SJ7
R_3	- 4K 25 W	T_3	- 2050
B_1	- 1.5 V.	M_2, M_3	- STEVENS-ARNOLD TYPE 172
B_2, B_3	- 45 V.	S_2	- PHOTOSWITCH
B_4, B_5	- 22½ V.		

FIG. 9 - SCHEMATIC FOR AUTOMATIC DISCHARGE SWITCH

follows:

The grid bias of the 6SJ7 pentode which is in series with a type 930 phototube and a 90 volt battery is critically adjusted so that an increase in light intensity on the photocell causes a current increase in the circuit. This current produces a large potential drop across the 6SJ7 pentode which is applied across the grid and cathode of a 2050 thyratron gas-filled tube with an electromagnetic relay in the plate circuit. When the thyratron is fired, current flows to energize the relay. The thyratron grid bias adjustment is made by varying the grid bias of the 6SJ7 with the photocell dark, until the tube just fires when the potentiomater is backed-off slightly; the thyratron now will fire only when light strikes the photocell. The thyratron permits the flow of current until the plate potential is made zero or negative for a short time. This was done by switching the plate potentials off momentarily.

The basic circuits for all three phototubes were similar. The complete sequence of events is as follows - with the drum and disc rotating at the proper speed and the camera shutter open, as well as other precautions which are necessary to photograph the trace, a single pole manual switch turns on one flash-light bulb which activates the first phototube. The voltage drop across the 6SJ7 tube instantly rises and this is impressed on the grid of the 2050 thyratron which causes the thyratron to fire and close a relay. This closure

turns on the two remaining light bulbs in the photocell box. As the disc continues to rotate, the second photocell is activated and goes through the same electronic procedure as the first. This causes the second thyratron to give a pulse to the single shot vibrator which turns on the cathode ray spot for a definite pulse length. Continuation of the disc rotation activates the third phototube and this opens the contacts of the two relays so as to break both sides of the charging current simultaneously.

Single Shot Vibrator:

The fast beam switch which was used throughout this study for rapid recording, employs the basic circuit of a 930 phototube, a 6SJ7 pentode, a 2050 thyratron and 12AU7 tube used as a single shot vibrator and shown in Figure 10. This square wave pulse is triggered by the basic photoswitch unit from the second thyratron. The pulse is of the order of 20 volts positive which when impressed on the C.R.O. control grid through the 0.5 μF. condenser (in the C.R.O. circuit) raises the grid potential to a value at which the electron beam flows causing the fluorescent spot to appear on the screen. When light enters the photocell and the thyratron fires, a sharp potential drop occurs at the plate of the thyratron which appears across the 100 mmf. condenser (in the vibrator circuit) as a negative "pip" voltage. One-half of the 12AU7 tube is normally conducting while the other half is not. When the negative triggering impulse is applied, the

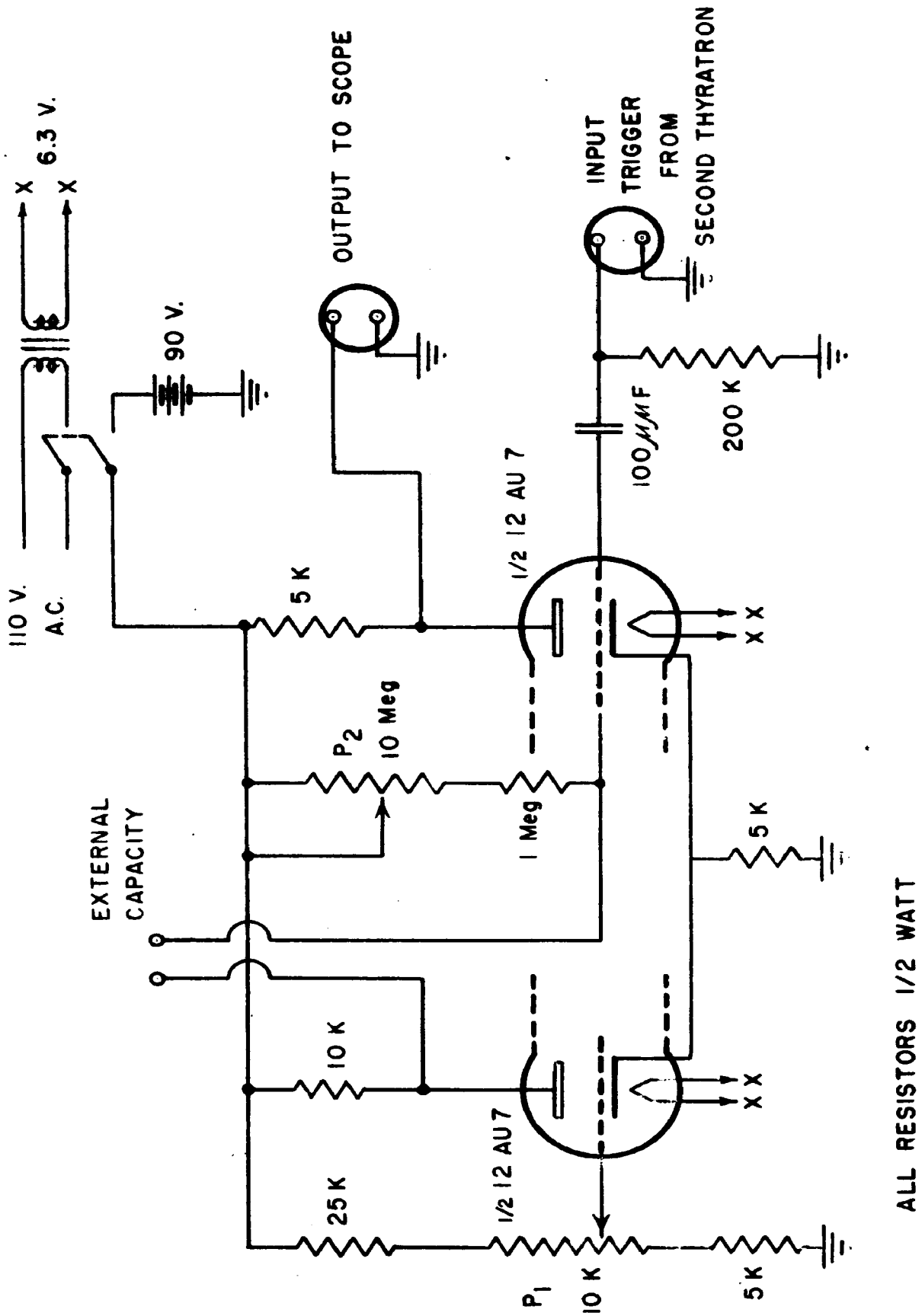


FIG. 10 - SCHEMATIC FOR SINGLE SHOT VIBRATOR

grid of the conducting half of the 12AU7 is forced beyond cut-off; thereby the tube ceases to conduct producing a sharp rise in its plate voltage, which is the start of the positive voltage pulse. The grid bias voltage of the second half of the 12AU7 is reduced to zero when the first half stops conducting, thus the second half starts conducting and produces a drop in its plate potential which sends a negative pulse through the condenser that pushes the grid of the first half of the 12AU7 even more negative and holds the tube in a non-conducting state until the charge on the condenser can drain off through suitable resistances. Once the grid voltage of the first half of the 12AU7 reaches the cut-off value and starts conducting again, the cathode bias voltage developed across the 5,000 ohm resistor turns off the second half of the 12AU7 raising its plate voltage; this sends a positive pulse through the condenser driving the grid of the first half of the 12AU7 even more positive. The plate voltage of the first half of the 12AU7 thus drops to its original value ending the pulse. The pulse length is determined by the values of the condenser across the external terminals and the potentiometer P_2. Increase of either the capacity or resistance or both increases the pulse length. With a 2μF condenser the maximum pulse is about 3.5 seconds, whereas a 0.1μF condenser produces a maximum pulse duration of 0.17 second. The sensitivity is controlled by the potentiometer P_1.

In order to adjust this unit to operate as a single shot

vibrator, a vacuum tube voltmeter is connected to the output plug and the potentiometer P_1 is set to about 70 volts. Since this setting is near the point of change from 70 to 90 volts (at which this device becomes a multivibrator) this adjustment is critical. This adjustment may also be made with an auxiliary C.R.O. by connecting the output to the horizontal plates and viewing the screen. If the unit operates as a multivibrator, a recurring pulse will be observed when the second thyratron in the switching box is fired. By backing off P_1, only a single pulse will be flashed on the screen.

The vibrator so adjusted gives a square wave pulse of 20 volts which is sufficient to raise the C.R.O. voltage to the point where electrons flow - before and after the pulse no electrons are available to fluoresce the screen.

EXPERIMENTAL

Introduction.

The preliminary work was a comparison by means of potentiometric measurements of the variations of the direct methods of measuring polarization, as defined earlier. Initially, three variations of the direct method were investigated, (i) the Haring method, (ii) the Fuch's method, hereafter called the "back" method, i.e., with the tip of the standard reference half-cell in back of the working electrode, and (iii) the so-called "front" method in which the tip of the standard reference half-cell is placed in front of the electrode under investigation. Later, a fourth variation was included, in which contact with the tip of the salt bridge is made from the back through a hole drilled in the active electrode.

The electrolytic cell, Figure 3, was filled with 500 ml. of the acid copper sulfate solution and the copper gauze and sheet metal electrodes were inserted in the correct slots. The reference electrodes were properly positioned, one in the well in back of the cathode, one in direct contact with the face of the cathode and at about the center, a similar one against the face of the anode and the fourth in the well in back of the anode. All potential values cited in the experimental work are those obtained by measuring the potential difference between the standard half cell, described earlier, and the electrode under investigation. Absolute values were

not required since only differences between static and dynamic values were of prime interest. To transpose these values to the reversible hydrogen scale, 0.673 volt should be subtracted from the measured potential.

The solution, working electrodes and reference electrodes were allowed to reach equilibrium. As indicated by measurement of static potentials between the reference electrodes the gauze and sheet metal electrodes when successive readings differed by not more than ±0.1 millivolt, these were considered the static potentials for the experimental conditions. A specified current was allowed to pass to electrolyse the solution. Readings were taken of the resulting potentials at appropriate intervals (usually five minutes). These measurements were continued over a period of time, depending upon the current density, until the values remained essentially constant. These steady values were designated the dynamic potentials and the differences between static and dynamic potentials were taken as the polarization of the electrodes in that solution at the specified current density and temperature.

Measurements by the Haring method using a Wolff potentiometer followed the procedure outlined in the original article[37]. It must be assumed in this method that the two gauze electrodes are non-polarizable and that their difference of potential when the current is flowing is due entirely to the IR drop through the solution. As the three compartments

are of equal dimensions, any difference between the potential measured between the cathode and the first gauze and the potential measured between the first gauze and the second gauze is then due to cathodic polarization. Similar calculations can be made for the anode polarization. Minor corrections are made to compensate for inequalities in the static potentials of the electrodes and gauzes.

Before any readings were taken, the solution was electrolyzed with an auxiliary electrode at a low current density (about 10^{-4} amps. $cm.^{-2}$) for a prolonged period (usually overnight) to remove impurities, generally metallic, from the solution. This procedure has been used in previous work in this laboratory and is recommended by Hicking and Salt[25,28] and re-emphasized by Bockris[85]. Before each polarization determination, the electrodes were allowed to decay to a stable potential to prevent any effect of previous polarization. If the previous static value was not reached, and the approach to this value was very slow, the new static value was used in calculating the new polarization potential. The time required to reach the static values was materially lessened by shorting the working electrodes. To obtain steady reproducible polarization values the procedure found necessary in this laboratory, namely to continue the electrolysis until a steady state is reached was followed. The time required to reach this steady potential depended upon the material of the electrodes, the electrolyte and the current

density. At high current densities, an hour was usually sufficient for copper in acid copper sulfate solution, but it required at least two hours for the platinum electrodes in sulfuric acid. At low current densities, however, much longer periods were necessary.

All the experiments were carried out at room temperature which varied from 20° to 26°C. This variation did not influence the conclusions since the polarization data were on a comparative basis and not absolute. Since all the measurements of polarization by the three methods were taken within such a short period, it may be assumed that the conditions of temperature, current density and concentration of the solution were constant.

In all the experiments with acid copper sulfate solution, no mechanical agitation was used; only the natural processes of convection, diffusion and electrical migration provided movement of ions in the solution. With the bright and platinized platinum in molar H_2SO_4, additional agitation was produced by the bubbles of liberated gases as they rose to the surface.

Potentiometric Measurements of Copper Polarization.

PRELIMINARY MEASUREMENTS

With the experimental arrangement described above, polarization data were determined on copper in acid copper sulfate solution at current densities ranging from 10^{-6} to 10^{-2} amperes per cm.^{2}. In the first series of experiments

only the "back" and "front" methods were compared. Table 1 summarizes and details the first experiment, listing the polarization data which were the averages of three or more runs. The probable error of measurement due to current fluctuation, changes in resistance and other variables amounted to ±0.3 millivolt.

At a current density of 10^{-6} amperes per cm.^{2}, the departure from reversibility was undetectable. At the next current density of 10^{-5} amperes per cm.^{2}, the departure from reversibility (or polarization) was detectable but in no case did it exceed one millivolt for either anode or cathode. Determinations beyond this current density showed greater deviations from the static potential and better reproducibility except at 10^{-2} amperes per cm.^{2} where high current drainage from the D.C. power source changed the current density during the run and fluctuations in polarization potentials were apparent.

Three general observations from the table may be listed: (1) a current density of 10^{-4} amperes per cm.^{2} or more is required before any appreciable departure from reversibility is important, (2) in this arrangement the "back" method gives much lower results than the "front" method, and (3) the reproducibility is good if precautions listed in the technique are followed.

Experience in obtaining the results summarized in Table 1 indicated that better current control was required to

TABLE 1

Current Density Amps. Cm.$^{-2}$	Position of Tip	Polarization in mv. Cathode	Polarization in mv. Anode	Comments
10^{-6}	Back Front	0.0-0.3	0.0-0.3	Continuous electrolysis for 7-1/2 hours. The potential changes were insignificant
10^{-5}	Back Front	0.29 0.97	0.51 0.75	Results variable; continued to rise after 10-3/4 hours of electrolysis. Values taken after 2-1/2 hours when they appeared most stable.
10^{-4}	Back Front	9.5 10.4	2.7 6.1	There was a rapid rise for the first 1/2 hour, then a slow drop which gradually levelled off at a stable value.
10^{-3}	Back Front	11.7 11.4 16.1 15.6	3.6 3.7 12.3 11.7	Two determinations on successive days showed a maximum deviation of 0.6 mv.
10^{-2}	Back Front	10.6 80.8	4.2 25.1	At this current density, variation in current becomes troublesome; duplicate readings were difficult to reproduce.

Notes - (i) Electrolyses carried out in an atmosphere of nitrogen at room temperature.
(ii) Current strength determined by microammeter and by IR drop over standard resistances.
(iii) Apparent surface area 32.2 cm.^{2}

Effect of Current Density on Polarization of Copper in Acid Copper Sulfate Solution by Front and Back Methods.

eliminate the fluctuation, and particularly the decrease of current with time. Consequently, in all the following experiments the automatic current regulator described in the Apparatus Section was used. To avoid certain repetitions in all the succeeding experiments it should be stated that the following conditions were maintained except in special cases when the variation will be specified:

(1) The apparent current density was maintained constant by the current regulator at 10 milliamps. per cm.^{2}, whatever the surface area.

(2) The back probe was placed in the well at the center rear of the electrode as shown in Fig. 3.

(3) The bevelled tip of the front probe was positioned near the center and placed firmly against the face of the electrode.

(4) The cathode and anode were inserted in the proper slots of the Haring cell (see Fig. 3) and occupied the full cross section of the cell.

(5) The gauzes were placed in the slots as described under "Haring Cell".

(6) Since the object of the experiments was to compare the different methods and to seek an explanation for any differences observed rather than to obtain an exact value of polarization potential, a freshly made acid copper sulfate solution was not always used but frequently an old solution was re-used. This may account for appreciable variations in

both static and dynamic potentials from one experiment to another. However, the solutions in all cases had been pre-electrolyzed and were maintained in a nitrogen atmosphere.

(7) The temperatures of the experiments were those of the room varying between 20 and 26°C.

Following the above directions, a run was made to compare the values by the front and back methods with the Haring cell values. Typical results are listed in Table 2.

TABLE 2

Electrode	Polarization in mv.		
	Back	Front	Haring Method
Cathode	9	86	71
Anode	5	41	27

Preliminary Polarization Measurements by the Back, Front and Haring Methods.

It is probable that when the electrodes completely filled the cross-sectional area as in the previous experiment that the diffusion of the liquid to the well in back of the electrodes was very slow or practically nil. To aid diffusion, in the next experiment the cathode was raised slightly from the bottom of the modified Haring cell. At the same time, the effect of the position of the tip of the front reference cell and of the distance from the cathode face to the front probe of the reference electrode was studied in an exploratory

manner. Measurements were also made by the back method and by the Haring method.

Using some previously electrolyzed and used acid copper sulfate solution the exact composition of which was not known but probably differed little from the original solution, the system was arranged to study only the cathodic values.

The cathode was raised 0.7 cm. from the bottom of the cell. The apparatus was exposed to the atmosphere. The results are summarized in Table 3. The numbers correspond to the position of the probe in contact with the cathode face as shown in Fig. 11.

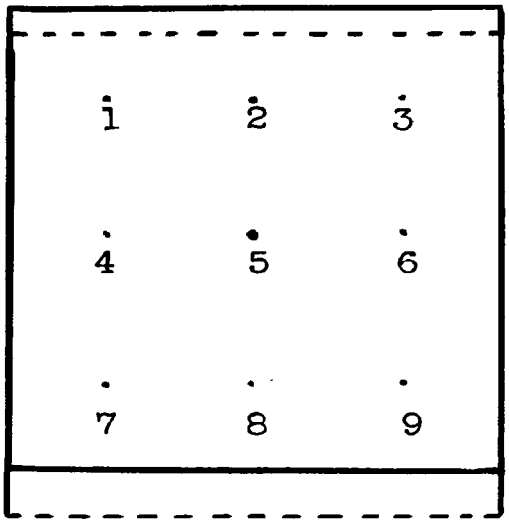


Fig. 11. Positions of Front Probe at Cathode Face for Table 3. Actual Size.

The following interesting conclusions may be deduced from this table: (1) The method with the reference electrode in back of the cathode still gives much lower values but the reproducibility is very good, ±0.3 mv. (2) The method with the reference electrode in front of the cathode gives consistently higher results than either the Haring method or the back method. (3) The potentials obtained by the front method varied over a range of 12 mv. depending on position

TABLE 3

Cell Measured	Stable State Potentials in Volts					
	Static	Dynamic				
		Position of Front Probe (Fig. 11)				
		1	2	3	4	5
Cathode vs. STD. Back	-+0.3555	-+0.3663	0.3662	0.3660	0.3657	0.3657
Cathode vs. STD. Front	-+0.3549	-+0.4202	0.4233	0.4201	0.4170	0.4241
Cathode vs. $Gauze_1$	+-0.0011	-+0.2226	0.2239	0.2232	0.2258	0.2256
$Gauze_1$ vs. $Gauze_2$	+-0.0008	-+0.1687	0.1686	0.1685	0.1661	0.1664

Method	Average	Cathodic Polarization in mv.				
Back	10.4	10.7	10.6	10.4	10.1	10.1
Front	68.4	65.3	68.4	65.2	65.1	69.2
Haring Cell	57.4	54.2	55.6	55.1	60.0	59.5

Cell Measured	Stable State Potentials in Volts				
	Static	Dynamic			
		Position of Front Probe (Fig. 11)			
		6	7	8	9
Cathode vs. STD. Back	-+0.3555	0.3659	0.3663	0.3657	0.3659
Cathode vs. STD. Front	-+0.3549	0.4205	0.4237	0.4285	0.4284
Cathode vs. $Gauze_1$	+-0.0011	0.2235	0.2255	0.2255	0.2250
$Gauze_1$ vs. $Gauze_2$	+-0.0008	0.1667	0.1690	0.1664	0.1660

Method	Avergae	Cathodic Polarization in mv.			
Back	10.4	10.3	10.7	10.1	10.3
Front	68.4	65.6	68.8	73.6	73.5
Haring Cell	57.4	57.1	56.8	59.4	59.3

Effect on Measured Potentials of Position of Probe on Cathode Face.

of the probe. An inspection of the table shows a consistent variation from one edge to the other with a maximum in the center and increasing near the bottom. From this and later observations this is definitely correlated with variations in current density due to leakage around the edge and especially at the bottom of the cathode and a net increase in current near the bottom. (4) Results by the Haring method are consistently lower than those by the front method, the difference in average values being 11 mv. or about 16%. (5) The differences in the results by the three methods are appreciably greater than the limits of reproducibility. The major purpose of this investigation is to seek an explanation for these differences.

An experiment was arranged to examine the relationship of the IR drop of the solution to the distance of the exploring tip from the front of the cathode. A micrometer screw with a metric scale and an attachment to hold the standard half cell was arranged in such a manner that the tip would be perpendicular to the face of the cathode near the center. In this case the solution was exposed to the atmosphere. For purposes of comparison, corresponding static and dynamic readings were taken by the three methods during the first half of the series when the probe was nearest to the cathode. Potential readings were taken at short distances (at first every 0.05 cm., then 0.10 cm.) away from the working electrode. On the assumption that the polarization remained constant in

the steady state, the IR drop through the solution can be calculated. If there were no IR drop at the tip of the Luggin capillary of the reference electrode, the curve obtained by plotting IR drop versus distance should give a straight line passing through the origin, i.e., no IR drop at 0.00 cm. Actually some deviation from a linear relationship is to be expected at the electrode-solution interface due to various factors which will be considered in the Discussion Section. The experimental data are given in Table 4.

The IR drops at increasing distances from the cathode are obtained by assuming that the value at 0.00 cm. in the table (83.0 mv.) is only polarization and subtracting this potential from the succeeding values in the column headed "Pol. + IR".

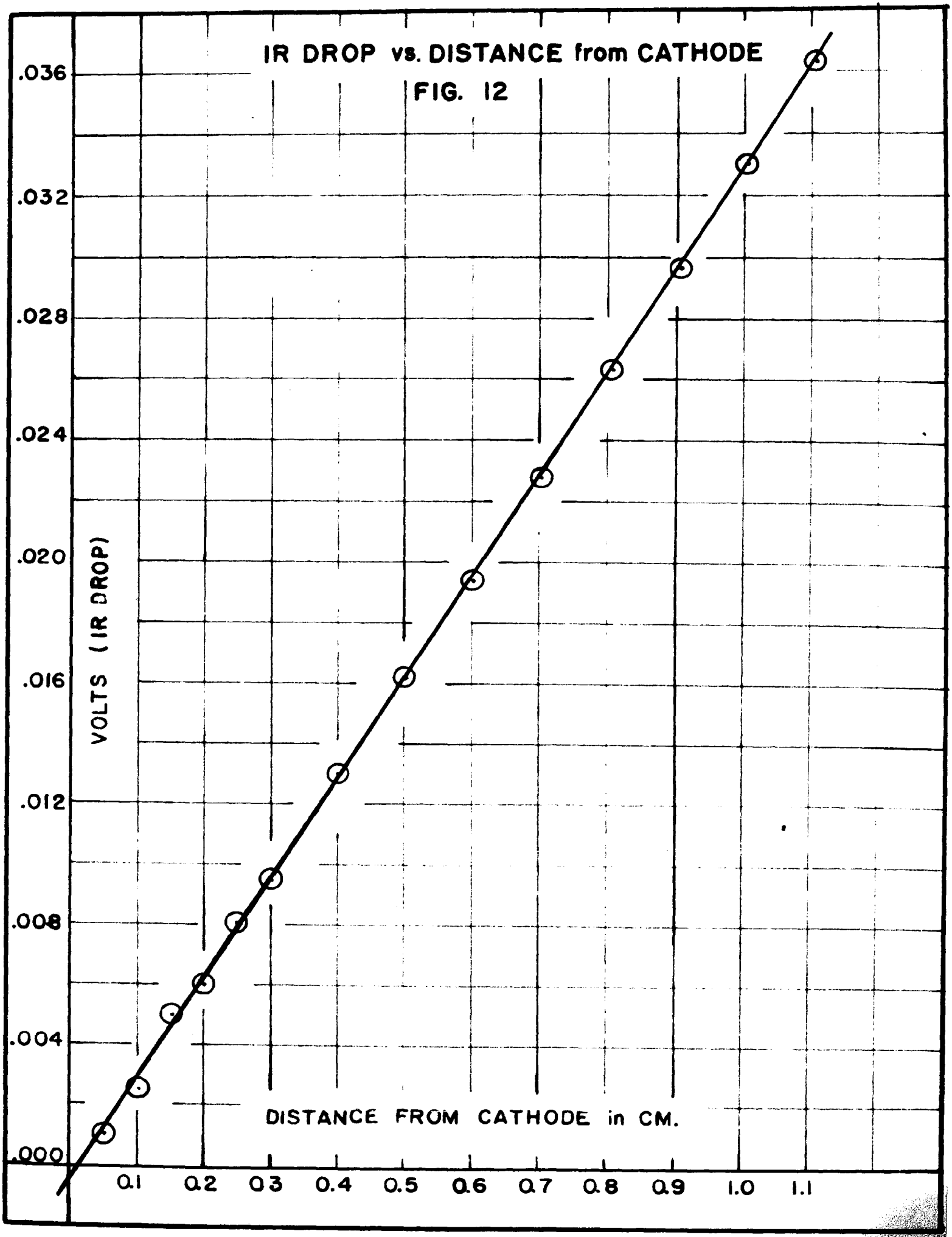
A plot of IR values, thus obtained, against distance from the face of the cathode is given in Figure 12. The approximately linear curve cuts the abscissa at 0.02 cm. and the ordinate at -0.6 mv. This difference slightly exceeds the experimental error of measurement and may be due to a small IR drop included in the first measurement; which may account for the slight shift in the line from 0.00 cm. Other possible factors are the following: (a) The tip of the search electrode has a certain amount of spring when placed firmly in contact with the active electrode. (b) The area immediately in front of the tip is a region of lower current density leading to the so-called "shielding effect", due to the

TABLE 4

Distance from Cathode in cm.	Potential Differences in Volts				
	Cathode vs. STD.Back	Cathode vs. STD.Front	STD. Back STD. Front	Cathode vs. $Gauze_1$	$Gauze_1$ vs. $Gauze_2$
0.00(Static)	-+0.3595	-+0.3585	0.0010	+-0.0003	+-0.0002
0.00(Dynamic)	0.3712	0.4415	0.0703	-+0.2578	-+0.1847
0.05	0.3711	0.4425	0.0714	0.2570	0.1840
0.10	0.3710	0.4440	0.0730	0.2572	0.1843
0.15	0.3709	0.4465	0.0756	0.2569	0.1837
0.20	0.3707	0.4475	0.0768	0.2568	0.1836
0.25	0.3706	0.4495	0.0789	0.2566	0.1836
0.30		0.4510			
0.40		0.4545			
0.50		0.4577			
0.60		0.4609			
0.70		0.4643			
0.80		0.4677			
0.90		0.4711			
1.00		0.4745			
1.10		0.4778			

Distance from Cathode in cm.	Polarization (mv.)		Pol. +IR	Calculated IR Drop (mv.)
	Back Method	Haring Method	Front Method (mv.)	
0.00(Static)				
0.00(Dynamic)	11.7	73.2	83.0	---
0.05	11.6	73.0	84.0	1.0
0.10	11.5	72.9	85.5	2.5
0.15	11.4	73.2	88.0	5.0
0.20	11.2	73.2	89.5	6.0
0.25	11.1	73.0	91.0	8.0
0.30			92.5	9.5
0.40			96.0	13.0
0.50			99.2	16.2
0.60			102.4	19.4
0.70			105.8	22.8
0.80			109.2	26.2
0.90			112.6	29.6
1.00			116.0	33.0
1.10			119.3	36.3

Effect on Measured Potentials of Distance of the Probe from the Cathode


IR DROP vs. DISTANCE from CATHODE
FIG. 12
VOLTS (IR DROP)
.036
.032
.028
.024
.020
.016
.012
.008
.004
.000
DISTANCE FROM CATHODE in CM.
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1

disturbance of the current lines by the tip. (c) Concentration changes at the cathode may influence the resistivity values near the electrode interface. In view of all these factors the linearity of the curve and the closeness of its intersection to the origin is surprising.

An inspection of this and the preceding tables shows that the back method gives much lower values than either of the other two. When the cathode was removed it was observed that the copper had plated on the back. Hence the polarization measured at the back would correspond to a lower current density than that at the front. A theoretical consideration shows that the potential difference measured between the standard half-cell and the active electrode is the potential difference developed between the reference cell and the metal in equilibrium with its ions in solution at the point nearest the reference through a path of least resistance. Since the current went around to the back of the electrode, the actual polarization so measured was the polarization at the back of the active electrode directly in front of the reference instead of in front of the cathode. This suggested that a study of the proper insulation of the back of the electrode should be made.

STUDY OF EXTENT OF INSULATION AND POSITION OF PROBES ON MEASURED POTENTIALS

To insure that the potential measured by the back method was that at the front surface, the back of the cathode and the

part of the electrode within the slot was coated with Unichrome Stop-Off Wax and a new series of measurements similar to those in Table 2 was carried out. The results appear in Table 5.

It should be pointed out that not all the values in the table represent independent quantities; one of the three potentials in the row set 1, 2 and 3 and one of the three in the set 5, 6 and 7 being dependent upon the other two in the set. It should be noticed that the value by the back method and the potential difference between the two standards when added (0.0645 + 0.0130 = 0.0775) give approximately the value (0.0770) of the polarization with the reference half-cell in front of the cathode which shows the precision with which polarization measurements can be made.

It should be especially noted that the back method still gives polarization values less than those by the front method, although the back reference is negative to the front reference in this as in previous experiments (compare Tables 2, 3 and 4). However, insulation of the back of the cathode materially reduced the difference.

In order to check the previous results two additional runs were made under the same conditions as those of Table 5. A summary of critical data is given in Table 6. The excellent reproducibility is clearly evident.

These results justified further investigation of the reason for the potential difference developed between the two reference electrodes. The cathode was insulated as in the

TABLE 5

Row Number	Cell Measured	Static Potential (volts)	Dynamic Potential (volts)	Difference (volts)
1	Cathode - $Gauze_1$	+-0.0005	-+0.2535	-+0.2540
2	Cathode - $Gauze_2$	+-0.0005	-+0.4335	0.4340
3	$Gauze_1$ - $Gauze_2$	0.0000	-+0.1802	0.1802
4	Cathode - Anode	0.0000	-+0.6310	0.6310
5	Cathode - Std. Back	-+0.3542	-+0.4187	0.0645
6	Cathode - Std. Front	-+0.3541	-+0.4311	0.0770
7	Std. Back - Std. Front	+-0.0001	-+0.0129	0.0130

Method		Polarization in Volts
Haring	(a)	0.2540-0.1802 = 0.0738
	(b)	0.4340-2(0.1802) = 0.0736
	Front	0.4311-0.3541 = 0.0770
	Back	0.4187-0.3542 = 0.0645

Effect on Measured Potentials on Insulating Back of Cathode

TABLE 6

Method	Polarization in mv.	
	Run 1	Run 2
Haring	71.5	73.3
Front	76.9	77.0
Back	63.7	64.4
STD. Back - STD. Front	-+13.4	-+12.9

Reproducibility of Cathodic Polarization Data of Copper

previous experiment but in addition the wax was extended to about 1/4" beyond the slot thus restricting the area to 21.2 $cm.^2$. No precautions were taken to protect the solution from the atmosphere. Results of three runs appear in Table 7, the first run in detail with the experimental values and for the other two the calculated polarization potentials only.

In all three cases, the polarity of the potential difference between the two reference half cells was reversed in respect to the previous runs (see previous Tables). By subtracting this potential difference, values within 0.2 mv. of the front method are obtained. The three results are not strictly comparable since the experiments were run on different days with the electrodes remaining in the same solution exposed to the atmosphere so that concentration changes might occur due to evaporation; the trend of the results, however, is in the same direction, which is the important thing.

TABLE 7

Measured Cell	Potential Differences in Volts		
	Static	Dynamic	Difference
Cathode-Gauze$_1$	-+0.0013	-+0.2042	-+0.2029
Cathode-Gauze$_2$	-+0.0024	-+0.3279	-+0.3255
Gauze$_1$-Gauze$_2$	-+0.0011	-+0.1236	-+0.1225
Cathode-Std. Back	-+0.3564	-+0.4633	-+0.1069
Cathode-Std. Front	-+0.3562	-+0.4327	-+0.0765
Std. Back - Std. Front	+-0.0003	+-0.0307	+-0.0304 (note polarity)

Method	Polarization in mv.		
	Run 1	Run 2	Run 3
Haring	80.4	89.9	82.6
Front	76.5	81.1	72.6
Back	106.9	107.6	98.7
Std. Back - Std. Front	+-30.4	+-26.3	+-26.0

Effect on Measured Potentials of Extending Insulation 1/4" on Front.

As a further check on these findings, two additional runs were made under the same conditions. In order to compare with the effects at the cathode, polarizations were also determined at the anode. The anode was similarly waxed off

as the cathode. The results appear in Table 8 and clearly support the previous findings.

TABLE 8

Method	Polarization (mv.)			
	Run 1		Run 2	
	Cathodic	Anodic	Cathodic	Anodic
Haring	87.3	16.1	91.8	17.0
Front	79.5	18.5	84.7	18.3
Back	106.9	1.8	112.5	1.4
Difference	+27.1		+27.6	
STD. Back-STD. Front		-16.5		-16.7

NOTE - Run (1) 79.5 + 27.1 = 106.6 ≈ 106.9
1.8 + 16.5 = 18.3 ≈ 18.5
Run (2) 84.7 + 27.6 = 112.3 ≈ 112.5
1.4 + 16.7 = 18.1 ≈ 18.3
} Deviation ±0.2 mv.

Anodic & Cathodic Polarization for Insulated Electrodes

A detailed consideration of these result will be found in the Discussion Section.

The next step in an attempt to clarify the relation of the stop-off wax and the position of the search electrode was a study of the various positions of the probe across the face of the working cathode. In order to extend the study to edges of the electrode, a 1/4" segment of the insulation was removed as indicated in Figure 13 which gives a diagrammatic sketch of the electrode and the approximate positions of the probe. The solution level was at about 1/4" above the top of the exposed

metal. Standard 1 (in back) was kept in a fixed position since it was found that moving it did not appreciably change the observed potential difference (see later for detailed information). Standard 2 (in front) was positioned in the various indicated locations as shown in the diagram. Standard 3 was a reference half cell the tip of which was maintained in a fixed position directly in front of the anode in order to check the results of the potential difference between standard 1 and standard 2. As seen by an inspection of the last two columns in Table 9, the values follow the same trend and the change in potential difference due to the position of the probe is of the same magnitude.

TABLE 9

Position of Tip	Potential Difference (volts)	
	STD.$_1$-STD.$_2$	STD.$_2$-STD.$_3$
1	+-0.0244	-+0.3546
2	0.0261	0.3564
3	0.0274	0.3574
4	0.0304	0.3591
5	0.0307	0.3604
6	0.0300	0.3603
7	0.0293	0.3590
8	0.0290	0.3595
9	0.0268	0.3560
10	0.0241	0.3535
11	0.0229	0.3524
12	0.0261	0.3514

Effect on Measured Potentials of Position of Probe as Indicated in Fig. 13.

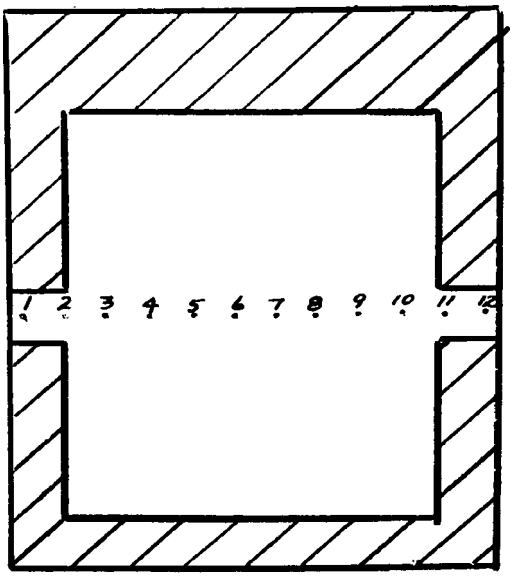


Fig. 13 Modified Cathode Showing Positions of Probe and Insulation. Actual Size.

The results of column 2 are shown graphically in Fig. 14. A duplicate run with nine positions across the electrode under investigation is reported in Table 10. The nine points were about equally spaced. The general pattern is similar to that of Table 9 and shown in Fig. 14.

TABLE 10

Position of Front Probe	Potential Difference (volts)	
	$STD._1-STD._2$	$STD._2-STD_3$
1	0.0020	0.3511
2	0.0223	0.3512
3	0.0219	0.3508
4	0.0271	0.3561
5	0.0284	0.3573
6	0.0289	0.3580
7	0.0275	0.3566
8	0.0227	0.3520
9	0.0223	0.3513

Effect of Measured Potentials of Position of Probe Similar to Table 9.

A third run was also made, including thirteen positions for the probe. In this case measurements were made also of the potential difference between the cathode and Standards 1 and 2. Positions No. 1 and No. 13 were at the extreme edge of the cathode.

TABLE 11

Position of Probe	Measured Potential Difference (volts)			
	$STD._1$-$STD._2$	$STD._2$-$STD._3$	Cathode-$STD._2$	Cathode-$STD._1$
Static	+-0.0002	-+0.0004	-+0.3526	-+0.3528
Dynamic 1	+-0.0215	-+0.3636	-+0.4290	-+0.4509
2	0.0196	0.3617	0.4322	0.4518
3	0.0218	0.3632	0.4301	0.4518
4	0.0242	0.3650	0.4285	0.4524
5	0.0250	0.3657	0.4274	0.4519
6	0.0250	0.3655	0.4277	0.4525
7	0.0250	0.3653	0.4277	0.4526
8	0.0251	0.3652	0.4279	0.4527
9	0.0242	0.3643	0.4285	0.4529
10	0.0219	0.3614	0.4309	0.4527
11	0.0194	0.3581	0.4331	0.4528
12	0.0194	0.3576	0.4334	0.4528
13	0.0202	0.3586	0.4325	0.4528

Effect on Measured Potentials of Position of Probe Similar to Tables 9 and 10.

An examination of the values of the first three potential difference columns in Table 11 again shows a general trend - a fairly constant value in the center with a slow decrease toward either edge. The slightly higher readings at positions No. 1 and No. 13 represent readings at the nearest possible

point to the edge of the electrode and may be due to a higher current density at these positions in comparison with Positions No. 2 or No. 12, about 0.2 cm. from the edges. This is shown graphically in Fig. 14. The consistency of the values in the fourth column of potentials indicate an experimental verification of a previously mentioned fact - that the standard half cell in back of the electrode is highly constant and reproducible.

The consistency of the results in the three tables (9, 10 and 11) conclusively demonstrates that the trend mentioned above is a real phenomenon which requires further study.

In order to determine the influence on the potentials of the uninsulated 1/4" segments at the edges of the electrode, in the next experiment this portion was also insulated, thus making a complete 1/4" band of wax around the entire edge of the electrode. Measurements were made at a series of equally spaced positions across the face as in the previous three runs. Results are given in Table 12.

At positions No. 1 and No. 12 the capillary probe was placed beyond the edge of the insulation and as close as possible to the edge of the cell wall. The polarity of the reference electrodes is indicated; Standard 1 (back) is negative in comparison with Standard 2 in position No. 1, whereas in position No. 2 the polarity of the standards is reversed. The results of this table along with those of Tables 9, 10 and 11 are shown in Fig. 14. The significance

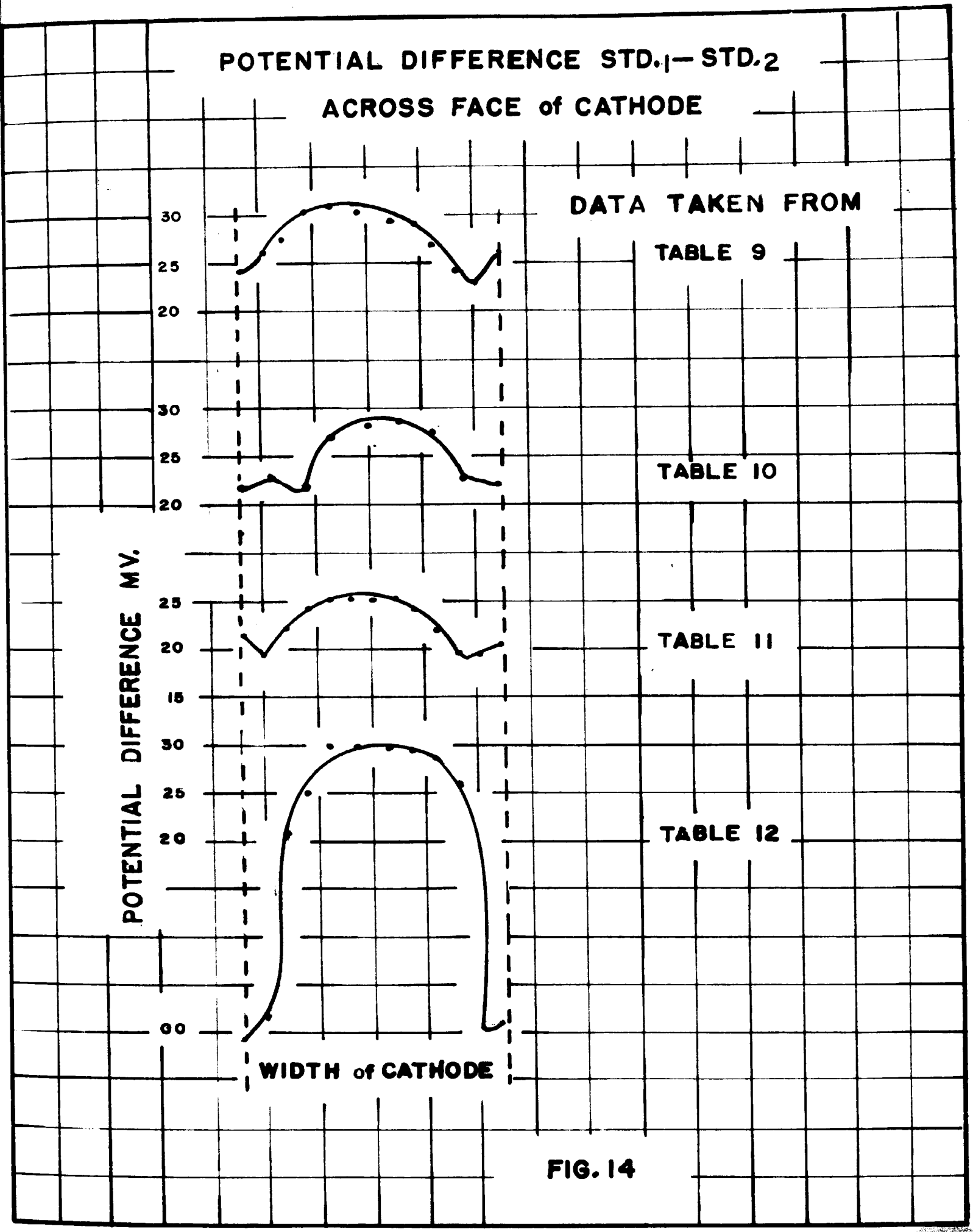

POTENTIAL DIFFERENCE STD.1 — STD.2
ACROSS FACE of CATHODE
DATA TAKEN FROM
TABLE 9
TABLE 10
TABLE 11
TABLE 12
POTENTIAL DIFFERENCE MV.
30
25
20
30
25
20
25
20
15
30
25
20
00
WIDTH of CATHODE

FIG. 14

TABLE 12

Probe Position	Potential Difference $STD._1$-$STD._2$ (volts)
1	-+0.0004
2	+-0.0018
3	+-0.0218
4	+-0.0249
5	+-0.0304
6	+-0.0297
7	+-0.0298
8	+-0.0297
9	+-0.0285
10	+-0.0264
11	+-0.0010
12	+-0.0030

Effect on Measured Potentials of Position of Probe When 1/4" Insulation on Front is Complete.

of the values measured and the polarity of the potentials will be considered later in the Discussion Section.

The results obtained up to this point indicate two factors which have a profound influence on the measured polarization values, (1) the extent to which insulation is applied especially near the edges and (2) the position of the front probe against the face of the electrode. As to the first factor, with no insulation on the back this difference between the front and back methods is about 60 to 80 mv., the back probe being negative (up through Table 4); with the back insulated this difference was reduced to 13 mv., with the same polarity (Tables 5 and 6); with the insulation extended 1/4" around the front edge, the sign of the back electrode changed to positive in respect to the front and the difference in potential was changed to 27 mv. (Tables 7 through 12) or a net change of 40 mv. The fact that the last arrangement obviously causes an increased current density at the edge of the insulation with the attendant increased polarization at the front

edge of the electrode suggests that the insulation should stop at the inner wall of the cell. This was done in the next series of experiments. As to the second factor mentioned above it is noted from Tables 9 through 12 and Figure 14 this potential difference (between front and back electrodes) remains fairly constant for positions in the central portion of the electrode and decreases uniformly toward the edges. It was desired to study further this factor under the new conditions. Consequently in the next experiment, the back, edges and a small rim extending only slightly beyond the slots were insulated thereby establishing the surface area to the cross-section of the cell, 30.6 sq. cm. Anodic and cathodic measurements were made with the two front probes, at the center and at the edge, with the back probe and by the Haring method. Results are summarized in Table 13.

Under these new conditions there is still the potential difference between the back probe and the front probe at the center, but it has been reduced to 15 mv. with the back probe still positive. However, when measurements were taken between the back probe and the probe at the front edge, the difference was only 8 mv. As previously found the values of the Haring cell method are consistently lower.

All previous results have indicated that the potentials measured by the back method correspond to the nearest exposed point on the cathode whether it be at the back, at the edge or at the front. The only way to make a direct measurement

TABLE 13

Run	Electrode	Polarization (volts)			
		Haring	Position of Standard		
			Front Center	Front Edge	Back
1	Cathode	0.0681	0.0772	0.0873	0.0928
2		0.0723	0.0779	0.0883	0.1002
3		0.0673	0.0766	0.0815	0.0910
4		0.0690	0.0767	0.0827	0.0921
5		0.0726	0.0819	0.0892	0.0970
Average		0.0697	0.0781	0.0858	0.0948
1	Anode	0.0150	0.0129	0.0218	0.0276
2		0.0151	0.0100	0.0197	0.0273
3		0.0132	0.0107	0.0177	0.0278
4		0.0140	0.0107	0.0185	0.0290
5		0.0139	0.0117	0.0176	0.0281
Average		0.0142	0.0112	0.0191	0.0280

Run	Electrode	Measured Potential Difference (volts)	
		STD.Back-STD:Center	STD.Back-STD.Edge
1	Cathode	+-0.0152	+-0.0048
2		0.0219	0.0114
3		0.0142	0.0097
4		0.0154	0.0090
5		0.0151	0.0076
Average		0.0164	0.0084
1	Anode	-+0.0146	-+0.0055
2		0.0175	0.0077
3		0.0169	0.0096
4		0.0180	0.0102
5		0.0163	0.0102
Average		0.0163	0.0096

Effect on Measured Potentials of Position of Probe and of Further Modification of Insulation.

by the back method with reference to the front center of the electrode is to bore a hole through the electrode at the center. Consequently for the next experiment, a 1/8" hole was drilled at the exact center of the cathode directly in front of the back probe. The same solution as before was used throughout the series of runs which covered a period of three days. Cathodic polarization values for four methods appear in Table 14.

TABLE 14

Run	Polarization (volts)				Measured Potential Difference, (volts) of Two Standards	
	Haring Cell	Position of Standard Electrode				
		Front, Center	Front, Edge	Back	Back-Center	Back-Edge
1	0.0668	0.0751	0.0803	0.0813	+-0.0056	+-0.0002
2	0.0683	0.0750	0.0809	0.0808	0.0057	0.0000
3	0.0677	0.0760	0.0798	0.0841	0.0082	0.0038
4	0.0669	0.0745	0.0800	0.0803	0.0059	0.0004
5	0.0681	0.0779	0.0825	0.0841	0.0060	0.0013
Average	0.0676	0.0757	0.0807	0.0821	0.0063	0.0011

Effect on Measured Potentials of Drilling a Hole in the Electrode.

While a complete consideration of these results is deferred until the Discussion Section the following points may be emphasized here as to the effect of boring a hole through the cathode: (1) the measured potential difference between the back probe and the front center has been reduced from 15 mv. shown in the previous table to 6 mv., (2) the measured potential difference between the back probe and the front

edge has been reduced from 7 mv. to 1 mv., (3) the polarization values by the back method are reduced by 13 mv. while those by the front method are decreased but slightly, (4) the values by the front method are greater by about 5 mv. at the edge than at the center, (5) the values by the Haring cell method are consistently lower than those by either of the other two as has been true in all previous cases in which the back of the electrode was insulated, (6) in agreement with previous tables, the degree of reproducibility of the measurements by each of the methods is surprisingly good.

Another method of measuring polarization by the direct method has the tip of the Luggin capillary inserted from the back through a hole in the electrode in such a manner that the tip is normal to the plane of the electrode-solution interface which should eliminate the IR drop and shielding effect associated with the front method. A discussion in greater detail may be found in the Theoretical Section of this dissertation.

In order to compare this method with the others under investigation, several runs were made in which the probing tip was so arranged that it passed through the 1/8" hole and the leading edge of the tip was flush with the electrode face. The probe for the front method was at the rim of the hole pressed lightly but firmly against the cathode. The same solution was used on different days so the concentration undoubtedly is not the same but this is of no consequence

since the point at issue is a comparison of the polarization values by the different methods in any one run.

TABLE 15

Method	Polarization (volts)			
	Run 1	Run 2	Run 3	Average
Haring	0.0718	0.0679	0.0643	0.0680
Front	0.0794	0.0734	0.0742	0.0757
Back (Tip in Hole)	0.0801	0.0743	0.0745	0.0763
Measured STD.Back-STD.Front	0.0007	0.0009	0.0002	0.0006

Effect on Measured Potentials of Placing Back Probe in Hole through the Center of Cathode

The results in each run of the method using the probe in the hole of the electrode and the front method are the same within the limits of error. The precision of determining polarization values is about one millivolt or less. This is much better than the accuracy of polarization values reported in the literature where 10 mv. is the best with 30 to 50 mv. not uncommon. If properly carried out it is safe to say that the two methods using the standard half cells compared in Table 15 give the same results. The Haring method gives consistently lower results.

EFFECT OF DISTANCE OF THE FRONT PROBE FROM THE CATHODE

As pointed out in the Theoretical Section, it is universally agreed that with the tip in front of the electrode

under investigation errors are introduced due to the presence of an IR drop and due to the shielding of the electrode by the tip of the reference cell. In general two methods have been used in an attempt to apply corrections for these effects. In one, the potential readings are taken at measured appreciable distances from the cathode and an extrapolation made to zero distance. In the second method, a single reading is taken at a specified distance away from the elctrode and a correction applied based on the bulk conductivity of the electrolyte. A critical test of the validity of these methods is decidedly in order. It may be recalled that a preliminary study of this effect was made before any insulation of the electrode was employed. Results appear in Table 4 and are shown in Figure 12.

As in the earlier experiment, a micrometer arrangement was used to hold the standard half cell and to measure the distance from the face of the cathode. The capillary tip of the reference electrode was placed in the bulk of the solution about 1.3 cm. away from the front-center of the cathode and then slowly brought to the face of the working electrode by the micrometer screw. Dynamic readings were taken every 0.1 cm. at first in the bulk and then as the probe approached the cathode, every 0.05 cm. or less until a constant potential value, signifying firm contact with the cathode, was reached. The values are reported in Table 16 and are presented graphically in Fig. 14.

TABLE 16

Reading on Micrometer (cm.)	Run 1			Run 2		
	Distance (cm.)	Potential (volts)	IR Drop (volts)	Distance (cm.)	Potential (volts)	IR Drop (volts)
4.0	1.34	0.4304	0.0196	1.40	0.4307	0.0206
3.9	1.24	0.4295	0.0187	1.30	0.4299	0.0198
3.8	1.14	0.4286	0.0176	1.20	0.4290	0.0189
3.7	1.04	0.4277	0.0169	1.10	0.4279	0.0178
3.6	0.94	0.4267	0.0159	1.00	0.4269	0.0168
3.5	0.84	0.4256	0.0148	0.90	0.4258	0.0157
3.4	0.74	0.4244	0.0136	0.80	0.4247	0.0147
3.3	0.64	0.4230	0.0122	0.70	0.4237	0.0136
3.2	0.54	0.4216	0.0108	0.60	0.4220	0.0119
3.1	0.44	0.4201	0.0093	0.50	0.4205	0.0104
3.0	0.34	0.4185	0.0078	0.40	0.4190	0.0089
2.9	0.24	0.4166	0.0058	0.30	0.4173	0.0072
2.8	0.14	0.4146	0.0036	0.20	0.4152	0.0051
2.75	0.09	0.4135	0.0027	0.15	---	---
2.70	0.04	0.4123	0.0015	0.10	0.4129	0.0028
2.68	0.02	0.4117	0.0009	---	---	---
2.66	0.00	0.4108	0.0000	---	---	---
2.64	0.00	0.4108	0.0000	---	---	---
2.60				0.00	0.4101	0.0000

Effect on Measured Potential of Distance of Front Probe from the Cathode.

The curves show a decided departure from linearity for distances less than 6 mm. from the electrode. Consequently corrections for IR drop based on either of the two methods outlined above will be in error. For example, as the dotted line in Fig. 15 shows, linear extrapolation from the bulk of the solution would produce an error of about 6 mv., even for this ideal condition of plane parallel electrodes with perpendicular current lines.

EFFECT OF POSITIONING OF BACK PROBE

Earlier results indicate an advantage of the back method in the avoidance of shielding and IR drop since the current lines do not normally go to the back of a properly insulated electrode. It was desirable to determine whether the positioning of the probe at the back of the electrode had any effect on the measured value. In order to make this possible, the cathode, the back of which was completely stopped-off, was moved into the next slot ordinarily occupied by a gauze electrode leaving a space behind for variation in the positioning of the probe. The locations used and values obtained are given in Table 17.

The consistent values for the dynamic potentials which show a maximum variation of 0.5 mv. indicate that if any IR drop occurs in back of an electrode which is properly insulated it is everywhere the same and thereby the standard half cell may be placed anywhere behind the electrode without the position of the probe affecting the potential value.

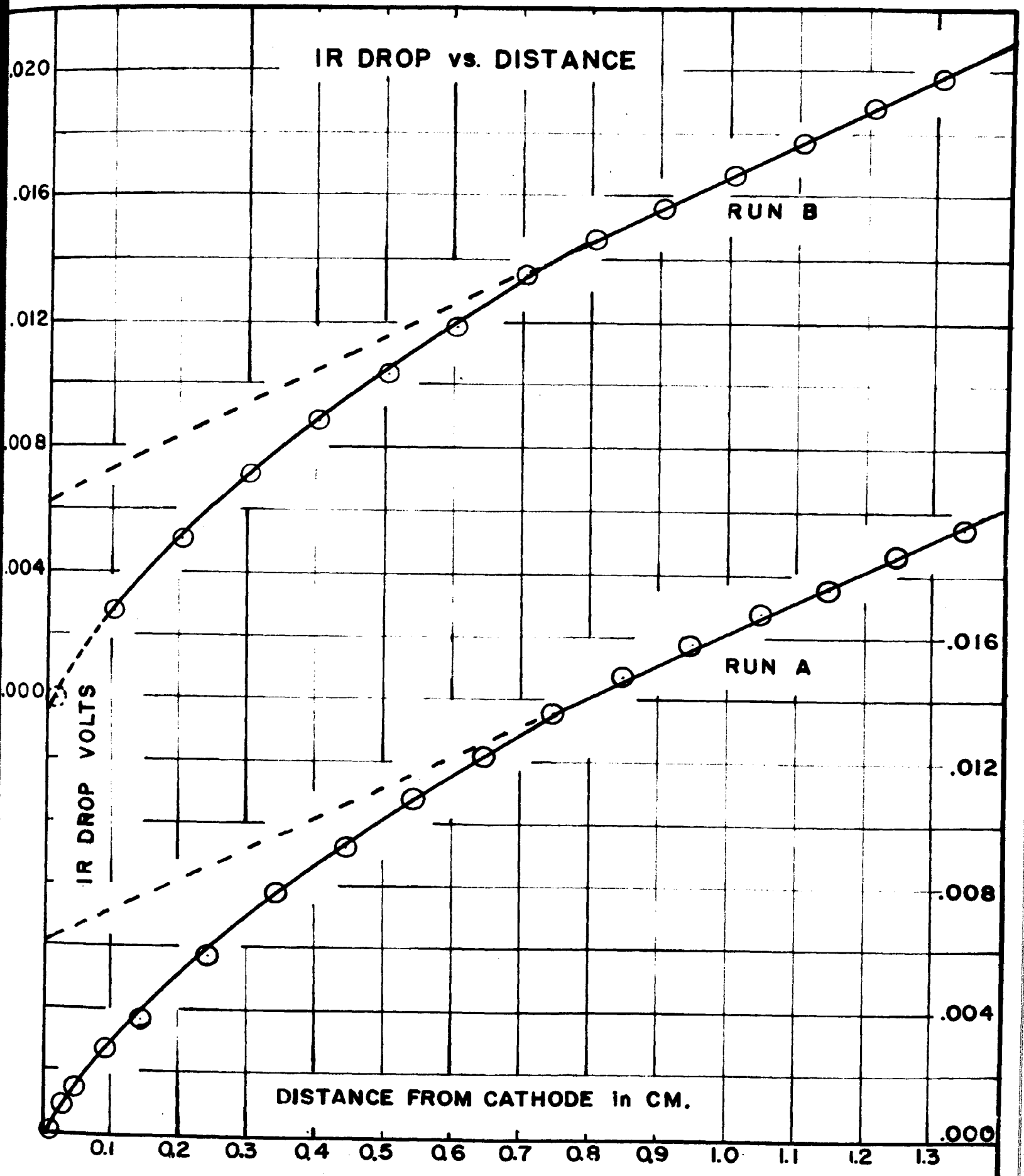

IR DROP vs. DISTANCE
RUN B
RUN A
IR DROP VOLTS
DISTANCE FROM CATHODE in CM.
.020
.016
.012
.008
.004
.000
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3

FIG. 15

TABLE 17

Position of Back Probe in Respect to Cathode Back		Dynamic Potential (volts)
Back & Tip in Contact	Right Hand Edge Left Hand Edge At Center	0.4361 0.4356 0.4355
Farthest away from Cathode	At Center Right Hand Edge Left Hand Edge	0.4361 0.4360 0.4361

Effect on Measured Potentials of the Position of the Back Probe.

In an earlier experiment - for which the results are given in Table 14 - it was found that with the tip of the reference electrode in the well behind the cathode and the front electrode at the edge of a hole through the center, five runs gave an average potential difference of 6 mv. In order to study this situation more thoroughly, in this case measurements could be made with the tip through the hole flush with the front surface and also when the tip was in the bulk of the solution in back of the electrode. The results appear in Table 18. As expected from previous observations, practically no difference in potential is noted between the two standards when they are in contact. However, when the back electrode was retracted into the body of the solution at the rear of the solution a potential difference of about 5 mv. was noted, corresponding to the result previously given in Table 14 when the probe was in the well.

TABLE 18

Position of Tips	Measured Potential Difference (volt)		
	Cathode-STD.$_1$ (in back)	Cathode-STD.$_2$ (in front)	STD.$_1$-STD.$_2$
Static Tips in Contact	0.3526	0.3524	0.0001
Dynamic Tips in Contact	0.4253	0.4252	0.0001
Tip No. 1 in Bulk	0.4309	0.4257	0.0051

Effect on Measured Potentials of Two Positions of the Probe behind and through the Cathode.

EFFECT ON MEASURED POTENTIALS OF POSITION OF PROBE BY THE FRONT AND HOLE METHODS WITH A SMALL CATHODE

Some previous experiments reported in Tables 9, 10 and 11, and shown in Fig. 14, showed a consistent variation in potential across the face of an insulated electrode completely filling the cell cross-section, which represents an ideal situation and one not usually found in research or industrial practice. In those cases in which only the back of the electrode was stopped-off, the potential remained nearly constant in the center half or third of the electrode surface and dropped off gradually toward the edges. In these experiments, the lateral positioning of the electrode could be established only approximately. In the next experiment, in order to make a more careful study of this potential distribution on a cathode not completely filling the cross-section, the probe was mounted on a micrometer screw arrangement which permitted accurate positioning. At the same time it was desirable to

explore the potential at points beyond the edges of the electrode. With this object the electrode was constructed as shown in Fig. 16 with all portions except the front central 2 x 2.5 cm. section stopped off with insulating wax. The anode was 30 sq. cm. in area. The other standard (No. 1) was in the well behind the electrode and maintained in one position.

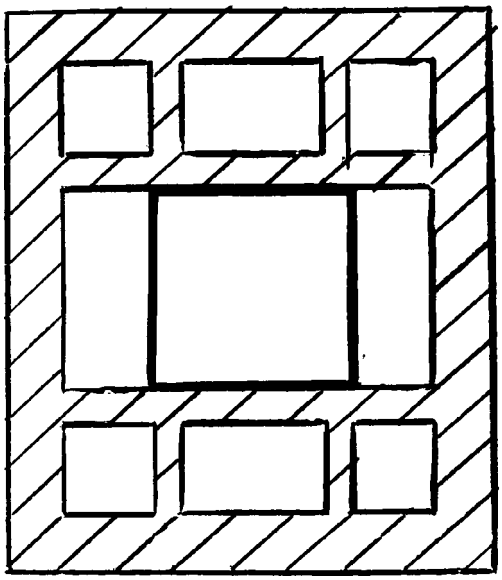


Fig. 16 Sketch of Small Cathode. Actual Size.

In the first experiment with this arrangement the potential difference was determined between the back standard and the front standard in various positions 2 mm. apart across the front face of and with the bevelled edge pressed firmly against the active cathode. The results are shown in Fig. 17 and indicate the great effect of the positioning of the probe on the magnitude of the measured polarization potential. The variation of potential difference between the two standards as the front probe is moved across the front face of the cathode is about 10 mv. representing an uncertainty of about 12% since in this case it may be recalled that the polarization potential is about 80 mv.; for higher current densities and other systems the variation might well be greater. The much greater symmetry of the variation shown here in comparison with the earlier results

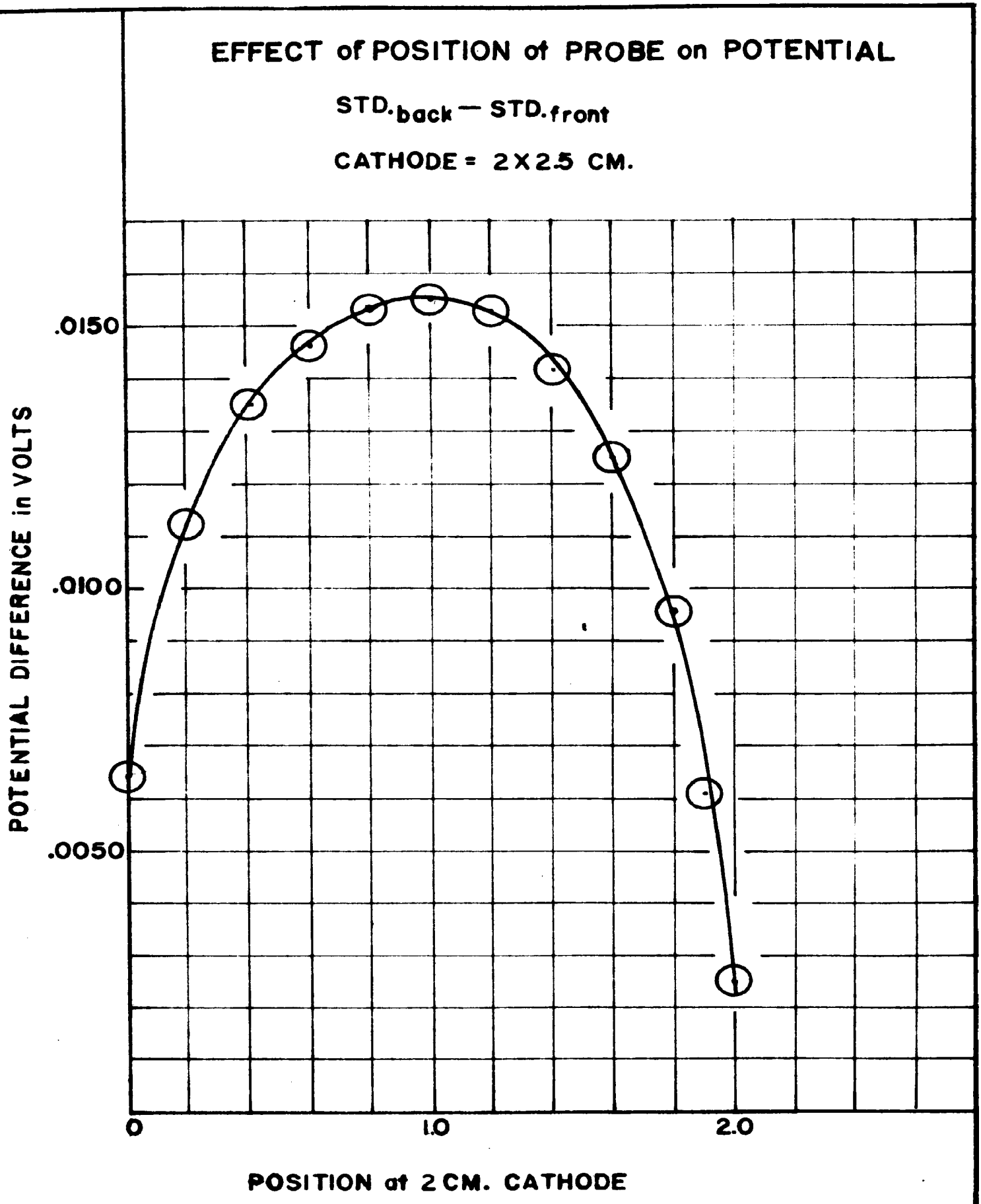

EFFECT of POSITION of PROBE on POTENTIAL
STD.back — STD.front
CATHODE = 2X2.5 CM.
.0150
.0100
.0050
POTENTIAL DIFFERENCE in VOLTS
0
1.0
2.0
POSITION at 2 CM. CATHODE

FIG. 17

is doubtless due to the greater accuracy possible in this experiment in the determination of the position of the probe.

In the second experiment with the same arrangement, the potential difference was measured between the cathode and the front standard at a similar set of positions across the front and extending about 0.6 cm. beyond the edge into the solution. The results appear in Fig. 18 and as previously observed the large symmetrical variation amounting to 5.4 mv. due to positioning is evident. In addition a rapid increase of about 10.0 mv. in potential difference is shown about 0.6 cm. beyond the edges of the active electrode.

Previous experiments (Tables 15 and 18) by the method with the probe through the hole ~~of~~ 12% the cathode to the front face indicated that almost identical results may be obtained with those measured by the front method. To correlate and verify this indication, a series of 1/8" holes, more or less equally spaced, was drilled through the 5 sq. cm. cathode, used in the two previous experiments, to accomodate the tip of the probe. Table 19 lists the values measured as the probe is moved from hole to hole from the left edge to the right edge. The front standard was positioned close to the center of the cathode and firmly in contact with it. Results in Table 19 confirm the previous experiments and conclusions.

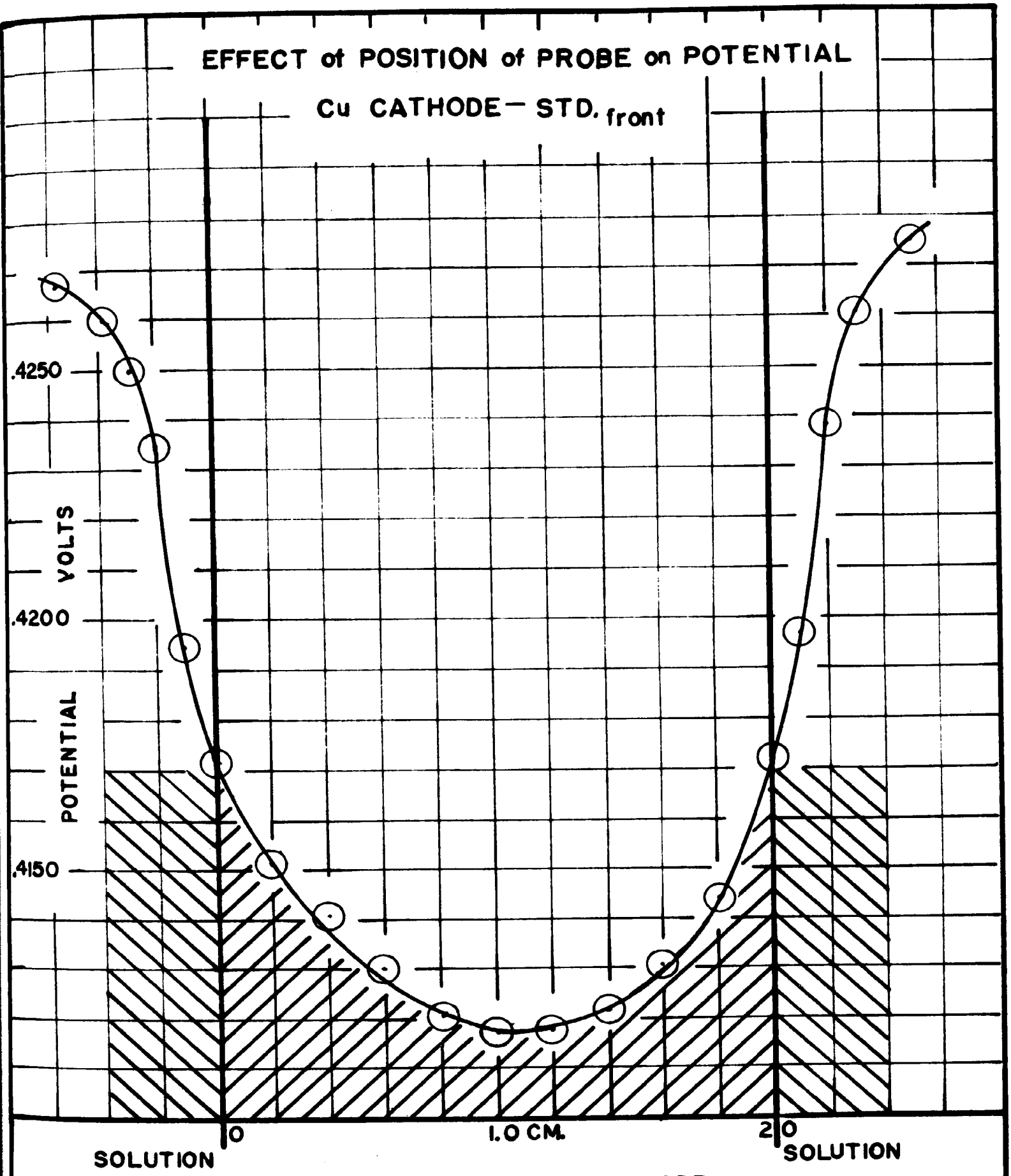

EFFECT of POSITION of PROBE on POTENTIAL
Cu CATHODE — STD. front
.4250
.4200
.4150
POTENTIAL VOLTS
0
1.0 CM.
2.0
SOLUTION
SOLUTION
POSITION OF PROBE AT CATHODE

FIG. 18

TABLE 19

	Cell Measured	Position of Hole	Run 1		Run 2	
			Difference of Potential (volts)	Polarization (volts)	Difference of Potential (volts)	Polarization (volts)
Static	Cathode vs. Std. Front		0.3581		0.3542	
	Cathode vs. Std. Hole	5	0.3585		0.3545	
Dynamic	Cathode vs. Std. Front		0.4229	0.0648	0.4222	0.0677
	Cathode vs. Std. Hole	1	0.4286	0.0701	0.4283	0.0738
		2	0.4267	0.0682	0.4253	0.0708
		3	0.4238	0.0653	0.4247	0.0702
		4	0.4230	0.0645	0.4225	0.0680
		5	0.4230	0.0645	0.4222	0.0677
		6	0.4228	0.0643	0.4226	0.0681
		7	0.4231	0.0646	0.4220	0.0675
		8	0.4242	0.0656	0.4214	0.0669
		9	0.4245	0.0670	0.4238	0.0693
		10	0.4272	0.0687	0.4252	0.0707

Effect on Measured Potentials of Position of Back Probe by the Hole Method.

Oscillographic Measurements.

INTRODUCTION

Results obtained up to this point by means of potentiometric measurements seem to indicate that the critical distinction among the different methods relates to the question of the presence of an IR drop varying from method to method and with the position of the probe. To continue this investigation further, it was proposed to study the natural decay curves of the polarization in an attempt to determine definitely whether the differences obtained in the previous work are due to a true polarization or to an IR drop. Due to the nature of the problem it was thought that the only instrument capable of giving an answer is the cathode-ray oscillograph in a time-potential study of the decay curve. As polarization decays more or less rapidly but an IR drop immediately, the time interval which would be of most value in distinguishing between them is that period of time from the exact moment of cessation of the electrolyzing current to a short time afterward, about 0.01 second. This brief time interval could give information of the presence of any IR component in the measured potential. The theoretical aspects have already been considered in the historical and theoretical parts of the dissertation and the details of the oscilloscope and necessary auxiliary equipment have been described in the Apparatus Section. The conditions of the experiments as specified previously (page 93) were maintained in the following work unless otherwise noted.

The first four plates show polarization decay curves for copper electrodes in acid copper sulfate solution.

The results in this section are presented by means of photographs and tables. The photographs represent oscillographic traces of the potentials (vertical axis) and their variation with time (horizontal axis). The stable potentials at the start are always indicated by a horizontal line at the upper left hand corner followed, after the interruption of the current, by the natural decay curve. In cases in which the exact potential is of interest, potential calibration lines also appear at the left hand side of the film; these can readily be distinguished from the trace of the dynamic potentials by the difference in length. The potential values for these calibration lines appear on the respective plates. The degree of amplification used in each case was such as to utilize nearly the full width of the film. In all cases, the rate of movement of the film was the same, namely, 0.26 milliseconds per millimeter. It should be stated also that it was possible by means of a comparator to measure to 0.1 mm. on the films.

DEPOLARIZATION CURVES FOR COPPER IN ACID COPPER SULFATE SOLUTION

General Remarks.

Plate I presents five films showing the general character and a comparison of the types of phenomena included in the measured potentials. Film A shows the reproducibility of three separate runs with a pure IR drop only. The measured

PLATE I

General



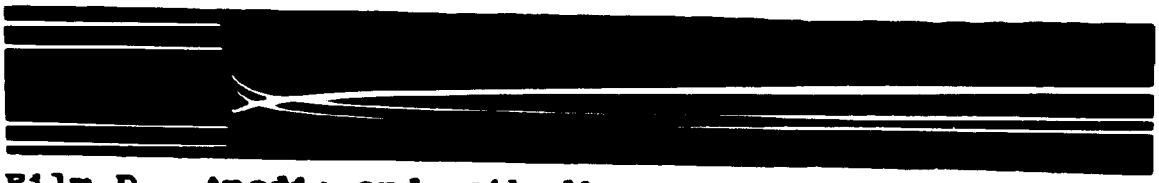
Film A - Oscillographic traces of an IR drop taken over a one ohm standard resistance. Three similar runs, only displaced by the balancing voltage.



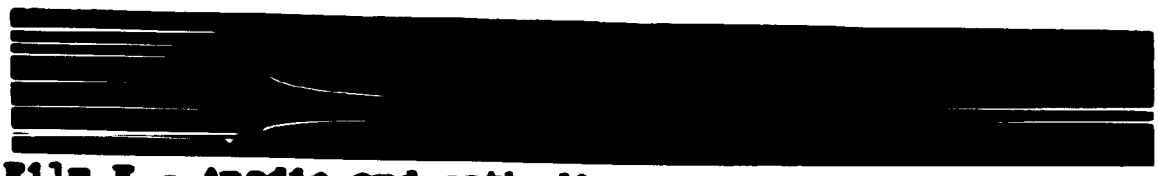
Film B - Comparison of a cathodic copper depolarization curve in acid copper sulfate at 10 Mamp. sq. cm. with IR drop over 1 ohm standard resistance.



Film C - Two cathodic copper depolarization curves under same conditions as Film B displaced slightly with the balancing voltage.



Film D - Anodic and cathodic copper depolarization curves by the front and back methods. Curves slightly displaced to avoid inability to follow traces. Cathodic decay downward, anodic decay upward.



Film E - Anodic and cathodic copper depolarization curves. Top line dynamic cathodic potential line by back method at 0.4475 V., second line by the front method at 0.4310 V., three calibration lines at 0.41, 0.38, 0.35 V., dynamic anodic potential line by front method at 0.3266 V. and by the back method at 0.3189 V. Both anodic and cathodic decay curves superpose.

potential difference was taken across a one ohm standard resistance in all cases. For clearness, the separate traces were arbitrarily displaced with respect to one another. The distance between the dynamic line and the corresponding lower line is characteristic of an IR drop. The fall of potential is so rapid that it naturally does not produce a trace on the film. In the analysis of later films of polarization decay curves such a displacement is considered an IR drop. It should be pointed out, however, that in the analysis where an IR drop is followed by a rapid depolarization, there is some uncertainty in determining the point between the end of the IR portion and the beginning of the depolarization. In an attempt to locate this point more accurately, a densitometer was tried. However, it was no more satisfactory than visual observation.

Film B of Plate I shows a direct comparison between a pure IR drop and a typical polarization decay curve for a copper cathode; the latter curve can be clearly followed with a densitometer to the point of cessation of current. This is typical of a depolarization decay apparently unaccompanied by an IR drop. In some later cases it will be observed that the total measured value may contain also an IR component.

Film C of Plate I shows two cathodic polarization decay curves for a copper cathode. These curves can be completely superimposed, thus proving the excellent reproducibility of the depolarization and of the instrumentation. As before these

curves can be followed back to the point of current interruption. Due to the rotation of the camera drum several times before the electrolyzing circuit was opened while the beam intensity was accidentally excessive, the initial trace appears extended all the way across the film. However, it is easily possible to discern the point of cessation of the current by the greater intensity of the trace in the left hand portion.

Film D of Plate I shows both anodic and cathodic depolarization curves for the same system measured by different methods. The two top lines are cathodic and the decay is downward to the static value whereas the two bottom lines are anodic and the decay is upward to the static value. The top cathodic curve is obtained by the back method and the lower one for the probe in the front center. The two curves are arbitrarily displaced from one another. Since the total decay is less in the second case it is evident that an IR component is present in the first case. A similar situation and explanation applies to the anodic curves.

Film E of Plate I illustrates depolarization curves similar to those of Film D, but the two potential lines for anodic and cathodic traces are not separated by the auxiliary bucking voltage. The two longer top lines in the upper left hand corner are the dynamic potential lines for the difference between the copper cathode and the standard reference electrodes. The first line is for the standard reference half cell in back of the cathode at a potential difference of

0.4475 volt. The second line is for the standard reference half cell in front of the electrode with the probe directly in contact with the face at a potential of 0.4310 volt. The decay curves due to depolarization superpose and are indistinguishable, indicating the same depolarization processes are occurring in both curves, the difference between the two dynamic lines indicating an IR drop of 16.5 mv. Similarly the anodic decay curves coincide as depolarization continues, the lower one for the reference in back indicating an IR drop. The film also shows typical calibration lines. After the first rapid decay, the cathodic and anodic curves appear to level off, the rate of decay decreases and appears to follow almost a straight line when it reaches the end of the strip of film, about 0.03 second after the cessation of the current. It appears that the decay curve returns to the static potential of the cell asymptotically. Both anodic and cathodic traces should coincide at the original static value after complete depolarization.

A certain number of additional remarks may be made with respect to observations from this preliminary plate. First, even in the case of a potential drop over a standard resistance, as in Films A and B, the trace is characterized by a slight horizontal displacement of about 0.3 mm. and a slight rounded "tail" at the beginning of the lower portion of the curve.

The inherent inductance associated with the various

components of the circuit (electrolytic cell, wire-wound resistors, etc.) provides a surge of current when the electrolyzing current is broken. This surge is due to the arcing of the contacts of the electromagnetic relay during a brief interval when they are opening. The current is then transposed into a voltage component and results in the horizontal blank space seen on the films following the interruption of the current. This blank space thus may be explained by assuming that the surge of potential at the moment of current interruption is impressed on the deflection plates of the C.R.O. and then decays rapidly. As an illustration of this explanation, it has been observed on some films, for example the anodic decay of Film D of Plate I, that an actual overshoot has occurred. The time element is very small and the rate of rise exceeds the writing speed of the screen and/or the photographic efficiency of the film, but in any event, it is not recorded. As this inductive potential decays, it is again picked up by the film and is recorded. While this process is occurring, the film is rotating continually, so that the time interval usually may be measured as a horizontal blank space instead of a continuous line. This space is of the order of 52 microseconds.

The capacitive effect operates in a different manner, opposing the change of potential which is occurring. It may be seen on the film as a slight rounding of the leading edge of a potential drop, e.g., see Film 1, Plate I.

With this technique, a large number of oscillographic traces of decay curves were recorded for a variety of conditions. With copper electrodes, in general, the curves show four features: (1) a blank space of about 0.3 mm. in the horizontal direction due to switching transients, (2) in some cases a vertical blank displacement representing an IR drop, (3) in all cases a very rapid decay gradually changing to, (4), a slow nearly linear decay. In this work the primary objective was to determine whether or not an IR drop occurs in any or all of these methods and if so what is its magnitude and cause. Incidentally it was found possible to distinguish somewhat arbitrarily the relative magnitudes of the rapid drop and the succeeding slow decay, although the former extended over varying periods of time ranging from 0.009 to 0.021 second after interruption of the current. There is a growing tendency among workers in the field to designate the rapid drop as due to "activation polarization" and the slow process as due to "concentration polarization", and these designations are employed hereafter. While it is of course realized that these two processes occur simultaneously, the procedure followed for the differentiation of these two types of polarization was to take arbitrarily the potential at which the decay curve becomes approximately linear as the end of the activation and the beginning of the concentration polarization stages. The numerical values given in the following pages for these types of polarization were obtained

by the use of this definition.

Cathodic Decay Curves by Various Methods.

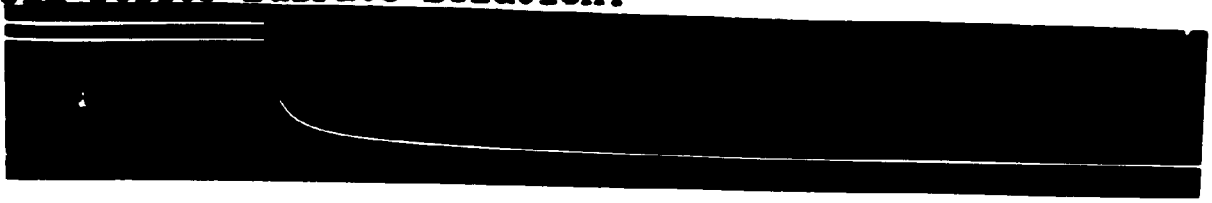
Plate II shows another series of films of measurements by various methods of the polarization decay of a copper cathode with a hole bored through the center. Film A shows two curves, one for the back method and the other for the front method. The top line is for the back method at a potential of 0.4439 volt, while the lower line is for the front method at 0.4336 volt. This difference of 0.0103 volt between the front and back methods is in general agreement with the potentiometric measurements taken under similar conditions and reported in Table 13. In the former work it was impossible to say whether this difference was an IR drop or a true polarization. The film, however, shows definitely that it is an IR drop.

The other four films of Plate II simplify the interpretation of the readings by showing only single depolarization curves on each with appropriate calibration lines.

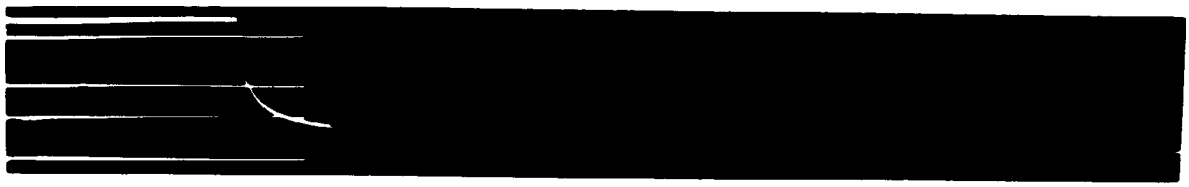
In Film B the probe was at the back of the cathode, in Film C at the front center, in Film D at the front edge and in Film E in the hole from the back and flush with the cathode face. Since all these photographs were taken with the same gain on the amplifier, it was possible to superpose the decay curves. When this is done, the decay portions of the curves coincide perfectly as far as can be determined; this of course is to be expected from inspection of Film A of this plate in

PLATE II

Cathodic Copper Depolarization Curves Measured by Various Methods Using a Polarizing Current of 10 Mamp./cm.^{2} in Acid Copper Sulfate Solution.



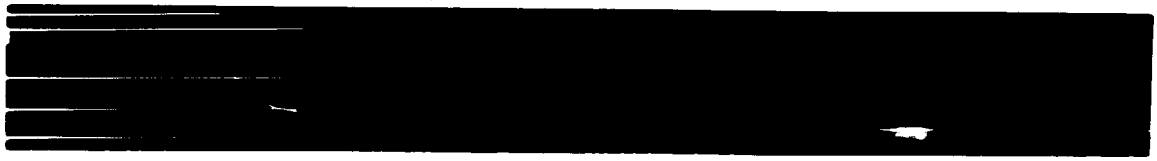
Film A - By both back and front methods. Top line dynamic potential line by the back method at 0.4439 V.; next dynamic potential by the front method at 0.4336 V.



Film B - Back method only. Dynamic potential at 0.4432 V.; calibration lines at 0.43, 0.40, 0.38 and 0.35 V. Double exposure with short time constant on decay curve.



Film C - Front method. Dynamic potential at 0.4340 V.; calibration lines at 0.42 (long), 0.39, and 0.36 V.



Film D - Standard at front edge. Dynamic potential at 0.4400 V.; calibration lines at 0.43, 0.40, 0.38 and 0.36 V.



Film E - Back method, hole in center. Dynamic potential at 0.4373 V.; calibration lines at 0.43, 0.40, 0.38 and 0.36 V.

which the superposition was automatic. When this superposition is done, it is found that the horizontal dynamic lines do not superimpose; the difference between them must be interpreted as an IR drop. The possibility can not be excluded that even in the case of the lowest dynamic line, that of Film C with the probe in the front center, a small IR drop is present. In the other cases definite additional IR components are noted as follows: in Film B (back method) 9.2 mv., Film D (front edge) 6 mv., and Film E (hole method) 3.3 mv.

The results shown on these last four films can be compared directly with those reported in Table 14 and 15, from which it will be seen that the difference in results by the same methods of measurement is from 3 to 6 mv. although the time interval between the two sets of experiments was approximately one year and no unusual precautions were taken to establish identical conditions. Detailed consideration of the numerical results obtained from these films is deferred to the Discussion Section.

Anodic Decay Curves by Various Methods.

Plate III shows self-depolarization traces by three different methods for a copper anode in acid copper sulfate solution. In these cases the change is a decrease in positive potential whereas in the cathodic films the change was a decrease in negative potential.

In Film A, the trace was taken by the back method, Film

PLATE III

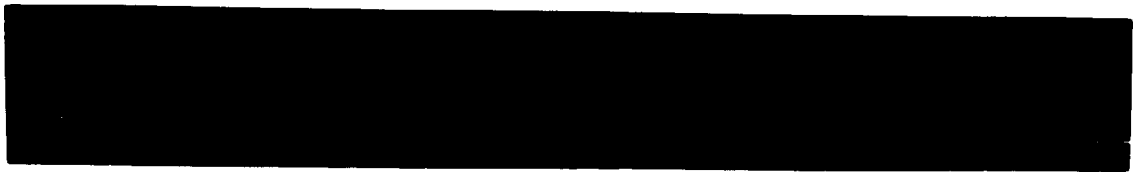
Anodic Copper Depolarization Curves Under Similar Conditions



Film A - Standard in back. Dynamic potential line at 0.3148 V.; calibration lines at 0.3248, 0.3348, 0.3448 and 0.3548 V.



Film B - Standard in front. Dynamic potential line at 0.3372 V.; calibration lines at 0.34 and 0.35 V.



Film C - Standard in back, hole in center. Dynamic potential at 0.3207 V.; calibration lines at 0.325, 0.335 and 0.345 V.

B by the front method and Film C with the probe inserted through the hole from the rear flush with the front face. By the superposition of the decay portions of the curves the differences in the dynamic potential lines, which constitute additional IR components, amount to 22.8 mv. in Film A (back method) and to 16.5 mv. in Film C (hole method), both related to Film B as a reference. The general pattern obtained for the different positions of the probe corresponds to those found for the cathode. The results will be considered in the Discussion Section.

Cathodic Decay Curves by Various Methods. Small Cathode.

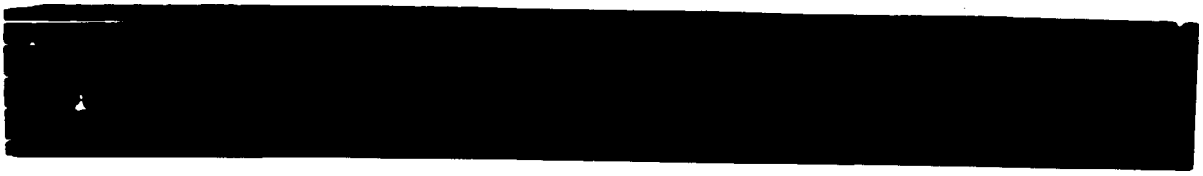
In Plate IV are shown cathodic decay curves obtained with the small cathode arrangement described on page 124 and illustrated in Fig. 15.

Film A was taken by back method and Film B by the front center method. Superposition of the two decay portions shows an additional IR component of 20.4 mv. in the former case.

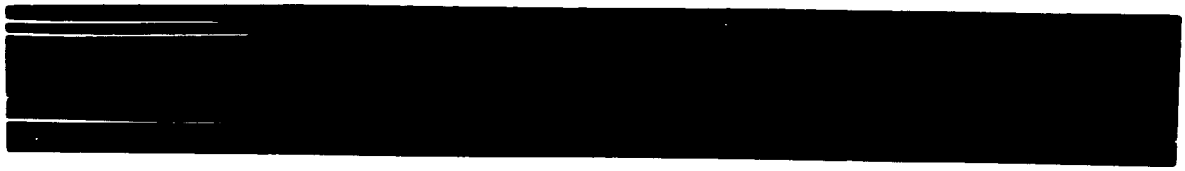
The latter result is verified by Film C of Plate IV which is a combination of Films A and B under the same experimental conditions. The top line is the dynamic potential by the back method at 0.4289 volt and a total decay of 0.0768 volt. The next lower line of the same length on the film is the dynamic potential by the front method at 0.4080 volt and a total decay of 0.0553 volt. The difference in dynamic potentials and measured total decay is due to an IR drop

PLATE IV

Cathodic Decay Curves by Various Methods. Small Cathode.



Film A - Standard in back. Dynamic potential line at 0.4357 V.; calibration lines at 0.42, 0.40, 0.38 and 0.36 V.



Film B - Standard in front. Dynamic potential line at 0.4158 V.; calibration lines at 0.41 and 0.37 V.



Film C - Standard in back and front. Dynamic potential for back at 0.4289 V., for front 0.4080 V.; calibration lines at 0.42, 0.40, 0.38 and 0.36 V.



Film D - Standard in front center, near hole in cathode. Dynamic potential at 0.4156 V.; calibration lines at 0.41, 0.39 and 0.37 V.



Film E - Standard in hole from back of cathode. Dynamic potential at 0.4156 V.; calibration lines at 0.41, 0.39 and 0.37 V.

included in the value by the back method. From the film this difference amounts to 20.9 mv. to be compared with 20.4 mv. as determined from film A and B. The decay curves by both methods superpose during the decay portions which are visible on the film and the potential drops to 0.3653 volt in 0.029 second after current interruption. The slower decay portion, here attributed to concentration polarization, is not completely identical in all parts in the time-potential curve, the deviation being quite small since the lines coincide in certain portions.

Films D and E can be discussed together since the only difference is the position of the tips of the standard half cells. In Film D, a hole was drilled through the cathode and the probe was placed in the opening from the front whereas in Film E the probe was in the same hole but the tip entered the hole from the rear and was flush with the cathode face. The dynamic potentials are identical at 0.4156 volt. There does not appear to be any IR drop since the trace can be followed up to the break of the current, although faintly.

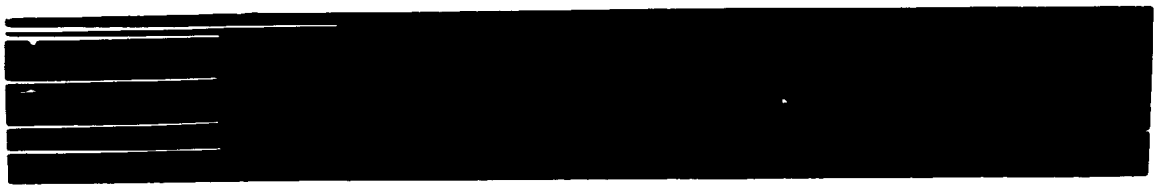
Effect on IR Drop of Distance of Front Probe from the Cathode.

Plate V shows four cathodic decay curves obtained with a probe in front of and at various accurately measured distances away from the cathode. Assuming that when the probe is in direct contact with the front of the cathode there is no IR drop, that when the probe is moved away from the cathode an IR

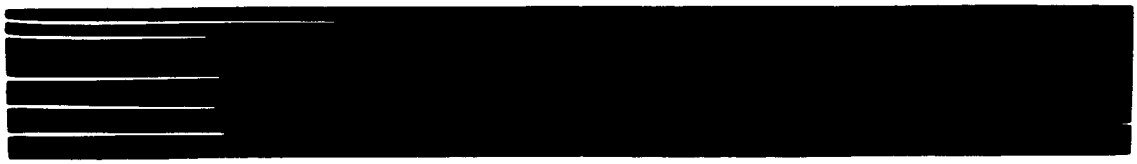
PLATE V



Film A - Probe 1.9 cm. away from cathode face. Dynamic potential at 0.4530 V.; calibration lines at 0.44, 0.41, 0.38 and 0.36 V. IR drop of 0.0223 V.



Film B - Probe 1.0 cm. away from cathode face. Dynamic potential at 0.4462 V.; calibration lines at 0.44, 0.41, 0.38 and 0.36 V. IR drop of 0.0146 V.



Film C - Probe 0.6 cm. away from cathode face. Dynamic potential at 0.4413 V.; calibration lines at 0.43, 0.40, 0.38 and 0.36 V. IR drop of 0.0096 V.



Film D - Probe at cathode face. Dynamic potential 0.4347 V.; calibration lines at 0.43, 0.40, 0.38 and 0.36 V. IR drop of 0.0007 V.

component equal to the resistance of the solution times the current from the cathode is included in the measured potential and that the decay process for the depolarization is the same in all cases, an IR drop can be calculated from the films and this can be compared with the potentiometric values taken simultaneously and with previous results shown in Fig. 15. The last assumption is justifiable since the copper depolarization is the same in all cases, and necessary because of the lack of distinction as to where an IR drop ceases and very rapid depolarization begins. By superposition of two films so that the decay curves coincide, the difference between the two dynamic lines shows a vertical displacement with no indication of an active potential and must be similar to a pure ohmic resistance as shown by Film A of Plate I. When calculated from the calibration lines on the individual films, the vertical displacement coincides with the difference of the dynamic potentials. This is to be expected since an IR component due to solution resistance is added to the polarization as the probe is moved away from the cathode. The results are shown in Table 20 and Fig. 19 where the values obtained oscillographically are shown and compared with previous potentiometric results. Inspection of the curves in Fig. 19 shows remarkable agreement especially in view of the fact that the measurements were taken approximately a year apart and no effort was made to duplicate the solutions. An extrapolation of the linear section of each curve, which

TABLE 20

Film	Distance of Probe from Cathode Face, cm.	IR Drop, volts Measured.
A	1.9	0.0223
B	1.0	0.0146
	1.3	0.0176
	1.6	0.0202
C	0.6	0.0096
	0.8	0.0122
D	0.00	0.0002
	0.1	0.0009
	0.2	0.0029
	0.3	0.0046
	0.4	0.0074

Effect on Measured Potential of Distance from Face of the Cathode. Data from Plate V.

corresponds to the common method for correcting the IR drop, leads to the same magnitude of error of 6 mv. in each case. This error is undoubtedly due to the shielding effect of the reference electrode.

Effect of Position of Front Probe across Cathode Face.

In Plate VI are shown cathodic decay curves obtained with the small cathode arrangement described on page 124 and illustrated in Fig. 16. In this series of films, the dynamic

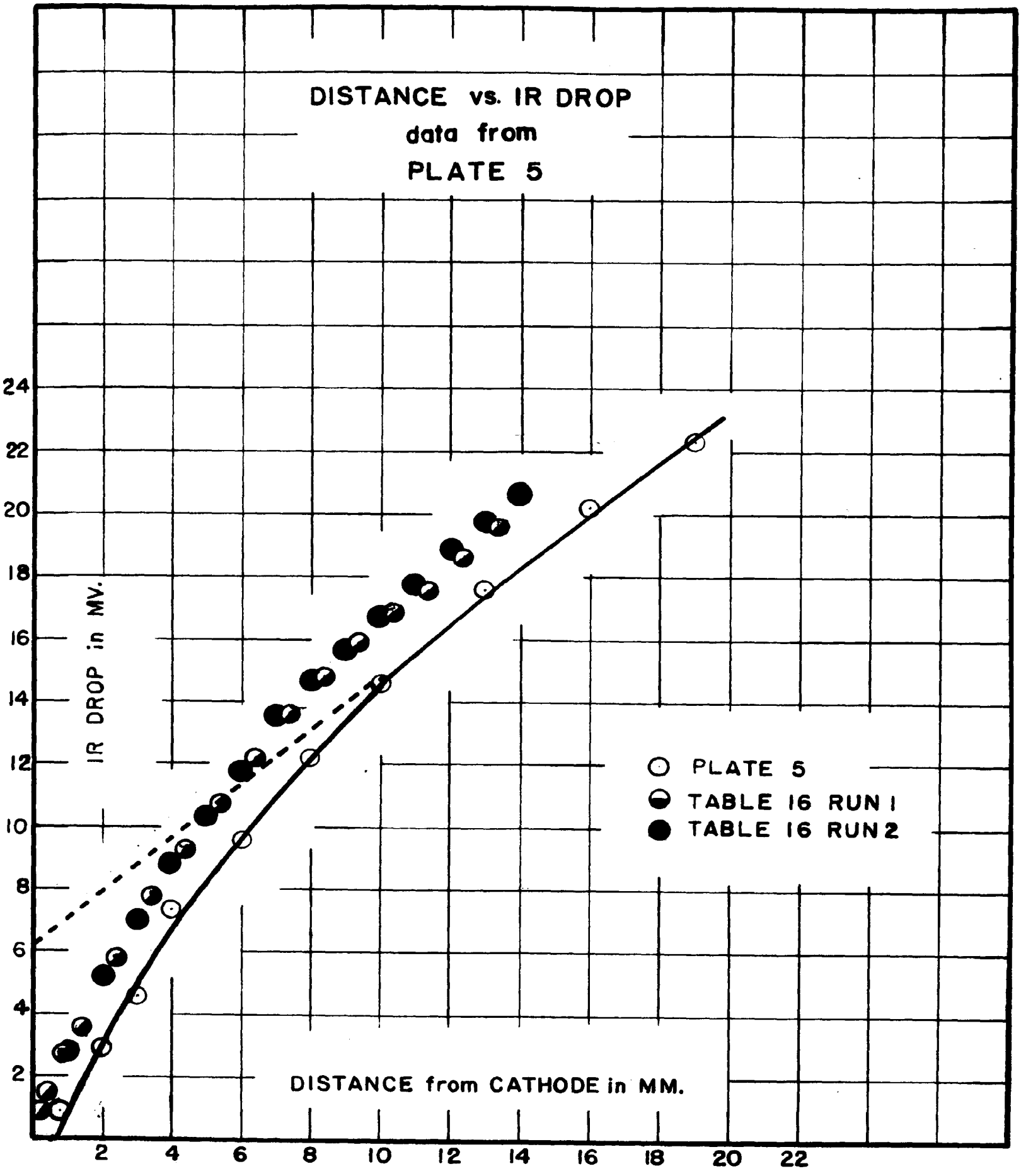
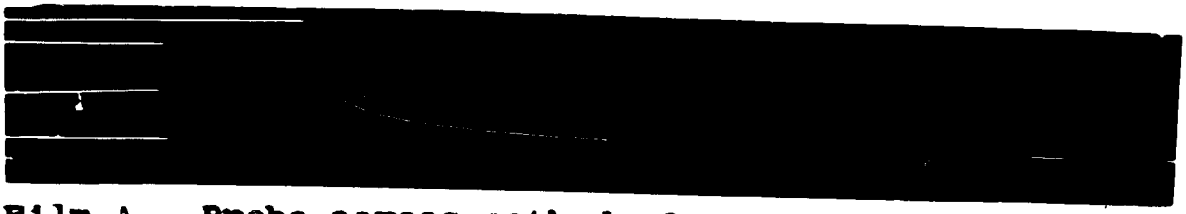

DISTANCE vs. IR DROP
data from
PLATE 5
IR DROP in MV.
DISTANCE from CATHODE in MM.
PLATE 5
TABLE 16 RUN 1
TABLE 16 RUN 2
2
4
6
8
10
12
14
16
18
20
22
24

FIG. 19

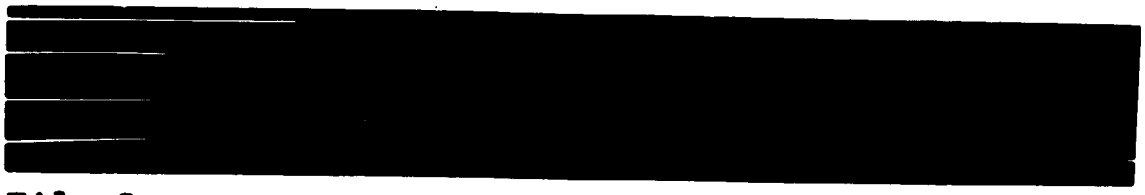
PLATE VI



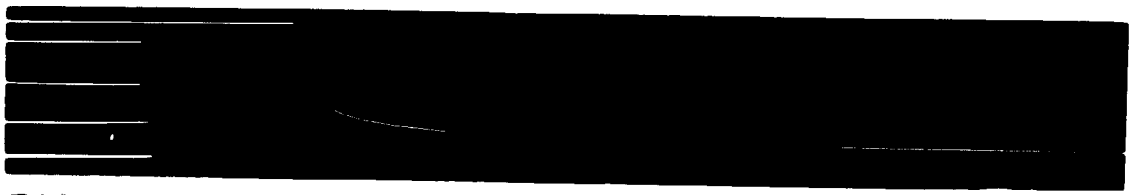
Film A - Probe across cathode face near center. Dynamic potential at 0.4204 V.; calibration lines at 0.41, 0.39 and 0.37 V. IR drop of 0.0009 V.



Film B - Probe across cathode face at 0.2 cm. from edge. Dynamic potential at 0.4237 V.; calibration lines at 0.41, 0.39 and 0.37 V. IR drop of 0.0024 V.



Film C - Probe across cathode face at edge. Dynamic potential at 0.4260 V.; calibration lines at 0.41, 0.39 and 0.37 V. IR drop of 0.0048 V.



Film D - Probe across cathode face 0.1 cm. beyond edge. Dynamic potential at 0.4314 V.; calibration lines at 0.42, 0.40, 0.38 and 0.36 V. IR drop of 0.0103 V.

potentials and decay curves are those for the front probe in different positions from the center to the edge of the cathode and beyond, comparable to the potentiometric measurements illustrated by Figure 17. Since the depolarization process is the same for all the decay curves, superposition of the traces show definitely that the increase in potential as the probe is moved laterally from the center to the edge is due to an IR drop and not an active polarization potential. The results of the experiment are listed in Table 21. These results are plotted in Fig. 20 together with a duplicate run; for further comparison the corresponding results from Figure 17 are also included. An inspection of Figure 20 shows excellent agreement both between the two sets of the potentiometric results and also the oscillographic results.

TABLE 21

Film	Position of Probe	Cathode vs. STD. Front	Measured Polarization	Change due to Position	Calibrated IR Drop
	0 mm. (Center)	0.4212	0.0642	0.0016	0.0014
A	2 mm.	0.4196	0.0626	0.0000	0.0000
	4 mm.	0.4203	0.0633	0.0007	0.0008
	5 mm.	0.4210	0.0640	0.0014	0.0015
	6 mm.	0.4210	0.0640	0.0014	0.0015
	7 mm.	0.4224	0.0654	0.0028	0.0029
B	8 mm.	0.4239	0.0669	0.0043	0.0044
C	9 mm.	0.4264	0.0694	0.0068	0.0066
D	10 mm. (Edge)	0.4317	0.0747	0.0121	0.0120
	11 mm.	0.4338	0.0768	0.0142	0.0140
	12 mm.	0.4343	0.0773	0.0147	0.0145

Effect (on Measured Potentials) of Lateral Position of Front Probe and on IR Drop Calibrated from Plate VI.

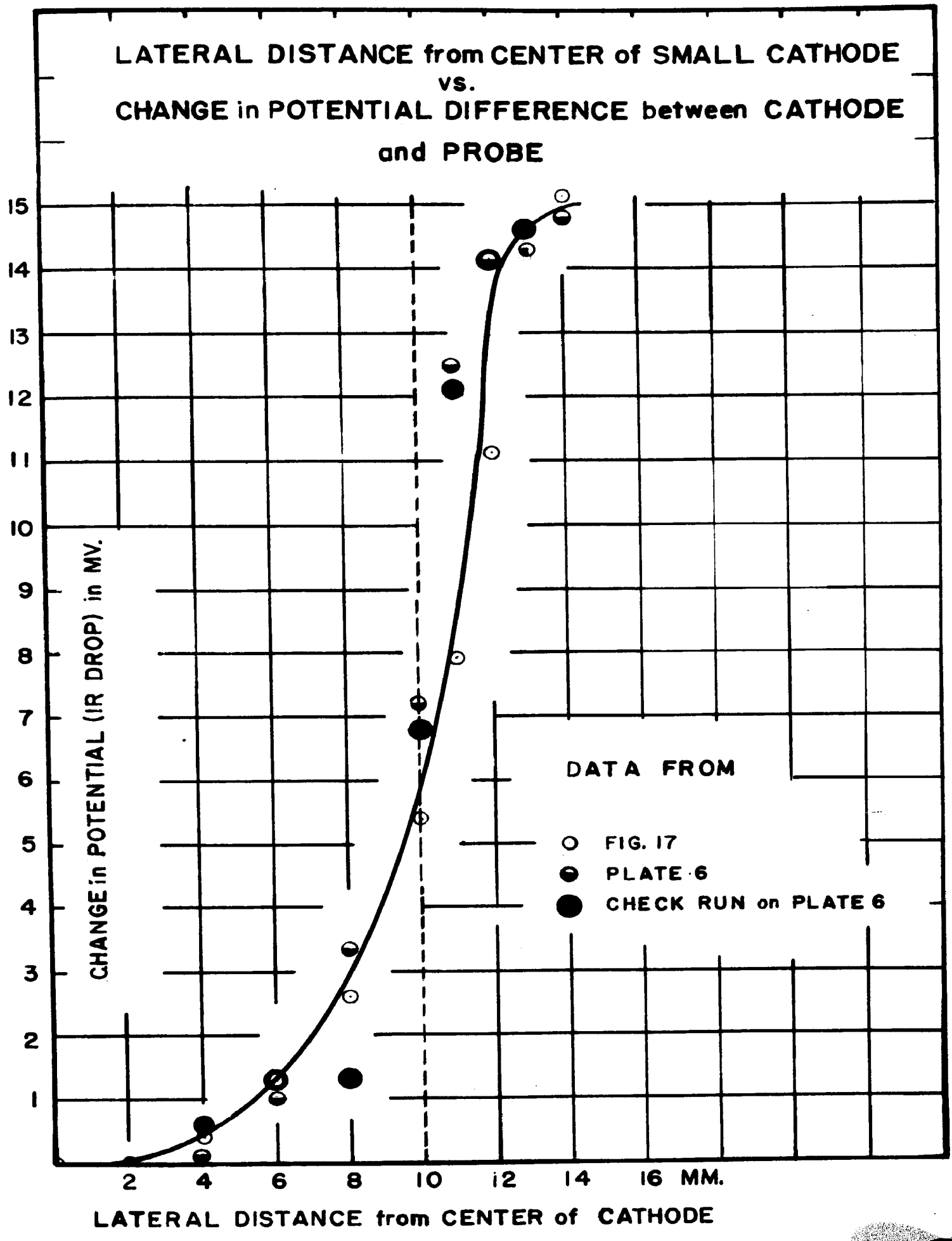

LATERAL DISTANCE from CENTER of SMALL CATHODE
vs.
CHANGE in POTENTIAL DIFFERENCE between CATHODE and PROBE
CHANGE in POTENTIAL (IR DROP) in MV.
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
DATA FROM
FIG. 17
PLATE 6
CHECK RUN on PLATE 6
2
4
6
8
10
12
14
16 MM.
LATERAL DISTANCE from CENTER of CATHODE

FIG. 20

Brief Summary of Results by Oscillographic Methods.

The original object of this research was to compare the various methods for determination of polarization potentials and to attempt to account as far as possible for any differences observed. Results obtained by the potentiometric measurements indicated marked differences in values among the different methods and by the same method under different conditions. It was impossible by potentiometric measurements to determine definitely whether these differences were due to a true polarization potential, an IR drop, or a combination of these. However, in some cases the evidence strongly indicated that the differences were due at least in part, to an IR drop. According to theory, it should be possible to determine definitely the difference between an IR drop and a true polarization photographically by means of a cathode ray oscillograph. Consequently, this method was applied to the study of the same systems as in the potentiometric work. Even by this method, in case a very rapid depolarization occurred accompanied by an IR drop, it was found difficult to determine definitely the point of distinction between the IR portion and rapid decay. However, the evidence indicated that in practically all cases a portion of the decay curve at least was due to an IR drop, the magnitude of which it is believed in most cases could be determined with a fair degree of certainty. In all cases where a true polarization is present it is possible to show without doubt by superposition

of films, the exact difference in IR drop between the two methods of measurement involved.

DEPOLARIZATION CURVES FOR PLATINUM ELECTRODES IN SULFURIC ACID

General Remarks.

The processes involved in the potential decay at platinum electrodes in sulfuric acid are distinctly different in nature and rate from those of copper in acid copper sulfate solution. However, the techniques available with this apparatus can be used here also to distinguish between an IR drop and a true potential, which is the only point of interest in this work.

Experiments with platinum electrodes which completely filled the cross section of the cell were carried out in molar sulfuric acid with a probe in front of and in back of the electrode. In all these cases gases were evolved at the electrodes, providing a source of agitation. The film speed was the same as in previous experiments. As other conditions are varied from one set of experiments to another, they will be specified.

The uncertainty in the determination of the transition point between IR drop and true depolarization experienced with copper electrodes still exists here.

Anodic Decay Curves for Bright Platinum.

Plate VII shows a set of anodic decay curves for bright platinum polarized at a current density of 1 ma. per cm.^{2} to a constant potential. Film A obtained with the probe in back indicates an IR drop of 0.0087 volt. Film B obtained with

PLATE VII

Anodic Decay Curves for Bright Platinum at 1 Mamp. per cm.^{2} in M H_2SO_4.



Film A - Standard in back. Dynamic potential line at 1.3052 V.; calibration lines at 1.29, 1.27 and 1.25 V. IR drop of 0.0087 V.



Film B - Standard in front. Dynamic potential line at 1.3058 V.; calibration lines at 1.29, 1.27 and 1.25 V. IR drop of 0.0079 V.



Film C - Standard in front, tip moved back from cathode face for an added IR drop of 0.0093 V. Dynamic potential at 1.3214 V.; calibration lines at 1.30, 1.28 and 1.26 V. Total IR drop of 0.0159 V., inherent IR drop of 0.0066 V.

the probe in direct contact with the front of the electrode shows an IR component of 0.0079 volt.

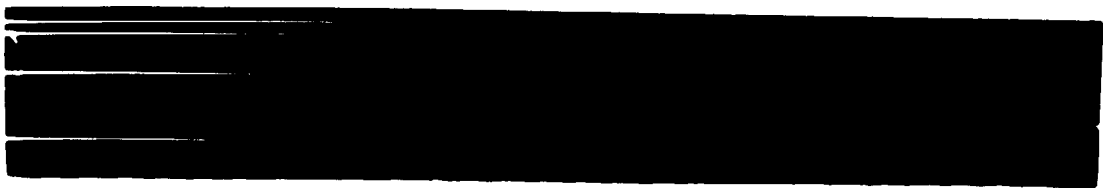
Film C of Plate VII is almost a duplicate of Film B with the variation that the tip was moved away from the anode so that a purposely included IR component of 0.0093 volt, as determined by the potentiometer, is measured in the total dynamic potential difference. Previous to the movement of the standard electrode away from the anode, the dynamic potential by the back method was 1.3101 volts and by the front method 1.3121 volts. After moving the front standard, the front dynamic potential difference was 1.3214 volts. This increased resistive potential is readily seen on the film as an added blank space at the point of current interruption. After introduction of 0.0093 volt, the total IR drop measured on the film is 0.0159 volt, whence the difference, 0.0066 volt, is inherent in the method and technique. This is to be compared to 0.0079 volt directly measured in Film B. This shows the extent to which a change in IR drop can be measured on the films.

Cathodic Decay Curves for Bright Platinum at 1 ma. per cm.^{2}

The next three plates show cathodic decay curves for bright platinum at different current densities. Plate VIII presents three different photographic traces of the cathodic decay of bright platinum in molar sulfuric acid following polarization at a current density of one milliampere per cm.^{2}.

PLATE VIII

Cathodic Decay Curves for Bright Platinum at 1 Mamp. per cm.^{2} in M H_2SO_4.



Film A - Standard in back. Dynamic potential line at 0.8614 V.; calibration lines 0.85, 0.83 and 0.81 V. No IR drop. Refer to text.



Film B - Standard in front. Dynamic potential line at 0.8627 V.; calibration lines at 0.85, 0.83 and 0.81 V. No IR drop. Refer to text.



Film C - Standards in back and in front. Dynamic potentials at 0.8626 and 0.8635 V. (Coincide on film.) Calibration lines at 0.85, 0.83 and 0.81 V. No IR drop. Refer to text.

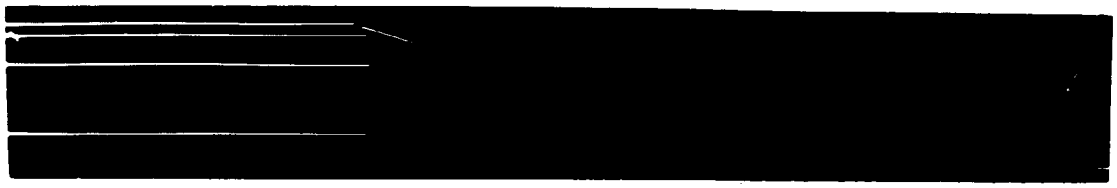
Film A is obtained by the back method, Film B by the front method, while on Film C, results by both the front and back methods are photographed together. If the method previously used with copper is employed in which the IR drop was considered to extend to the point at which the trace resumes after the blank space, then it would be concluded from these films that no IR drop is involved. However, if the measurement is made down to the approximately linear section, the values obtained are as follows for the three films: for A, 0.0071 volt; for B, 0.0056 volt; and for C, 0.0090 volt. The differences may be due to inductive or capacitive effects or to an extremely rapid depolarization phenomenon hitherto undetected, and made evident here by the excessive speed of film movement.It might be pointed out here that without this very high resolution of time, it would have appeared as an IR drop. It may be remarked also that in contrast to all the films previously taken, this particular set shows ambiguity in determining whether the first rapid stage is really an IR drop or an exceedingly rapid potential decay.

Cathodic Decay Curves for Bright Platinum at 10 ma. per cm.^{2}

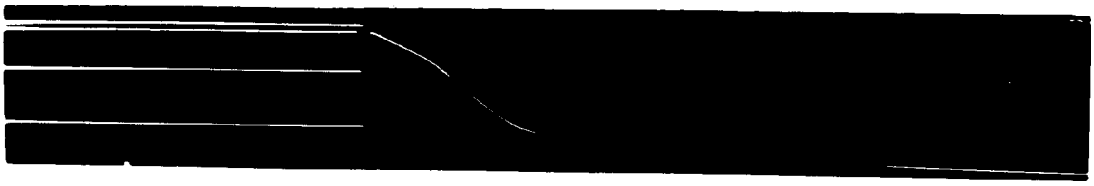
Plate IX shows cathodic polarization decay curves for bright platinum in molar sulfuric acid at a polarizing current density of 10 ma. per cm.^{2}. The films are in the same order as in the previous plate, namely, A is for the back method, B for the front method and C combines the traces for the two

PLATE IX

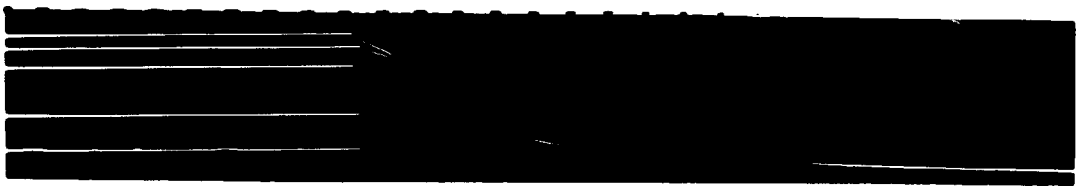
Cathodic Decay Curves of Bright Platinum at 10 Mamp. per cm.^{2} in M H_2SO_4.



Film A - Standard in back. Dynamic potential at 0.9272 V.; calibration lines at 0.90, 0.86 and 0.82 V.



Film B - Standard in front. Dynamic potential at 0.9430 V.; calibration lines at 0.92, 0.87 and 0.82 V.



Film C - Standards in back and in front. Dynamic potentials at 0.9300 and 0.9560 V.; calibration lines at 0.89, 0.86 and 0.83 V.

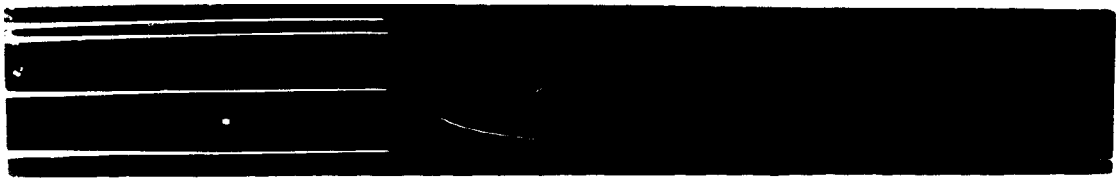
methods. For films A and B, the dynamic potential is the top line at the left, the others being the usual calibration lines. In film C the top line is the dynamic potential line for the front method while the second line is that for the back method. The IR drops measured from the films are as follows: for Film A, 0.0085 volt, for B, 0.0299 volt, for C by the front method 0.0201 volt and by the back method 0.0165 volt. Agreement here is not as good as desired but this may be due to the effects of pronounced gas evolution. In this case the larger IR value is given by the front method. The difference may be explained as due to gas bubbles in front of the cathode face.

Cathodic Decay Curves for Bright Platinum at 50 ma. per $cm.^2$

Plate X shows the traces obtained by recording the dynamic cathodic potential decay for bright platinum in molar sulfuric acid at a current density of 50 ma. per $cm.^2$. In this experiment, the front of the electrode was stopped off for 1/4" around theedges. The three films follow the same order as the last two plates. In Film C the upper line is for the back method while the second line is for the front method. Measured values for IR drops are as follows: for Film A, 0.0650 volt; for B, 0.0420 volt; for C (back method), 0.0680 volt, and (front method), 0.0280 volt. Comparison of these results with those from Plates VIII and IX shows that the effect of the higher current density, as may be expected,

PLATE X

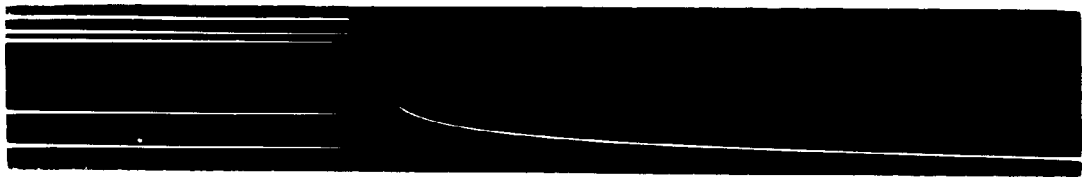
Cathodic Decay Curves for Bright Platinum at 50 Mamp. per $cm.^2$ in M H_2SO_4. 1/4" Insulated Rim on Front Face.



Film A - Standard in back. Dynamic potential line at 1.0862 V.; calibration lines at 1.05, 0.95 and 0.85 V.



Film B - Standard in front. Dynamic potential line at 1.0437 V.; calibration lines at 1.00, 0.90 and 0.80 V.



Film C - Standards in front and in back. Dynamic potential lines at 1.0875 (back) and 1.0478 V. (front); calibration lines at 1.02, 0.92 and 0.82 V.

is to increase greatly the IR drop, for example, for the front method from zero up to 0.042 volt. The reversal of the relative magnitudes of the IR drops by front and back methods in Plates IX and X is no doubt attributable to the effect of the insulation at the front edge which, as in the case of copper, increases current density at the edges and thus increases the polarization. The results obtained here indicate that a considerable component of this effect is due to the IR drop.

Summary of Results for Bright Platinum.

It may be stated that an IR component is always noted; it increases rapidly with increased current density, differs markedly from one method to another and with the method of insulating the cathode.

DISCUSSION OF RESULTS

As stated in the Introduction the primary objects of this research were to compare directly the various methods for the measurement of polarization and to attempt to account for and to eliminate the differences observed. Throughout the Experimental Section, in connection with the presentation of the tables, some attention was given to the significance of the information contained in the results. This was especially true of the preliminary work in the first four tables because of its bearing on the future planning of the research. In the present section primary attention is given to the relation of all the experimental results to the primary objectives of this research.

The conclusions reached in the Discussion apply equally to the experiments with copper in acid copper sulfate and with bright platinum in sulfuric acid. There seems no reason to suppose that they would not be equally valid for other systems as well. In the first experiment in which the methods were compared, the results showed that the polarization given by the back method was much less than by the other two. Since in this experiment the back of the cathode was not insulated, it was considered that this might have been largely responsible for the difference. The succeeding experiments in which different degrees of insulation were used verified this suspicion. In the first instance, only the back and edge of the cathode were insulated. This resulted

in an increased polarization by the back method from approximately 10 mv. to 64 mv., but was still lower than by the front center method by 13 mv. The next step was to insulate around the front extending 1/4" beyond the cell walls; this resulted in an increase in the potential by the back method of approximately 40 mv. from the previous value which made it 27 mv. more than that by the front center method. This is to be expected since the total surface area was appreciably reduced, thus increasing the effective current density particularly at the edge, which is the point at which polarization would be measured by the back method. It should be pointed out also that measurement by the back method would include an appreciable IR drop due to the current which normally flowed to the insulated portion being deflected toward the body of the solution. The next step, therefore, was to decrease the insulation back to the edge of the cell in an attempt to secure uniform current distribution. When this was done the difference between the back and the front center was reduced to 15 mv. When the front probe was moved to the edge the difference was reduced to 8 mv. In a further extension of this study, both potentiometrically and oscillographically (Plate VI, p. 148), the positive potential difference between the back standard and the front standard in a series of positions from the center to either edge was found to decrease progressively from the center to the edge. When a hole was drilled through the center of the electrode the potential difference between

the standards was further decreased and when the back electrode was inserted into the hole and flush with the front face the difference was completely eliminated.

The low values of polarization obtained by the back method with the uninsulated cathode were obviously due to the abnormally low current density at the back of the cathode. After the back and edges were insulated the pronounced increase observed was due to the much higher current density at the nearest exposed point of contact. However, due to the screening effect of the wall on the metal in the slot holding the cathode in place, the current density was still less than the average value and the polarization was thus less than that by the front method. The validity of this explanation was demonstrated by extending the insulation 1/4" around the front edge (always maintaining the average current density on the exposed front surface) which increased the measured polarization value. The explanation of this increased potential was given above as being due to the combined effects of an increased current density, and hence polarization, at the exposed edge of the cathode and of the inclusion of an IR drop across the face of the insulation. When a 1/4" segment at the center of the insulating rim was removed as shown at positions No. 1 and 12 in Figure 13 (p. 107) and also Tables 9 through 11 (pages 107-109), a slight increase in potential in front of this newly exposed section was observed; this also is logically explained as due to the concentration of current

lines to this segment from the neighboring insulated areas. The progressive decrease of positive potential from the center toward the edges, as shown in Figures 14 (p. 111), 17 (p. 125), and 20 (p. 150) and Plate VI (p. 148) was definitely shown by means of the oscillographic traces to be an IR drop across the face of the cathode. The source of this IR drop is in the flow of positive current from the center toward the edges. This, in turn, is due to the higher concentration of copper ions at the center of the electrode solution interface. It is well known that due to the decrease in density of the electrolyte resulting from the deposition of ions at the cathode interface, the solution flows upward along the cathode face. In a cell of this type, it is to be expected that the upward flow will be greater at the center, decreasing toward the edges, thus resulting in a higher copper ion concentration at the center. This explanation accounts for the observation noted above that the difference in potential between the back and front probes was reduced when the latter was moved from the center to the edge. This will also explain the potential difference observed between any two probes so located as to include different portions of this IR drop. The experimentally demonstrated IR drop and its attendant explanation throw light on the differences in polarization values obtained by different experimental arrangements.

As pointed out earlier in the Discussion, when the front probe was moved to the edge of the exposed electrode the

polarization value obtained was nearly the same as that from the back, which is to be expected since both measurements were with respect to approximately the same spot on the electrode. Another method to accomplish the same objective is to bore a hole through the cathode and to position the two probes as near together as possible, that is, with the back probe in the hole and flush with the front face and the front probe adjacent to the hole. In this case, as expected, the two methods gave identical results. This agreement merely signified that the two probes are measuring the potential at the same point on the electrode. However, this value is undoubtedly not the true polarization because of the screening effect of the front probe. When the back probe was withdrawn from the hole, a small difference of potential was observed, again due to an inclusion of an IR drop to an equipotential line. Any further changes in the position of the back probe have no effect since no new current lines remain to be followed.

In order to obtain more information for systems with non-uniform current distribution, several experiments were carried out with a small cathode in this same cell. (For details see Fig. 16, p. 124.) In this case, the same general trend was indicated with a large enhancement of the effects of a resistive potential. This brings out more forcibly the practical importance of the position of the probe and of the lack of uniform current density. This was further confirmed

in a series of measurements with the back probe through a series of holes across the face of the electrode.

The existence of a hitherto neglected IR drop component across the electrode has been experimentally demonstrated and its origin explained. In measurements by the front method, an IR drop is unavoidably included and must be corrected for either by an extrapolation procedure or by use of the bulk conductivity value. Both of these methods lead to erroneous results as demonstrated in experiments in which measurements were taken at known distances from the cathode. It appears from a series of potentiometric and oscillographic experiments (Plate V, p. 144) in which measurements were made with a front probe at different very accurately measured distances from the cathode that neither of these methods furnishes an accurate correction to be applied to the total measured value. The difficulty arises from two sources: (1) The resistance of the solution between the tip and the electrode varies in a non-linear manner with distance from the electrode and much more rapidly as the electrode is approached. This latter effect is due to extreme variations in concentration near the electrode. (2) The probe in front of the electrode has the effect of shielding the electrode surface from its normal share of current lines, thus decreasing the current density at the point at which polarization is measured. This effect also rapidly becomes more serious as the probe is brought closer to the electrode surface. These effects act

in opposite directions in such a manner as to compensate each other partially. The nature of the curvature of the curves shown in Figure 19 (p. 147) demonstrates that the effect of shielding increases more rapidly as the electrode is approached, even over-balancing the effect of IR which normally would produce a curvature in the upward direction near the electrode surface. Since neither of these methods gives the proper correction, the front method can never give true polarization data.

Throughout this discussion, the extreme significance of any departure from uniform current distribution has been made evident. From this single point of view the Haring cell should be the ideal arrangement. However, the results obtained in this research show that there must be other disturbing factors since in all cases the values obtained by the Haring method are consistently lower than those by the front or back method when properly applied. The results by the Haring method are fairly reproducible and, providing a high degree of accuracy is not required, it represents a convenient technical tool. The results of the experiments definitely indicate that even with the Haring method, the back of the electrodes should be insulated.

As has been pointed out above, the values by the front method are highly dependent upon the position of the probe, both laterally and longitudinally with respect to the face of the cathode. In this regard the back method possesses a

distinct advantage in that the positioning is not critical. The value obtained in this case is that measured to the nearest exposed point on the electrode. The results of the experiments indicate that this method will give a correct measure of true polarization at the average current density of the experiment, if, and only if, the properly insulated electrode should correspond exactly to the cross-section of the cell, a condition not usually obtained in practice. In case the latter condition cannot be fulfilled, the back method will still give the most nearly correct polarization value if a small hole is bored through the center of the electrode. Experimental results indicate that even in this case best results will be obtained if the inside of the hole is insulated. To approximate this, the probe of the back electrode can be inserted into the uninsulated hole and flush with the front face.

For basic fundamental studies of true polarization the final recommendations based upon the results of this work are: (1) a cell of uniform cross-section with the exposed portion of the electrode filling the entire cross-section and all other portions of the electrode being insulated; (2) a compartment behind the electrode which contains the probe of the reference electrode and is filled with the same solution as the cell proper; (3) a small hole, the inside of which is insulated, is bored through the center of the electrode; (4) as an alternative to the foregoing, the pierced and insulated

electrode may form the end of the cell, to the rear of which is attached a suitable chamber containing the probe and the solution; (5) if a uniform cross-section is not possible, the best procedure is to use the hole method, i.e., with the probe of the electrode inserted from the back through the hole and the tip flush with the front face.

SUMMARY AND CONCLUSIONS

The results from Table 1 (page 92) showed that the most suitable current density for this research was 10 milliamperes per sq. cm.

For the observed values for polarization in nine different positions on the front of the cathode, the polarization falls off laterally from the center to the edges and the general trend is an increase from the top to the bottom and at a greater rate as the bottom of the cell is approached. This was to be expected since it was discovered that some current was going to the rear of the electrode and the electrode was raised from the bottom.

Tables 2 (p. 94) and 3 (p. 96) as well as comparable results selected from Table 4 (p. 99) show that the polarization potentials measured by the Haring cell method are consistently lower than those by the front method. Under the conditions of these measurements the values by the back method are very much lower and not even comparable to those by the front method. This was later shown to be due to the fact that the back of the cathode was not insulated.

Preceding the experiments for Tables 5 (p. 103) and 6 (p. 104) the back and edges were insulated. This materially reduced the difference between the back and front method. However, the back method still gave lower results by approximately 13 mv.

Prior to the experiments for Tables 7 through 12 (pages

105-109, 112) the insulation was extended 1/4" on the face of the cathode. This resulted in an increase of potential difference of about 40 mv. for the back method which gave it a value about 27 mv. higher than by the front method; the value by the front method remaining approximately the same.

The fact that the last arrangement obviously caused an increased current density at the edge of the insulation, with the attendant increased polarization at the front edge of the electrode, suggested that the insulation should stop at the inner wall of the cell. Results in Table 13 (p. 114) showed that this was in fact the case; the potential difference between the front center and back standards decreased to about 15 mv. When the front probe was moved to the edge of the insulation, the difference was further reduced. The lowest value, amounting to 8 mv., was obtained when the exposed metal occupied the exact cross-sectional area of the cell.

All the experiments so far have definitely demonstrated that the back method gives the true polarization for a given current density when the insulation extends over the back, around the edge and corresponds to the cross-section of the cell. Only by this means can a uniform distribution of current density be assured. These results show that the importance of the extent of limiting the insulation can not be over-emphasized.

A second factor under investigation in this series of experiments was the effect of lateral positioning of the front

probe and its relation to the insulation. The importance of this positioning is indicated by the results of Tables 9 through 12 (pages 107-109, 112) and Figure 14 (p. 111) which show that the potential difference between the front and back probes remains fairly constant for positions in the central section and decreases uniformly to the exposed edges of the electrode. If the insulation extends into the solution and the probe is placed in front of the insulation erroneous results are obtained which in the case studied amounted to 30 mv. (Table 12 , p. 112; Fig. 14, p. 111). In the above arrangement where uniform current distribution is not obtained, true polarization values can not be determined by any method.

In order to get a measurement by the back method for a polarization at the front center, a hole was bored through the center of the cathode. The following is a summary of the results obtained: (1) The measured potential difference between the back probe and the front center has been reduced from 15 mv., shown in the previous table, to 6 mv.; (2) the measured potential difference between the back probe and the front edge has been reduced from 7 mv. to 1 mv.; (3) the polarization values by the back method are reduced by 13 mv., while those by the front method are decreased but slightly; (4) the values by the front method are greater by about 5 mv. at the edge than at the center; (5) the values by the Haring cell method are consistently lower than those by either of the

other two as has been true in all previous cases in which the back of the electrode was insulated; and (6) in agreement with previous tables, the degree of reproducibility of the measurements by each of the methods is surprisingly good.

Results obtained in Table 15 (p. 117), by extending the probe from the back through the hole flush with the front face, showed that the polarization measured by the back probe was reduced by about 6 mv. and corresponded almost exactly to the front method at the same point. This is further supported by Table 18 (p. 123) in that the measured polarization is increased by retracting the probe into the bulk of the solution in back of the electrode.

Measurements by the front method may involve an IR drop, a shielding effect, or both. Results of Table 16 (p. 119), Figures 15 (p. 121) and 19 (p. 147) and Plate V (p. 144) indicate that corrections for the IR drop using the bulk conductivity may be in error, and in this relatively ideal situation may be about 6 mv. or 7%. Thus no exact value of polarization can be obtained by the front method even when the best accepted methods for applying corrections are used.

The results in Table 17 (p. 122) show that the polarization values obtained by the back probe is the same within ±0.3 mv. regardless of its position in the rear of a properly insulated electrode.

Results of Fig. 17 (p. 122) and 18 (p. 123) and Plate VI (p. 148) illustrate the large variations of potential differences due to non-ideal current distribution resulting from

the use of a small cathode as frequently applied in practice. Much more serious errors enter if the probe is moved even slightly beyond the edge of the electrode, a distance of 4 mm. adding 9 mv. to the potential measured at the extreme edge. Confirmation of the variations due to non-uniform current distribution is given in Table 19 (p. 128) using the method with the probe in the hole and flush with the cathode face.

In all the instances in which measurements were made simultaneously by the various methods, and the back of the electrode was properly insulated the Haring cell gave consistently lower values for polarization by approximately 7 mv. than the front method. This was undoubtedly due to inherent errors in correcting for the IR drop and to the inaccuracy of the assumptions involved. The results are highly reproducible and, if errors of the above magnitude are acceptable, it represents a useful technical tool.

All the measurements with the potentiometer strongly indicated that the difference in potential between the back and front probe and, in general, between any two probes, was due to an IR drop. The later work with the oscillograph conclusively demonstrated that this was in fact the case. An explanation for the occurrence of this IR drop was given which fitted all cases observed.

On the basis of this research it is concluded that the back method gives precise and reproducible values to within

1 millivolt provided that precautions be taken to insure uniform current distribution and to insulate properly the electrode. The hole method, which is a modification of the back method, is capable of giving satisfactory results if suitable precautions and design are employed.

As the historical survey shows, the best values reported in the literature for polarization seldom claim an accuracy of 10 mv., 50 mv. being not uncommon. It is generallyconsidered that copper is among the most difficult metals with which to secure stable static values. In this research it was possible not only to reproduce static values on large sheets of copper to less than 1 mv. but to obtain equally good reproducibility for polarization data even as high as 80 mv.

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