THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

PART I

THE DISTRIBUTION OF THE POTENTIAL IN A UNIFORM COLUMN OF ELECTROLYTE DURING ELECTROLYSIS

AND

PART II

THE ANALYSIS OF ACTIVATION OVERPOTENTIAL INTO EXPONENTIALLY DECAYING COMPONENTS

A THESIS

SUBMITTED TO THE GRADUATE FACULTY

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BY

LUTHER WHITFIELD MARKS III

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APPROVED BY

[illegible]

R. G. Fowler

Kenneth E. Brook

John C. Brixey

H. O. Rays

THESIS COMMITTEE

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PART I

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GENERAL INTRODUCTION

The observation of the similarity in the proposed mechanisms of electrical conduction through electrolytes and through ionized gases suggested to Professor William Schriever that space charge, known to exist in gases, might also exist, though small in magnitude, in electrolytes undergoing electrolysis. Several investigations, beginning in 1923 and culminating in the work of Reed[1] in 1948, yielded results in conformity with the foregoing hypothesis. Since this was in contradiction to the assumptions of electrical neutrality found in many places in electrochemical literature, there were serious objections raised after the publication of these results. Part I will deal in detail with additional investigations of these effects and the conclusions derived therefrom.

During these investigations an examination of what happens to

the "space charge" immediately after electrolysis ceases led eventually to the discovery of an apparently new and interesting relation concerning the decay of overpotential with time; in Part I will be mentioned the way that this came about. Part II will deal separately with this decay phenomenon; an explanation will be given.

PART I

CHAPTER I

INTRODUCTION

History of Local Work

In earlier researches at the University of Oklahoma it was found that during electrolysis the potential gradient along the center of a uniform column of electrolyte between plane parallel electrodes, was not constant. The cause of this non-uniformity had been interpreted as macroscopic space charge, the density of this charge being constant over any cross section of the column. Since the present investigation lends evidence that factors other than space charge were instrumental in producing these observed variations in the potential gradient, it seems proper to review the basic assumptions which led to the space charge interpretation. These may be stated as follows:

(a) The cross sectional area of the column of electrolyte is uniform throughout its entire length between the electrodes.

(b) There is no variation in concentration in the measurable portion of the column during 15 minutes of electrolysis.

(c) The electric field is then everywhere in a direction normal to the electrodes which are situated at the ends of the column of electrolyte.

(It is seen that this requires that the current density be uniform over the electrode surface as well as over any transverse cross section of the column.) Since the probe (exploring electrode), by means of which the potential difference was measured, is very small compared with the cross sectional area of the column, this third assumption should be true everywhere except in a small volume about the axis of the column which includes the probe.

The horizontal plate glass trough which contained the electrolyte was 8.0 cm wide and the solution was 8.0 cm deep; the plane electrodes were 40.0 cm apart with faces parallel to each other and perpendicular to the sides of the trough. If we consider the origin of coordinates at the cathode surface and the x-axis along the long axis of the trough, then we may consider the horizontal and vertical directions to be the y- and z-axes respectively.

Poisson's equation, under these conditions takes the form,

$$1. \qquad \frac{d^2V}{dx^2} = -\frac{dE_x}{dx} = -\frac{4\pi}{\epsilon}\rho \quad , \quad E_y = E_z = 0$$

where V is the potential at a point whose perpendicular distance from the cathode is x, ρ is the space charge (net charge per unit volume), ϵ is the dielectric constant of the solution, and E_x, E_y, and E_z are the rectangular components of the electric field strength. Thus, any change in the electric field between two points at distances, x_1 and x_2, from the cathode is due to a net charge in the interlying region. This is illustrated for both positive and negative charges in Figure 1. The positive charges act as "sources" and the negative charges act as "sinks".

Every criticism of a space charge interpretation must ultimately fall back on one or more of these three assumptions. (This, however, does

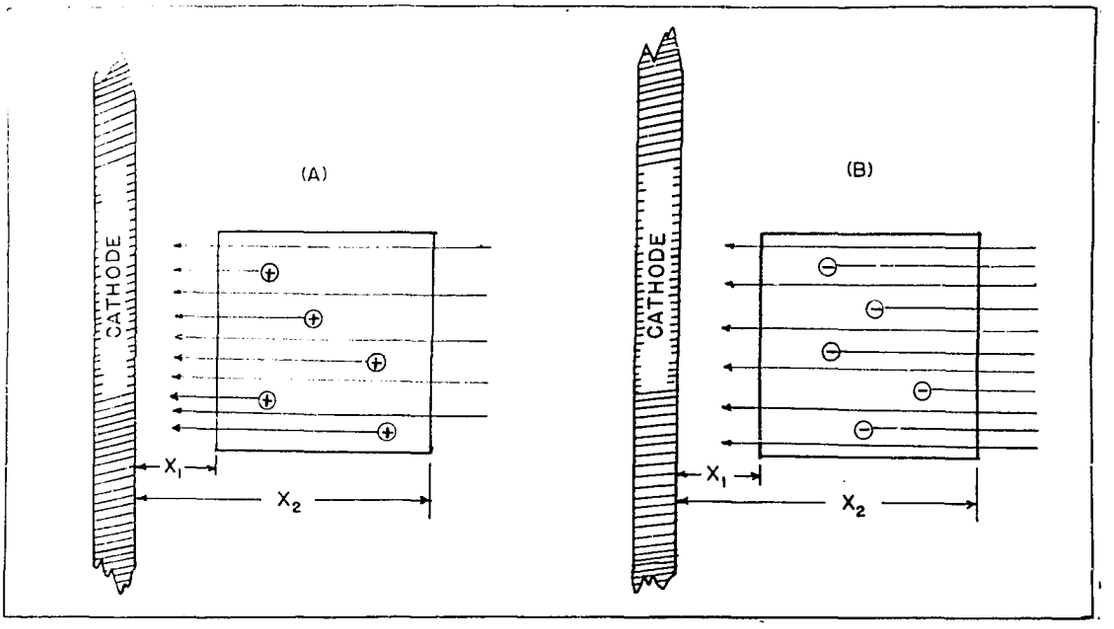

FIGURE 1. EFFECT OF SPACE CHARGE ON THE ELECTRIC FIELD.

require one further supposition, that the method of determining the potential at a point in the solution leads to correct results.)

That the first assumption listed (concerning cross sectional area) is important was realized early in the work. Reed in 1929[2](p.28) was able to detect non-uniformities in the walls of a porcelain trough that was used to contain the electrolyte. Since that time glass troughs with accurately plane walls and bottoms have been employed. The width and depth of the solution have been held constant to within one tenth of one millimeter in 80 throughout the entire length of the column. Variations in width of this order do not affect the potential gradient to a measurable extent.

Much of the adverse criticism of the space charge explanation has arisen because of the second assumption which concerns concentration. However, even long before the publication of Reed's results in 1949, Martin[3] in 1938 had carried out an investigation to ascertain whether

concentration changes did occur which would account for the variation in the potential gradient as observed still earlier by Brooking[4] and others. Martin found no such changes in concentration. Then again, after Reed and Schriever's publication[5], Pickett[6] repeated the investigation for concentration changes with improved apparatus and found evidence of such variations only very near the current electrodes, but these changes were less than one per cent, much too small to account for the potential gradients observed.

At the time the present research was begun (Spring 1953) there was planned a third simultaneous investigation to determine the magnitude of the concentration changes during DC electrolysis by still more refined methods. Though this was not carried out as planned, the work to be described in Part I of this thesis will demonstrate the validity of the results obtained by Martin and Pickett.

Very little reportedly has been done to check the accuracy of the third assumption ($E_y = E_z = 0$); indeed in only the first thesis by Roller[7] (p.39) is there any mention of an attempt to verify this supposition. Professor William Schriever stated that both Brooking[4](1933) and Reed[1] (1948) made measurements laterally in the trough and found no significant changes in the potential at points not close to the electrodes; no records of such measurements were made. Furthermore, criticisms[17,23,24] of Reed and Schriever's publication[5] have in no wise touched on the validity of this assumption.

The following is Roller's statement of the assumption, and of his attempt to check it.

> It is assumed that the electric field in the electrolyte was unidirectional and normal to the electrodes in the region of the liquid invaded by the platinum pointers. This assumption seems justified when it is considered that the dielectric constant of the liquid is high and that the region explored by the pointers was close to the longitudinal axis of the liquid. Indeed it was found experimentally that raising and lowering the pointers to different levels in the electrolyte seemed tc have no appreciable effect on the electrometer readings. (The underscorings have been added.)

Roller measured the potential difference between two platinum probes, set a fixed distance apart, which could be moved axially along the trough.

In addition to the researches already cited, concerning the three assumptions, there are other theses[8,9,10] in which are discussed improvements of measuring technique, reproducibility, and calculation of space charge in accord with these three hypotheses.

Present Work

This present research initially was planned to be an investigation of the potential gradient in a conducting electrolyte between "reversible" Ag/AgCl electrodes. Essentially the same procedure outlined by Reed[1] was followed and, for a 0.0024 N KCl solution with the Ag/AgCl current electrodes (described later), there occurred significant deviations in the potential gradient after 20 minutes of electrolysis as far out as 10 cm from the cathode (see Figure 6).

While this experimental work was being carried out there arose the following fundamental consideration, which is vitally connected with the third assumption: If net positive or negative charge densities exist out in the interior of the solution as suggested in the space charge interpretation, and there are no lateral components of the electric field, then the charges would move toward the sides of the column, to a minimum energy configuration.

At first it was believed that these charges (supposedly ions), due to their low mobilities, might not move far in the 15 minutes during which the electrolysis took place. This idea proved untenable because measurements of the decay of the potential at various points in the solution after the current ceased, showed that the charge did disappear rapidly. (See Part II.) This work revealed that the potential of all points throughout the column of electrolyte, excluding regions very near the electrodes, were at the same potential very shortly after the current was turned off, that is, in two to three minutes; in fact throughout most of the trough the potential was constant in less than thirty seconds. If then the charges are annulled so rapidly when electrolysis ceases, it is reasonable that they must also somehow be discharged or removed as quickly even while electrolysis occurs.

It was this consideration which stimulated a thorough investigation of lateral and vertical potential distributions at various distances from the electrodes. Subsequently it will be shown that the resulting data led to causes, other than space charge, for the non-uniform potential gradients which had been observed by previous researchers. Observations, such as significant fractions of the current going to the backs of the electrodes, diving toward the lower edges of the electrodes, going to certain spots on the electrode surface, and even rising upward toward the top edges of the anode, will be discussed. If the current diverges from or converges toward some region of the electrode surface, then lateral components of the electric field must exist and assumption three must be invalid.

The Purpose of Part I of the Present Investigation

It can be seen from the preceding discussion that the original plan for the research had to be altered. The purpose then became, primarily, to establish what, and how, effects other than space charge could produce the non-uniform potential gradients which have been reported by previous researchers.

CHAPTER II

APPARATUS

The apparatus used throughout this work was essentially the same as that employed by Reed[1](p.24) except for some changes in the electrical circuit, the construction of a new type of probe for work in $CuSO_4$, the device for moving the probe laterally, and a few other minor alterations. The use of a vertical cell was new.

The Cells

The horizontal trough was the same as that used by Reed[1](p.24). The vertical cell was constructed similarly of slabs of plate glass with the same tolerance of 0.1 mm in width throughout its length. The four sides and one end were enclosed, the inside dimensions being 65 cm tall x 9 cm x 9 cm. The column of electrolyte between the current electrodes was made to be a rectangular parallelepiped 35 cm x 9 cm x 9 cm except for the space occupied by the Lucite rods and the glass tube for supporting the probe; these will be described later.

The Electrodes

The probe for work in chloride solutions was of much the same construction as that used by Reed[1](p.26). (A complete description is given in Appendix I.) The bare metal-tipped probes, such as those used

by Reed[1], Ferguson[8], and others, fluctuated in self potential considerably even though the maximum electrometer current was only about 10^{-10} amp/cm^2. This difficulty was corrected by constructing a probe of a new design shown in Figure 2(B). The bare wire was inserted into the finished hollow probe to within a short distance from the tip. The electrolyte could then enter the tip and cover the exposed wire. This accomplished two important results; first, the area exposed to the solution was greater and thus the current density was reduced, and second, the probe-to-solution e.m.f. was not disturbed when the electrolyte was stirred. In some cases the end of the bare wire was coiled, see Figure 2(B), in order to increase even more the area in contact with the electrolyte while in another case a piece of copper, from the same stock as the current electrode, was used. The electrolyte rose inside the tube of the probe to the height of the solution on the outside.

The Ag/AgCl current electrodes, used in the horizontal trough, were made from 99.9 percent pure silver, 0.063 inch thick. The 10 cm long silver plates were machined to fit freely inside the trough, and were, at the top edge, silver-soldered into a machined slot in a brass holder. (The procedure for plating the chloride on the silver surfaces is described in Appendix I.) The electrolytic copper electrodes, made from a copper sheet 1/8 inch thick, were mounted in the same manner. (The preparation of the copper surfaces is discussed in Appendix I). The platinum electrodes were those used by Ferguson[8](p.12).

Supports for the Pointer, the Trough, and the Current Electrodes

The optical bench, the rider used for positioning the probe along

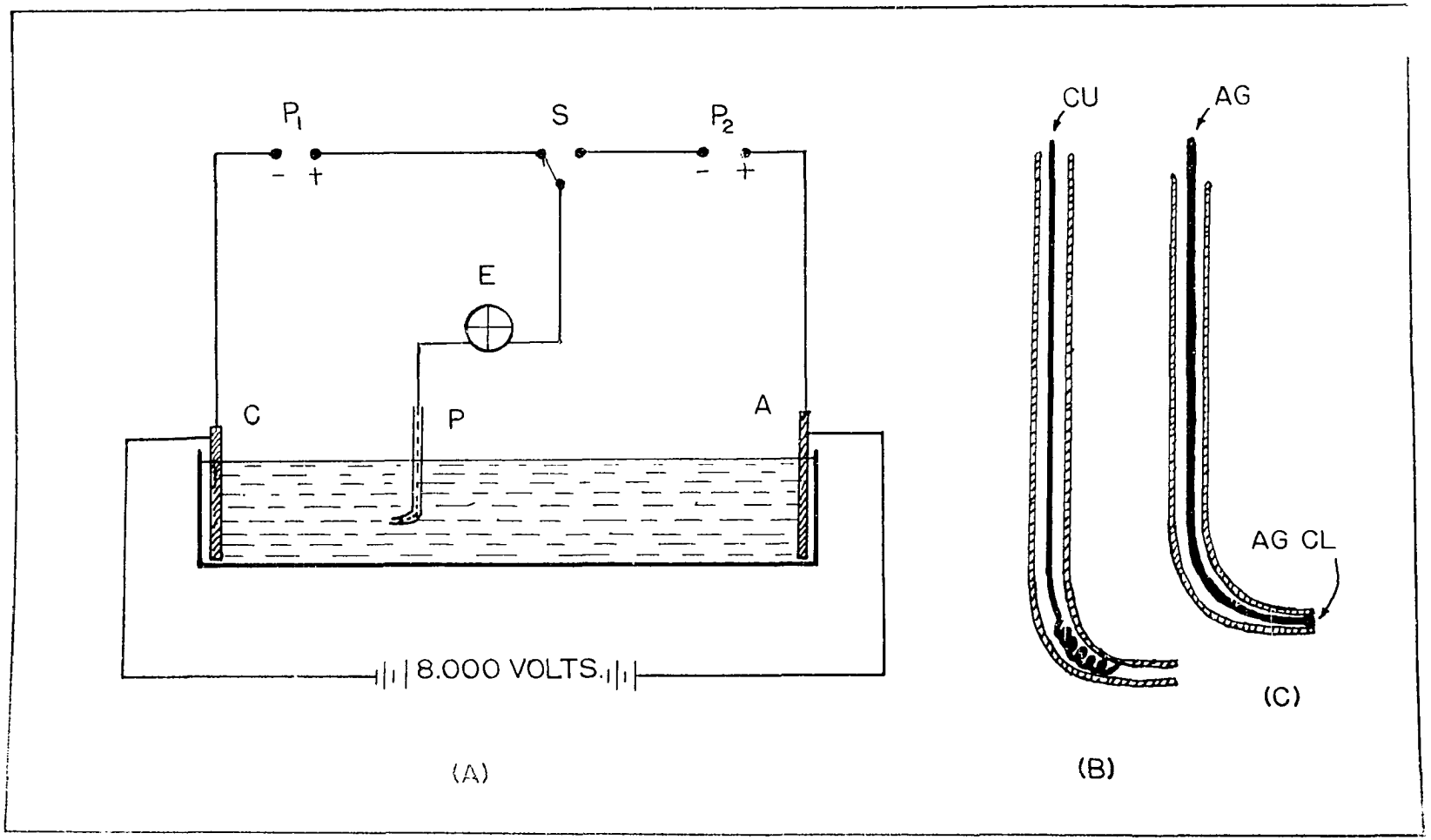

FIGURE 2. SCHEMATIC DIAGRAM OF THE APPARATUS.

the axis of the trough, the turn table for orienting the probe, and the supports for the trough and current electrodes, were the same as those used by Reed[1].

To permit moving the pointer laterally in the horizontal trough a bar of one inch square steel, six inches in length, was mounted horizontally, corner up, upon a specially constructed optical bench rider, with the axis of the bar perpendicular to that of the bench. This permitted the second rider, which carried the probe, to move laterally across the trough. Vertically on this second rider was mounted a screw drive which permitted the raising and lowering of the pointer above and below the axis of the trough. This device did not permit adjustments of sufficient precision to maintain the probe at a fixed distance from the electrode surface. Thus each time an off-axis setting of the probe was made a new zero reading was determined with the probe tip just touching the electrode. This device permitted the probe to be positioned at practically any point in the electrolyte.

The Electrode Assembly for The Vertical Cell

In Figure 3 the three Lucite rods L, each carefully machined to a length of 350.0 mm, acted as separators for the electrodes E. Holes were drilled and threaded into the ends of the rods to admit copper plated cap screws, which clamped three of the corners of each electrode onto the ends of the rods. In the remaining corner of each electrode a hole was drilled large enough to permit a 3/8 inch diameter glass tube T, to pass through freely. This tube was about 70 cm long and closed at the bottom.

The tube extended in each direction from the two probes [see Figure 3(B)] so that it would remain in the holes while the probes were positioned at any point between the current electrodes. (This length of T necessitated the 65 cm long tank.) The stems of the two probes P, with their points 16 cm apart and oriented in opposite directions, were passed through holes in the walls of T and each bent upward inside at right angles as shown in Figure 3(C). Next two small tubes t, of such bore that they would just slip over the probe stems were inserted at the top of T and lowered until they slipped over the ends of the probe tubes. A copper wire of size 20 B.&S. gauge, with the insulation removed for several centimeters near the end, was inserted into each of the tubes t down to within approximately one centimeter of each probe tip. The tube T was then filled with sealing wax to a few cm above the top probe. This served to insulate the two probe systems. The probes were of such a length that they could be moved vertically along the axis of the cell; also they could be rotated any place along an arc, the radius of which was the same as the distance of the axis from the center of T. When the electrode system was lowered into the vertical tank, the electrolyte could then enter the probe tips and make contact with the bare copper wires. (The electrolyte rose in each of the probe systems to the height of the electrolyte in the cell.)

Either of the probes could be positioned to within ±0.01 cm in the vertical cell by means of a vertical cathetometer. The cathetometer crosshair was focused on the probe tip. Any off axis measurements could be made by rotating tube T holding the probes and also correspondingly rotating and refocusing the cathetometer. Since the electrode assembly and cathetometer scale were not mounted rigidly together, it was necessary

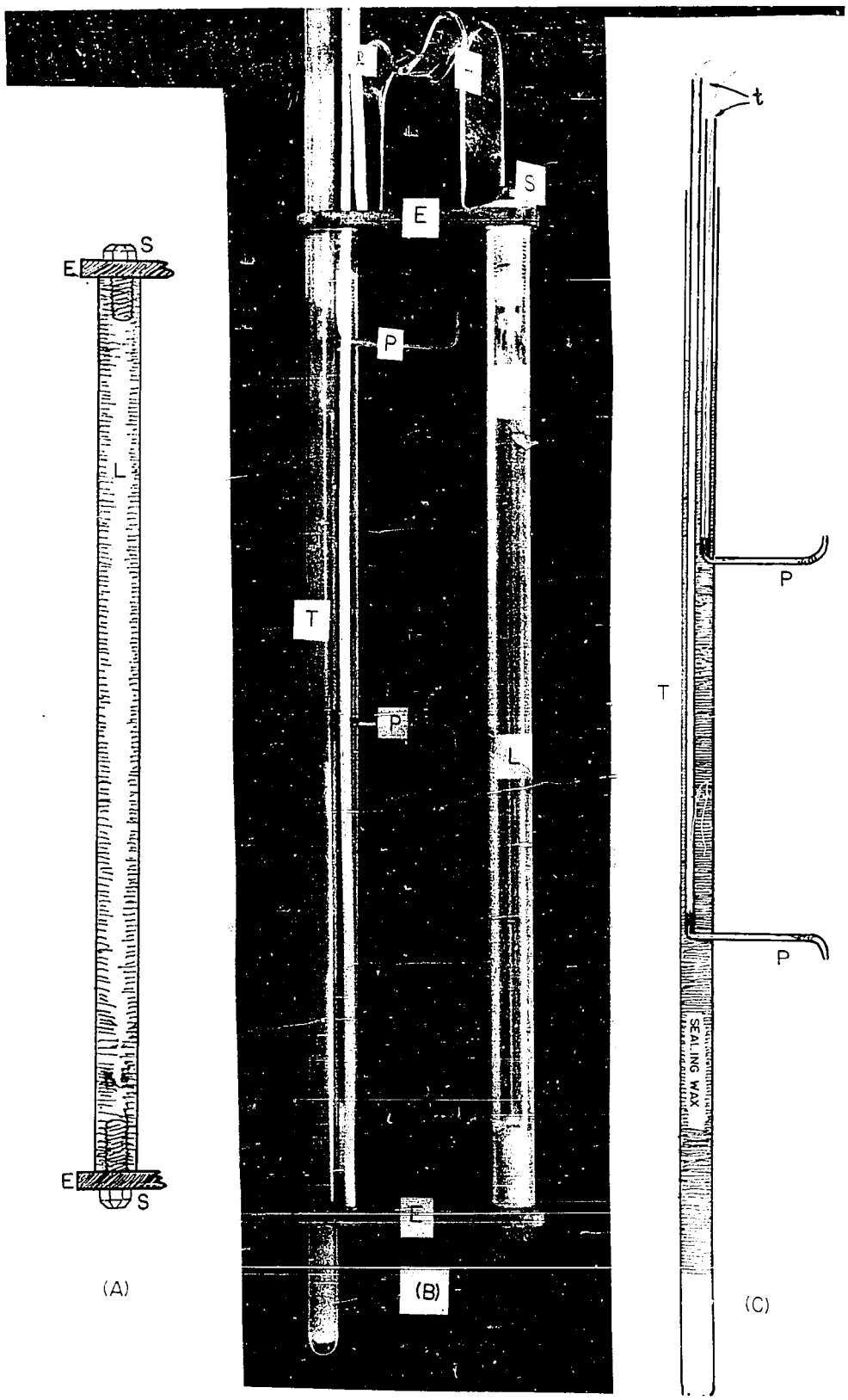

FIGURE 3. ELECTRODE SYSTEM FOR THE VERTICAL CELL.

repeatedly to check for any relative shift. This was done simply by taking a new zero position on the cathetometer scale when the crosshair was focused on one of the probe tips resting against the surface of the corresponding current electrode. To permit the removal of the system from the tank, a Lucite handle H was attached as shown.

The current leads ℓ were made of size 10 B.&S. gauge copper wires threaded on the lower ends. The existing plastic insulation was pulled back near the threaded ends which would be in the electrolyte, and several coats of "Krylon", an acrylic plastic, were sprayed on, each coat being allowed to dry independently. The insulation was then pulled back down over the dried plastic and two spray coats of plastic were applied over this insulation on each lead.

The electrodes for the vertical cell were made from a 1/4 inch thick electrolytic copper plate. They were cut in the form of a square of such size that they fit the inside of the vertical tank closely yet so they could be moved easily without binding. In addition to the holes drilled in the current electrodes to admit the bolts and the tube T one hole was drilled and threaded 3/16 inch deep on the top side of each electrode to receive the threaded ends of the copper leads. Another hole was made in the top electrode to permit the lead from the lower electrode to pass through. The backs and edges of the electrodes were covered with four coats of "Krylon". The faces had previously been carefully flattened on a belt sander and rubbed and polished to a smooth finish with progressively finer grades of emery paper. For a description of the final cleaning of the copper electrodes see Appendix I.

The Alignment of the Electrodes

A rapid alignment of the electrodes in the horizontal trough was accomplished by the use of an inverted T-beam. The beam was constructed of two strips of aluminum 1/4 inch thick and 400.0 mm long, the edge of one being held firmly to the center (lengthwise) of the other by screws. The ends were machined accurately perpendicular to the sides of the inverted T-beam. Three legs one centimeter high held the beam up off the floor of the horizontal trough.

To align the electrodes the T-beam was placed inside the horizontal trough which in turn was placed in position upon its support. The electrodes were then placed inside the trough at the ends of the beam and clamped to their holders. With the sides of the inverted T-beam parallel to the sides of the trough, the electrodes were adjusted flush with the ends of the beam. The electrodes were then accurately parallel to each other, perpendicular to the axis of the trough, and the proper distance apart.

The Ag/AgCl electrodes were prevented from coming in contact with the aluminum beam by inserting thin sheets of "Saran" plastic. Although this changed slightly the distance of separation of the electrodes, this change could be easily corrected for by use of the probe and its vernier scale after the beam was removed.

The Electrical Circuits

A schematic diagram of the electrical circuits is shown in Figure 4.

The entire system is that described by Reed except for the addition

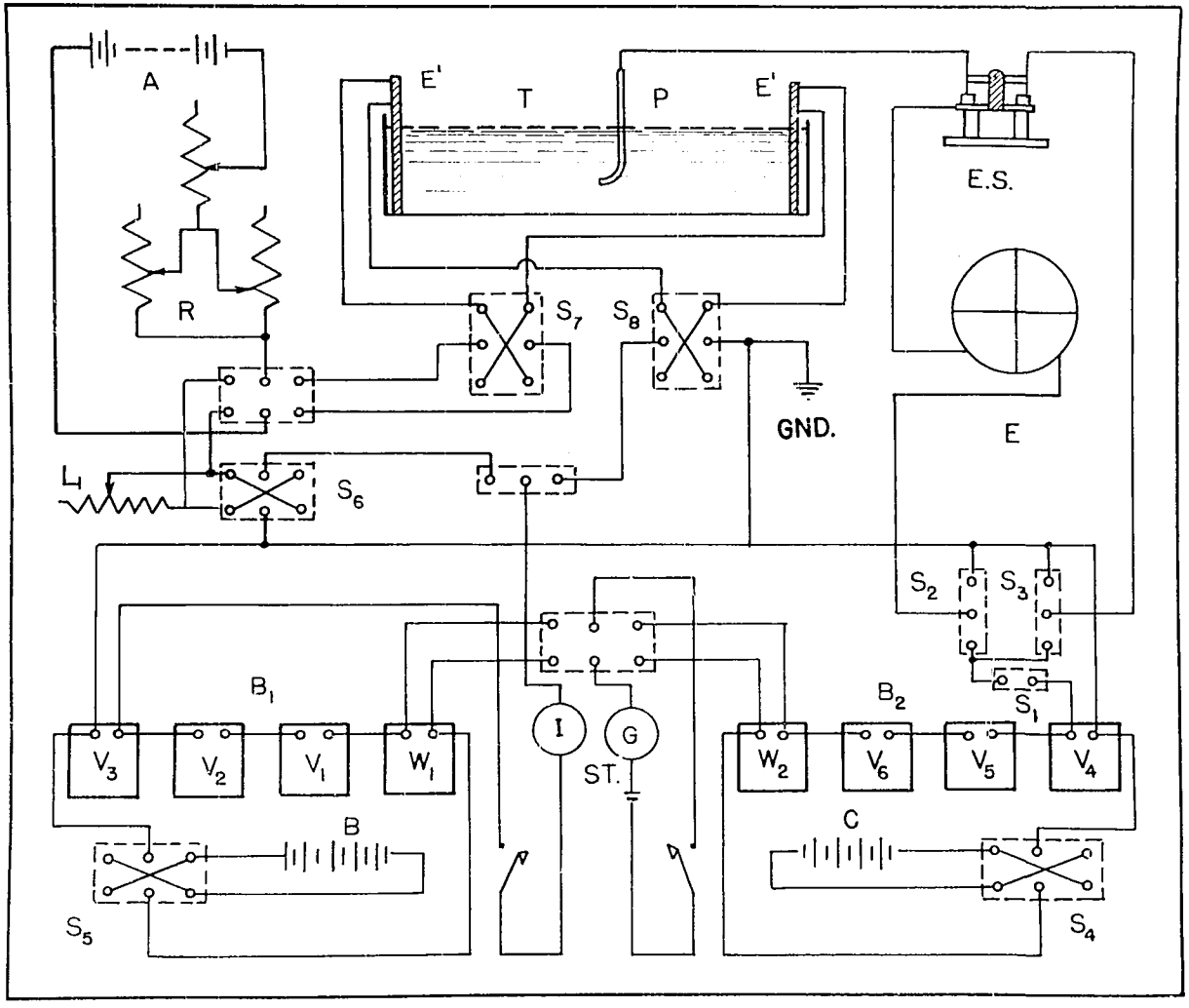

FIGURE 4. SCHEMATIC DIAGRAM OF THE ELECTRICAL CIRCUITS.

of five reversing switches, S_4, S_5, S_6, S_7, and S_8, which serve to change quickly the ground connection from the cathode to anode with simultaneous reversals in the other circuits. The standard cell polarity was also necessarily reversed with each reversal of these switches. The reversing switch S_7 determines which electrode will be the cathode.

The electrometer needle was charged to a potential of 135 volts rather than the 112.5 as used by Reed[1]. This produced a sensitivity of approximately 1.55 mv/mm but this was not constant over the entire length of the ground glass scale. Consequently a calibration table was made which, for the entire range of the electrometer scale, remained very accurate when the electrometer system was kept at a temperature of $30 \pm 1^{\circ}C$, the calibration temperature.

The vertical cell and cathetometer were housed in the same heat-insulated cabinet and the same electrical circuits were used, as for the horizontal trough apparatus.

CHAPTER III

PROCEDURE AND RESULTS

The deviations from a linear rise in potential between the cathode and the anode were determined in the following 0.0024 N solutions:

Solution	Cell	Electrodes	Total Potential Difference
1. KCl	Horizontal	Ag/AgCl (unbacked)	8000 mv
2. HCl	"	Ag/AgCl (unbacked)	2600 mv
3. HCl	"	Ag/AgCl (backed)	3200 mv
4. $CuSO_4$	"	Cu (old)	8000 mv
5. $CuSO_4$	"	Cu (backed)	8000 mv
6. $CuSO_4$	Vertical	Cu (backed)	7000 mv

The designation "backed" refers to the coating of the backs and edges of the current electrodes with an acrylic plastic (Krylon) which prevented electrical conduction to these parts. "Old" refers to a pair of unbacked copper electrodes used by previous workers. The total potential differences were chosen such that the current density in each case was approximately 5×10^{-5} amp/cm^2.

Measurements of the potential distributions in cross section planes were carried out for each of the above cases except the first, KCl.

Two methods were used for the determination of the deviations from a linear rise in potential. The first method was essentially the

same as the "Standard Curve Method with constant potential difference" described by Reed[1]. This method was used only in the first and second cases. The second method was designed to correct for certain types of changes at the current electrodes for which the "standard curve method" could not correct. It, too, was carried out with a constant potential difference. In both cases the apparatus for measuring the potentials was the same. The probe, placed at a desired position in the trough, was used to determine the variation with time of the potential at that point. The current was passed through the electrolyte and the potential across the cell was maintained at the value listed under Total Potential Difference. The deviations were measured, as was done by Reed[1](p.37), at one minute intervals over a period of fifteen minutes (20 minutes in the case of KCl). The solution was then stirred, the probes moved to a new position, and the system allowed to rest for 15 minutes (20 minutes). The procedure was then repeated. Such a series of measurements is designated a "run".

The Standard Curve Method

Repeated observations of the potential at a given point in the trough did not duplicate; there was a progressive change. This lack of duplication was caused by unavoidable changes in the electrode-solution interfaces. Reed[1](p.41) claimed that good reproduction of data could be obtained by compensating for this change in the following manner:

> When observations were being made in say, the anode half of the trough, a certain point in that region was selected as a standard reference point. Runs were made, first at this standard point, then at a desired point, and then back at the standard point. The pointer was then moved to another point, where a run was made. Then another run was made at the standard point, etc. For observations in the anode half of the trough the 36 cm point (from the cathode) was used as the standard point. In the cathode half of

> the trough, the 20 cm point was used.
> To obtain the first datum for the standard curve, the deviations existing at the end of the first minute, for all of the runs that were made at the 36 cm point, before and after runs were made at other points, were averaged. This gave the standard value of the deviation at the end of the first minute. To obtain the second datum, the deviations at the end of two minutes were averaged. This procedure was repeated until standard values of deviation were found for all of the 15 times of current flow from one to 15 minutes. These were plotted to obtain the standard curve. By the same method, the standard curve at 20 cm was obtained.
> The deviation-time curves for the different points of observation were standardized by means of the standard curve, in the following manner. The two runs at the standard point, taken before and after the run at another point, say at 32 cm, were averaged, point by point, in the same way the standard curve was obtained. Then a set of differences was obtained by subtracting each datum for this average curve from the corresponding datum for the standard curve. Each of these differences applied as a correction to the corresponding datum of the curve at 32 cm served to standardize that curve.

This has previously been referred to as the Standard Curve Method.

In this investigation, for KCl the points 8 cm and 36 cm from the cathode were chosen as standard points in the cathode and anode sections respectively. Two points near the center of the trough were corrected by both the 8 cm standard point and the 36 cm standard point and the averages of a few runs in each case were found to agree within two millivolts. Six runs at a point within one centimeter of the cathode, after correction by this method, yielded values having an Average Deviation of the order of five millivolts.

The Second Correction Method

A careful study of the Standard Curve Method revealed that it would <u>properly</u> correct for changes occuring simultaneously at both electrodes <u>only</u> if an increase in the potential drop between cathode and solution were accompanied by a corresponding decrease in the magnitude of

the potential drop between anode and solution. In some cases this condition was approximated because, with an increase in the cathode drop, the current decreased and consequently the anode drop decreased. This type of change can be seen in the 5, 10, and 15 minute curves for $CuSO_4$ obtained by Reed[1](p.82). The cathode drop increased with time and correspondingly the anode drop decreased, hence the deviation-distance curve moved upward remaining approximately parallel to its initial position. To make a prediction as to whether this would occur would be impossible without knowing all the factors causing the drops at both electrodes.

In the case of HCl between Ag/AgCl electrodes the above condition did not exist. The cathode drop increased over a series of runs extending for several days and also the anode drop gradually increased in magnitude. This caused a rotation in the deviation-distance curve rather than a shift of the curve up or down. The points near the center of the trough, about which the rotation occurred, varied little while the standard points varied considerably in opposite directions. In applying a standard curve correction to the points near the point of rotation, one would be allowing for a change which did not occur.

To correct for these simultaneous changes at both electrodes properly the following simpler and faster procedure was devised. All points at which the potential was desired were determined beforehand and then, beginning with the one nearest the cathode, the runs were carried out at every second point progressively from the cathode to the anode, and then from anode to cathode at the points which were skipped. This series had to be carried out as one unit in order to preserve the progressive change in each electrode. The entire series required a full day. The

next series was carried out on the same points except in the reverse order; then two similar series were done beginning at the anode and progressing toward the cathode and back again on the points first chosen. If the progressive change of the electrodes proceeded at a constant rate during all four series of runs, it can be seen that the average of the four potentials for each point would correspond to the potential at that point at a time half way through a complete series of eight traversals of the trough. For each series of runs in the horizontal trough it would have been ideal to include all points on each traversal of the trough but the time required would have been too great. In the vertical cell, when only a portion of the column was mapped, this was done. The above procedure for determining the deviations from a linear rise in potential gave duplicable results.

Correction Applied to Potential Measured by Probe

The "chemical e.m.f." correction applied by Reed[1](p.39) leads to incorrect results. He assumed the potential difference measured between a current electrode and the probe at a distance x from the electrode, (after the correction for the orientation of the probe was applied), was the algebraic sum of the fall of potential from electrode to probe and the electrode-probe "chemical e.m.f."; the latter was measured prior to electrolysis. When such corrections were applied to measurements made at a point in the solution, first with respect to the cathode and then with respect to the anode, see Figure 2(A), it was found that the difference between the two determinations of the potential at the point was equal to the sum of the two observed "chemical e.m.f.'s". This is true since the

potential indicated by potentiometer P_2 will equal to 8000 mv minus the potential indicated by P_1.

Figure 5 shows graphically how the "chemical e.m.f." correction would affect the measured distribution of potential between the electrodes. The cathode and anode chemical e.m.f. corrections, for several systems used by Reed[1](p.109) were of the same order of magnitude; thus he must have applied the anode correction in the wrong direction and obtained apparent consistency. However, it is difficult to see how this could account for his deviation-distance curve for $NiSO_4$[1](p.100) unless the anode distribution was arbitrarily adjusted to fit the cathode distribution. It is significant that, even if this were done, the space charges calculated from his curves would be the same as though there were no chemical e.m.f. correction since the curvatures of the curve were not changed.

For the various probes used throughout the work, the corrections for the orientation of the probe were approximately equal to those found by Reed (between 5 and 10 mv).

Method for Off-Axis Measurements of Potential

For making off-axis measurements of potential the previously described apparatus for adjusting the probe off the axis of the column of electrolyte was employed. It was important in these measurements that the probe tip be the same distance from the electrode surface for every pair of runs which were to be compared. To accomplish this, for each off-axis-setting of the probe, the zero reading (with the pointer against the electrode surface) was taken and then the probe was moved the desired distance from this position. In certain cases it was found that the lateral settings could be made by merely sliding the rider carrying the probe laterally

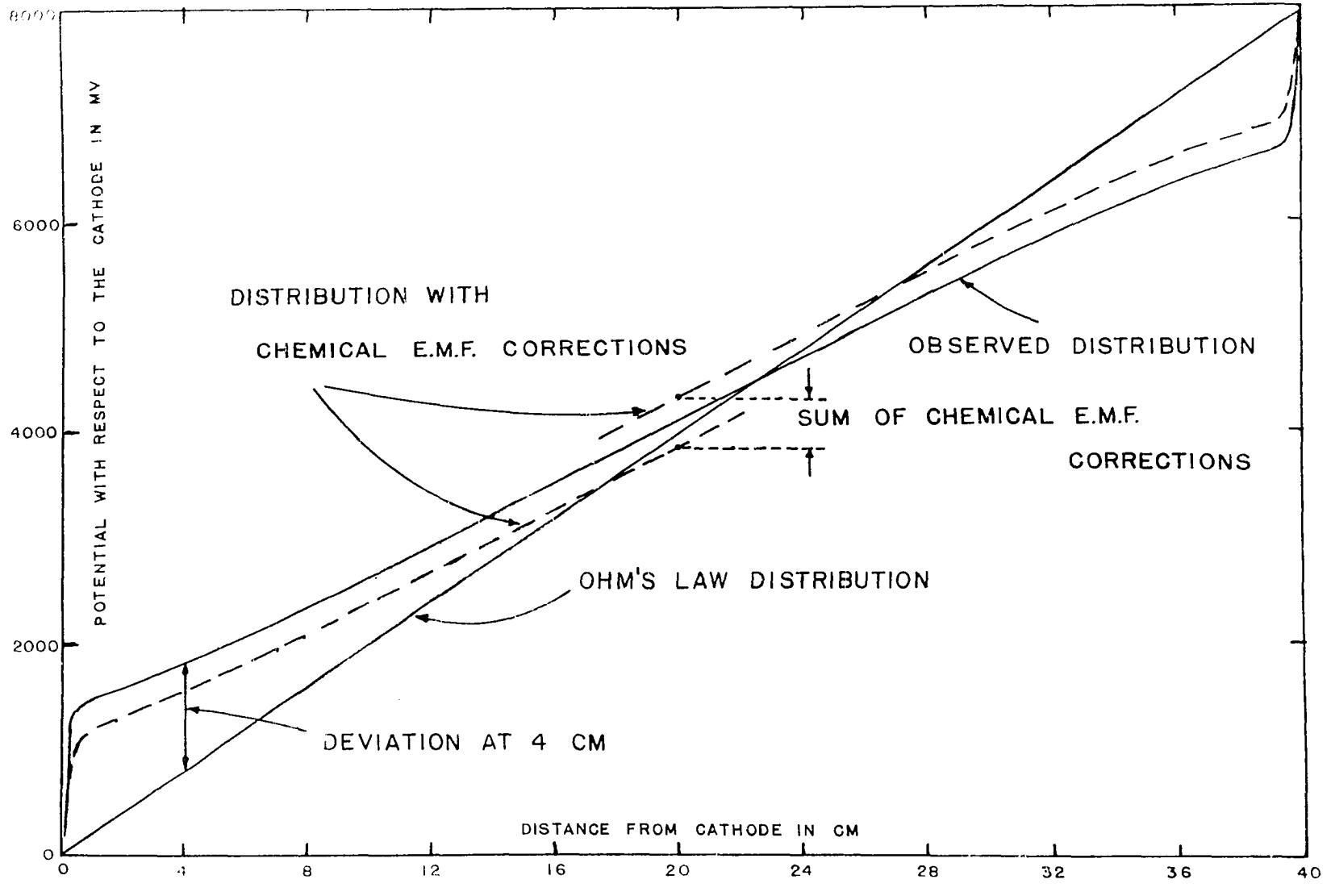

FIGURE 5. CHEMICAL E.M.F. CORRECTION TO POTENTIAL DISTRIBUTION

the desired distances without determining a new zero position for each setting. However, since parallelism between the rider way and the electrode surface could not always be obtained this procedure was not always permissible.

To compensate for over-all changes which might occur at the electrode surface the following procedure was followed. The potential was measured at one minute intervals during 15 minutes of electrolysis at a given distance from the electrode surface along the axis of the column. The solution was stirred, the probe was moved to an off-axis position such that the probe was the same distance from the electrode surface as it was for the previous setting, and the system was allowed to rest 15 minutes. Then a "run" was carried out to determine the potential each minute at this off-axis position during 15 minutes of electrolysis. Next the probe was moved back to its former position on the axis and a second run taken there. The averages of the data for the two runs taken on the axis were then compared with the corresponding potentials for the off-axis run.

When a more complete mapping of the potentials in a cross section plane was desired, the procedure just described was carried out for several points over the section. All the runs on the axis were then averaged to form a "standard" run. The average of the two runs, taken on the axis before and after a given run off the axis, was subtracted from the standard run and this difference was applied as a correction to the run taken off the axis in order to "standardize" it.

Usually the potential at a given position varied so little between runs that two or more off-axis runs could be made before making another run on the axis. Indeed, when the differences in potential over a cross

section plane were significant, they were larger than the variations between runs due to electrode changes.

Experimental Results

The first part of this investigation was carried out in accord with the procedure described by Reed[1] in order to determine whether "space charge" existed in a chloride solution between "reversible" Ag/AgCl electrodes. The first two sets of deviation-distance curves are similar to those obtained by Reed for other types of electrodes and solutions. The previously described Standard Curve Method was employed to obtain deviation-time curves for a horizontal column of KCl solution between unbacked Ag/AgCl electrodes. These curves are shown in Figure 6. In the same figure is shown the deviation, after both 3 and 20 minutes of electrolysis, as a function of the distance from the cathode. The average of five runs was used to determine each point on the deviation-time curves. The total number of runs for all the curves was 119.

The standard curve procedure was also employed to obtain data for a horizontal column of HCl solution between unbacked Ag/AgCl electrodes. The data are shown in the form of curves in Figure 7. The average of six runs was used to determine each point 1.0 cm or less from an electrode. The points at 16, 20, and 24 cm from the cathode were not standardized; they are respectively the means of six, nine, and six runs. Each of the remaining points was determined by the average of five runs. The total number of runs was 125.

When measurements were made laterally across a section of the trough to determine whether the "space charge" was apparently drifting toward the sides, potential distributions were obtained which led to an

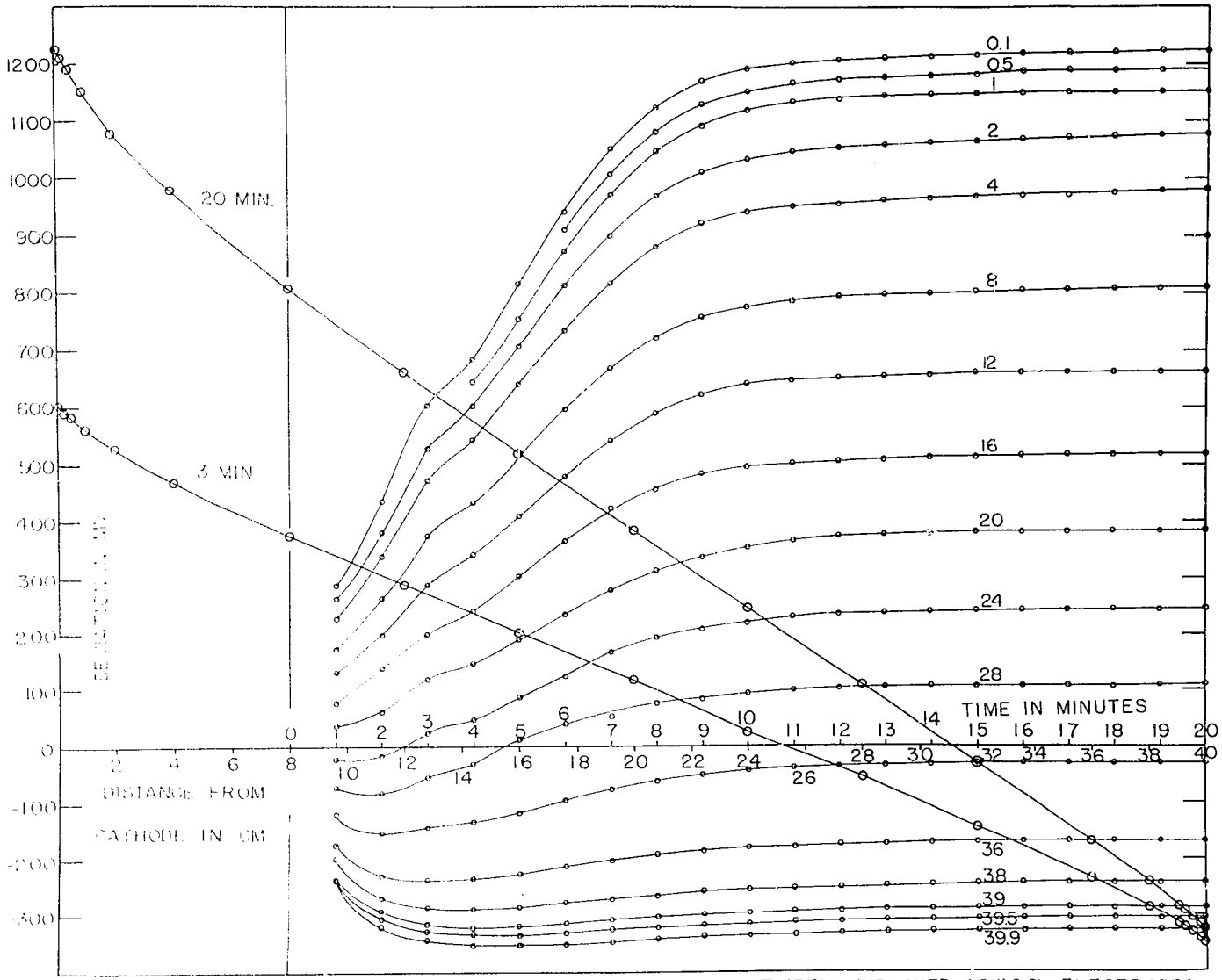

FIGURE 4. POLARIZATION DATA FOR A 0.0024 N KCL SOLUTION BETWEEN UNBACKED AG/AGCL ELECTRODES.

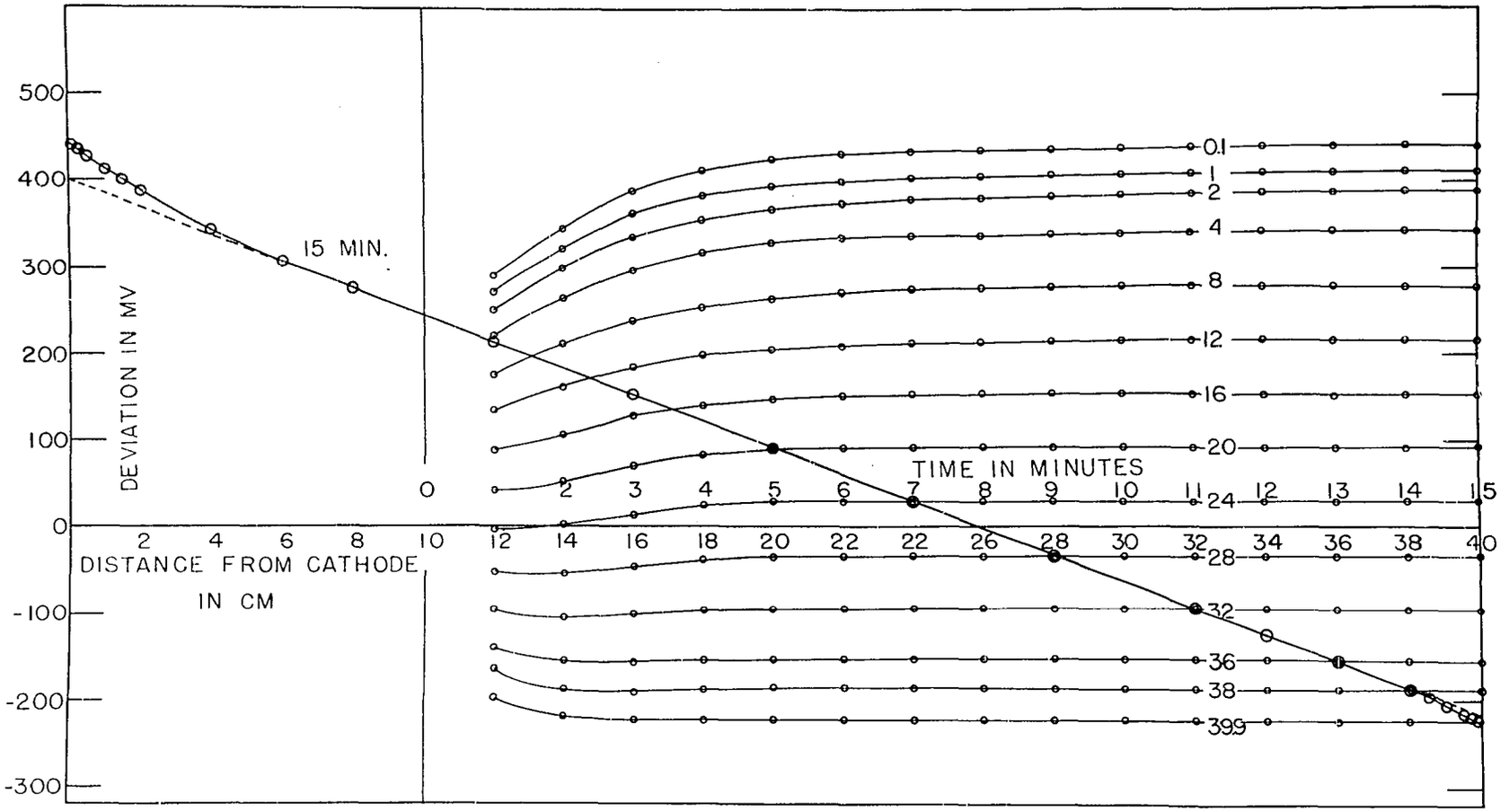

FIGURE 7. DEVIATION DATA FOR A 0.0024 N H CL SOLUTION BETWEEN UNBACKED AG/AG CL ELECTRODES.

entirely different interpretation of the first two sets of data. This third set of data and the measurements which ensued are discussed below.

The lateral distributions of the potential in the same HCl solution between unbacked Ag/AgCl electrodes is shown in Figure 8. The data for the three curves were obtained as previously described at 0.5, 2.0, and 4.0 cm from the cathode. The ordinates represent the potential differences between a point at the center of the section and the points to the right and left of center.

These lateral distributions of potential with unbacked Ag/AgCl electrodes were interpreted as being caused by a fraction of the current passing around the edge of the electrode to the back side of the cathode.

To test what effect covering the back and edges of the cathode with a non-conductor would have, lateral (also vertical) distributions of the potential were determined. These lateral and vertical distributions of the potential in the horizontal column of HCl solution between backed Ag/AgCl electrodes are shown respectively by the lower and upper curves in Figures 9(A) and 9(B). The data were obtained at 0.2 cm from the cathode and 0.1 cm from the anode. The ordinates represent the potential differences between a point at the center of the section and the other points represented by the abcissas.

To determine the effect of backing the electrodes on the potential gradient along the axis of the column of electrolyte the previously described "Second Correction Method" was employed. The deviation-time data for this HCl solution between backed Ag/AgCl electrodes are shown in Figure 10. Each point was determined by the average of six runs. The total number of runs was 126.

The data depicted by Figure 10 indicate that the non-uniform

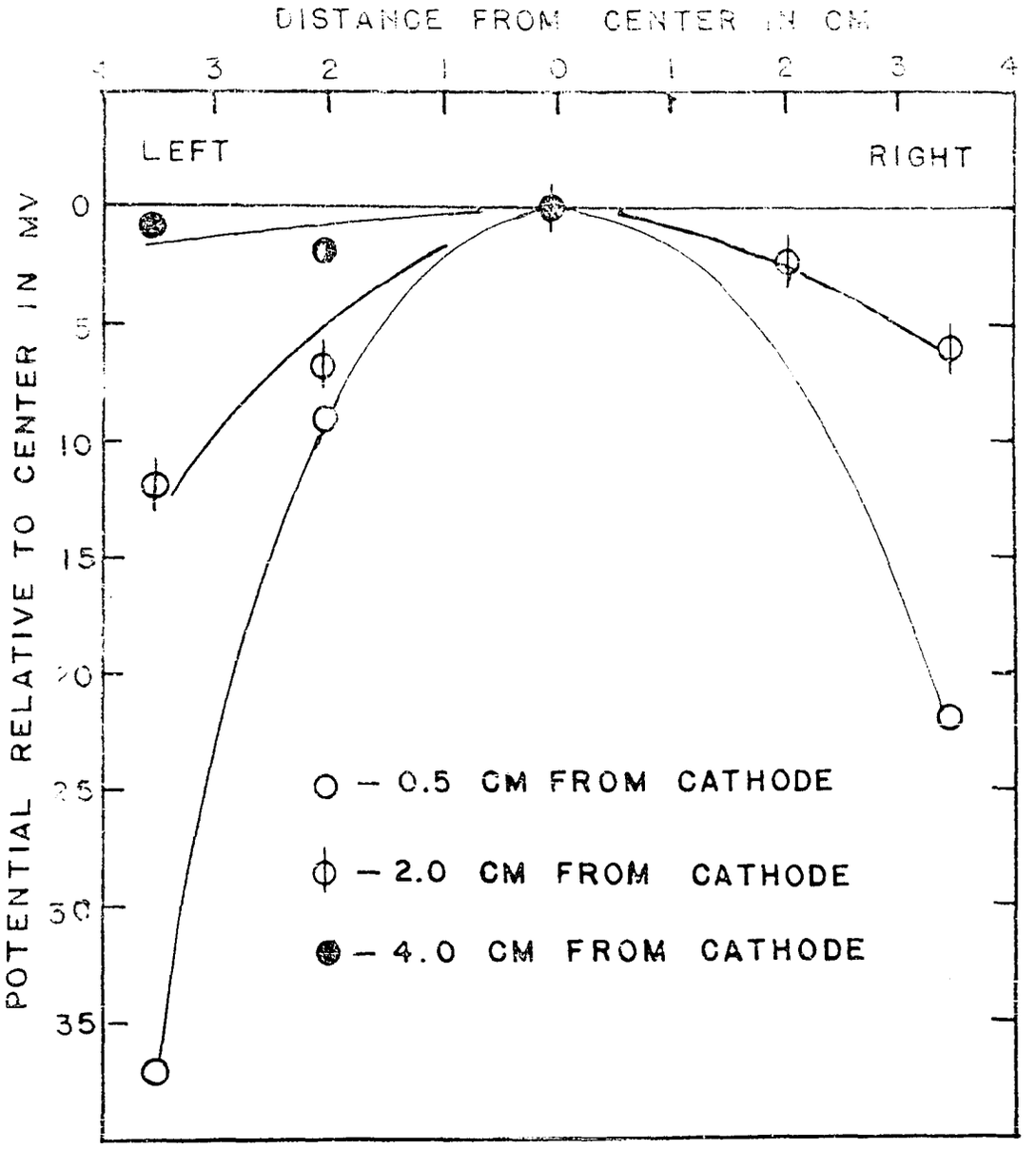

FIGURE 8. LATERAL DISTRIBUTIONS OF POTENTIAL IN A 0.0024 N HCL SOLUTION NEAR AN UNBACKED AG/AG CL CATHODE.

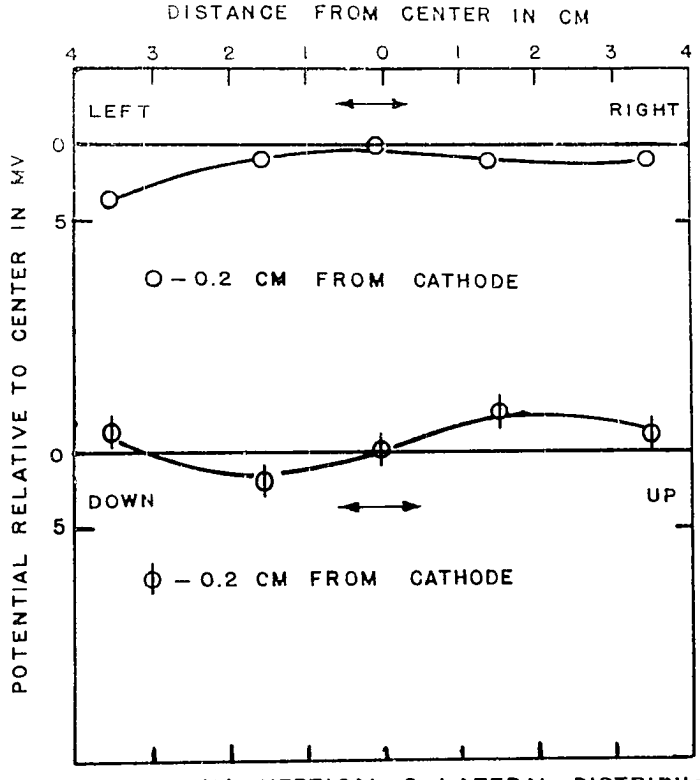

FIGURE 9(A). VERTICAL & LATERAL DISTRIBUTIONS OF POTENTIAL IN A 0.0024 N H CL SOLUTION NEAR A BACKED AG/AG CL CATHODE

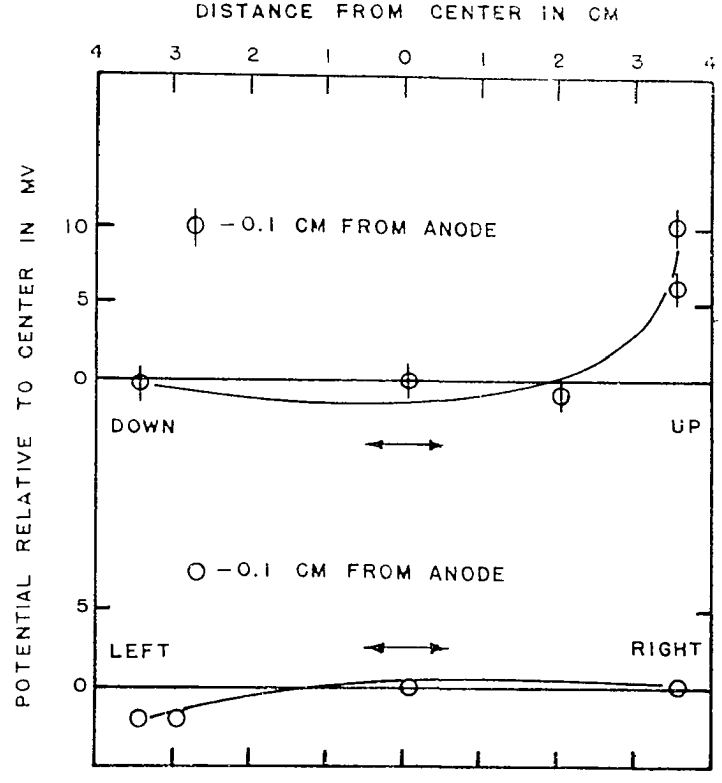

FIGURE 9(B). VERTICAL & LATERAL DISTRIBUTIONS OF POTENTIAL IN 0.0024 N H CL SOLUTION NEAR A BACKED AG/AG CL ANODE

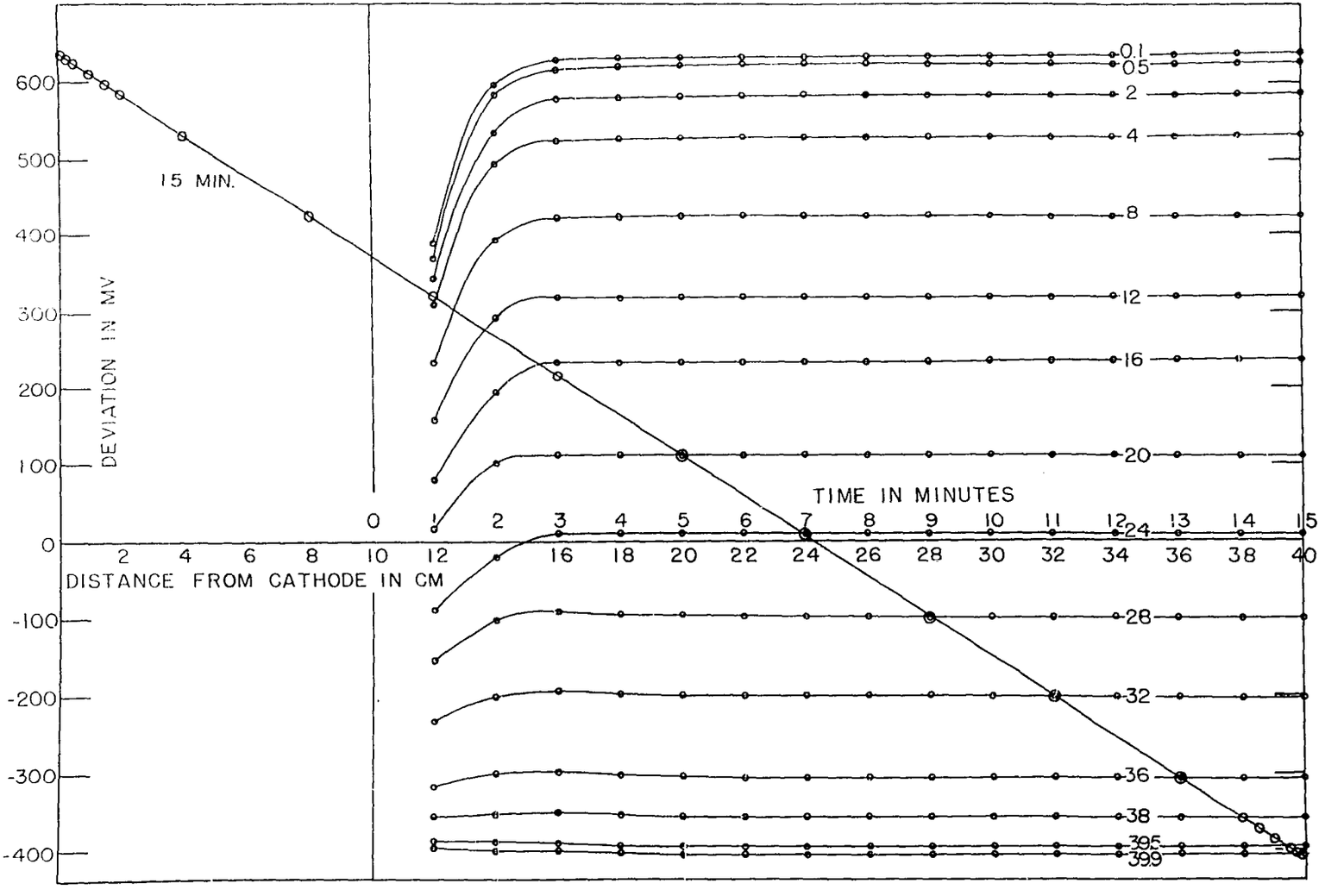

FIGURE 10. DEVIATION DATA FOR A 0.0024 N H CL SOLUTION BETWEEN BACKED AG/AG CL ELECTRODES.

potential gradients observed by previous workers were caused by non-uniform current density distributions over a section of the trough. Since much work had been done with copper electrodes in $CuSO_4$ solution in previous investigations, it was decided to make further tests with this system. A particular copper cathode used by Reed and others was on hand.

Reed[1] had employed the Standard Curve Method to obtain deviation data with this "old" copper cathode in $CuSO_4$. To determine whether a non-uniform distribution of current density over the cathode surface could have produced the non-uniform potential gradients which he observed at this electrode, lateral distributions of the potential were determined. After the cleaning procedure described by Reed[1](p.119) was carried out, certain areas of the cathode remained lighter colored as the electrolysis progressed. These areas are indicated in Figure 11(A). In Figure 11(B) are shown the lateral distributions of the potential along a horizontal line passing through the axis and 0.3 cm from the cathode, and also along a line 2 cm above this line. The ordinates of the points represent the potential difference between a point on the axis of the column and the points indicated by their abcissas. These data lead to a simple interpretation of the potential gradients near this electrode as described by Reed.

This cathode had a thick deposit of copper near the edges on the back of the electrode; the dotted line around the sides and bottom in Figure 11(A) indicates the extent of the deposit. This strengthened the belief that a significant fraction of current was going to the back of the electrode.

If the non-uniform deposits on the cathode surface were produced because of regions of different crystal structure then annealing should

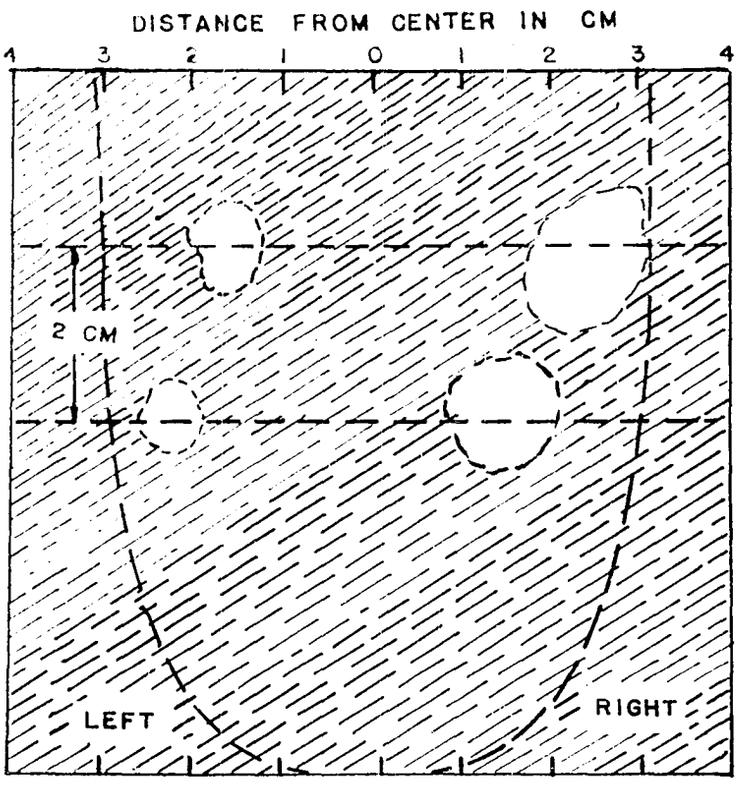

FIGURE 11 (A). SURFACE IRREGULARITIES ON AN OLD COPPER CATHODE

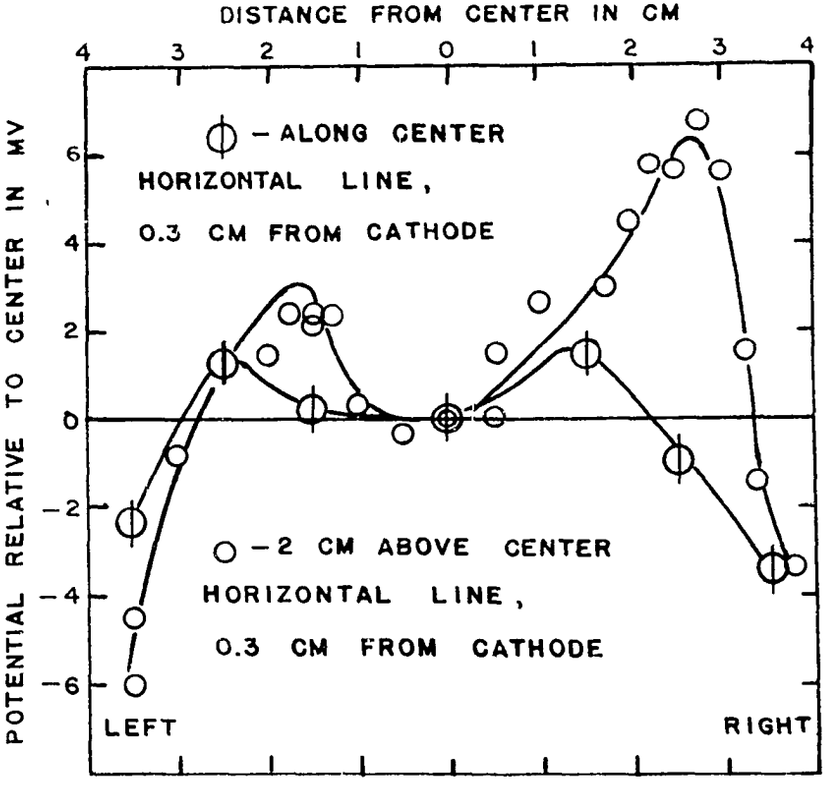

FIGURE 11 (B). LATERAL DISTRIBUTIONS OF POTENTIAL IN A 0.0024 N $CuSO_4$ SOLUTION NEAR AN OLD COPPER CATHODE

remove them. New copper electrodes were prepared by annealing, flattening the surfaces, and covering the backs and edges of copper sheets with "Krylon" as described in Appendix I. The lateral and vertical distributions of potential after 15 minutes of electrolysis at 0.5 cm from the electrodes are shown in Figure 12(A) for the new copper cathode and in 12(B) for the new copper anode in a $CuSO_4$ solution. In Figure 13(A) are shown the deviation-time data for a point 0.5 cm from the cathode at six different depths in the column. Similar data for a point 0.5 cm from the anode are shown in Figure 13(C).

A correlation between the vertical distributions of the potential at the electrodes and the potential gradients at different depths was obtained by determining deviation-distance curves after 15 minutes of electrolysis for several depths. The results are shown in Figure 13(B). Each point along the axis of the trough represents the mean of four runs. The total number of runs was 76. For the other deviation-distance curves in this figure each point represents the average of two runs.

Even with backed electrodes the potential was not the same at all points in a vertical section of the column of electrolyte. It was considered possible that some contamination from the atmosphere was changing the conductivity of the solution or perhaps accelerating or changing the electrode reaction near this surface. To test this possibility the top surface of the electrolyte was covered with a glass plate which fit nicely into the trough between the electrodes, and which had two small aperatures to permit insertion of the probe. With freshly cleaned copper electrodes in $CuSO_4$ solution, it was found that at a fixed distance from the anode the potential was the same at all levels in the column (compare with

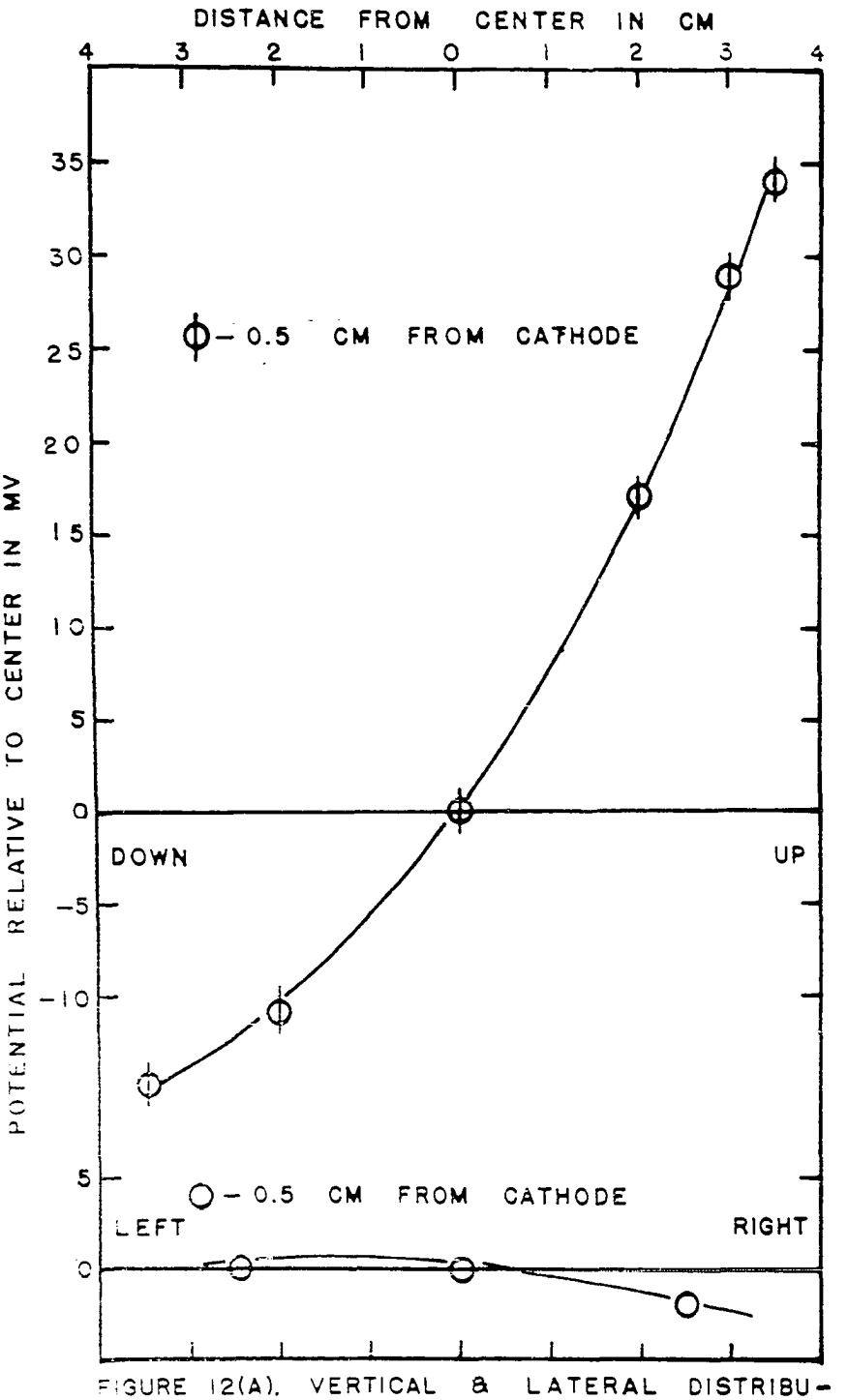

FIGURE 12(A). VERTICAL & LATERAL DISTRIBUTIONS OF POTENTIAL IN A 0.0024 N $CuSO_4$ SOLUTION NEAR A BACKED COPPER CATHODE

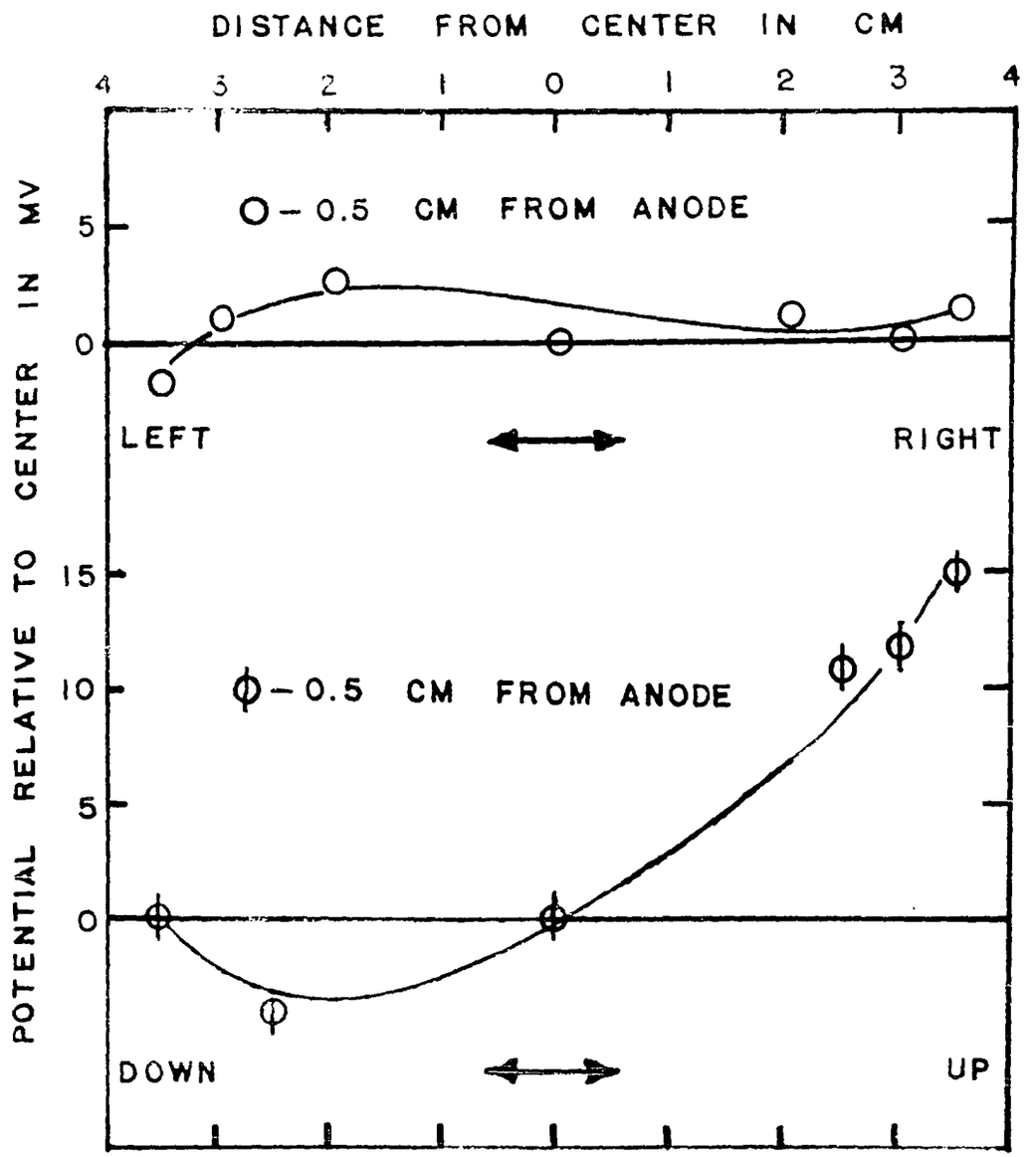

FIGURE 12(B). LATERAL & VERTICAL DISTRIBUTIONS OF POTENTIAL IN A 0.0024 N $CuSO_4$ SOLUTION NEAR A BACKED COPPER ANODE

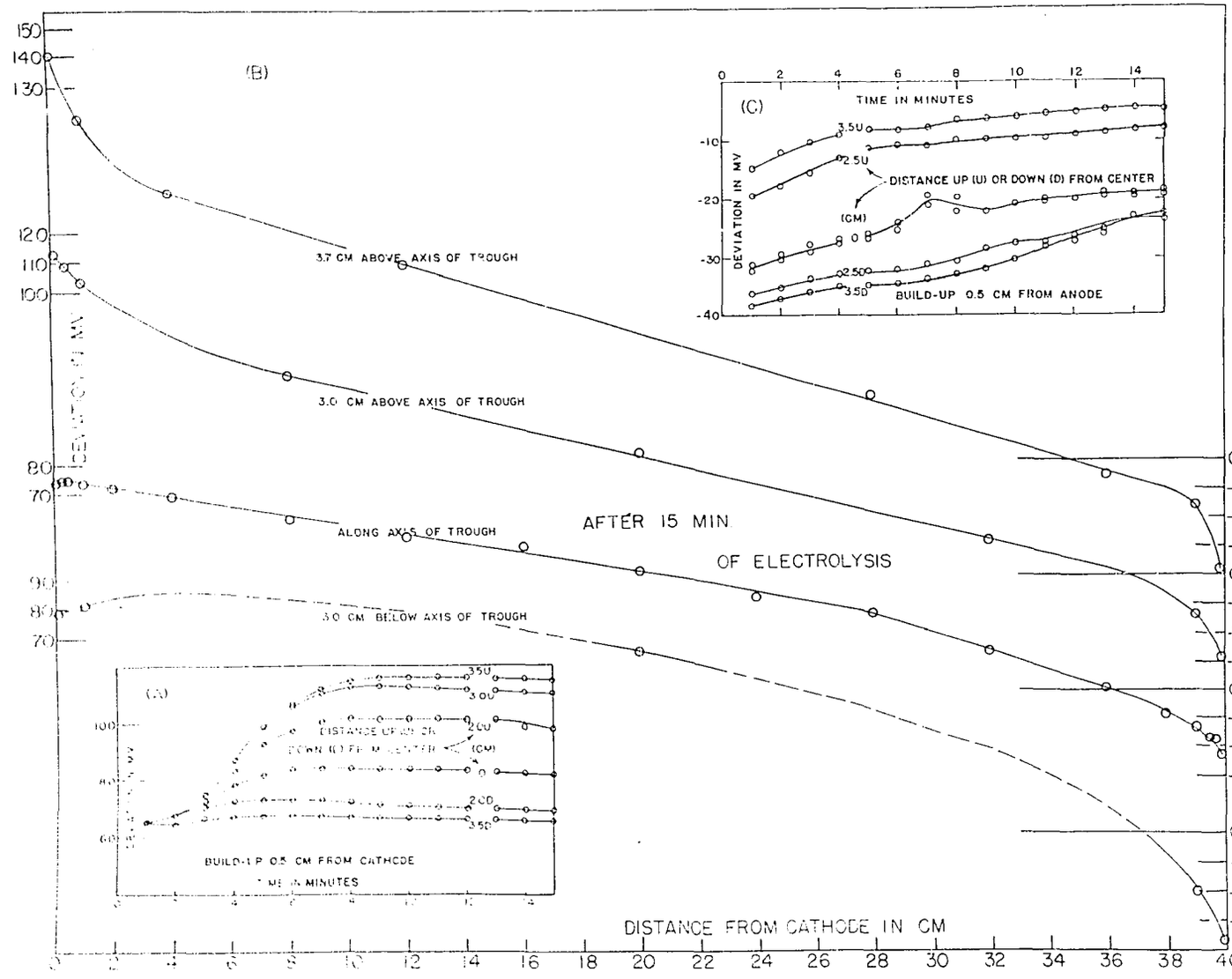

FIGURE 13. DEVIATION DATA AT SEVERAL DEPTHS FOR BACKED COPPER ELECTRODES IN A 0.0024 N $CuSO_4$ SOLUTION.

Figure 12(B) for data without the glass cover). However, the vertical distribution of the potential near the cathode was not improved by the glass cover.

To test whether the non-uniformity at the anode was a condition of the electrode itself near the top, two examinations were carried out. First, it was found that this effect was exhibited by both electrodes when used as anodes, and second, the potentials read at 1 cm below the surface and 1 cm from the bottom were exactly the same for a full trough as with the trough half full.

In copper coulometric work, where it is important that the anode reaction be the transfer of copper from the electrode into the solution and the cathode reaction be the deposit of copper onto the electrode, acid solutions of $CuSO_4$ are used. For this reason H_2SO_4 was added to the 0.0024 N $CuSO_4$ solution between backed copper electrodes; this made the acid concentration approximately 0.0024 N. This produced a vertical distribution of potential at the anode which was almost uniform but it did not improve the vertical distribution of potential near the cathode. Similar results were obtained for a $CuCl_2$ solution when HCl was added.

Since the procedures just outlined produced no improvement in the vertical distribution of potential at the cathode, it must have a different cause. Natural convection, due to a change in the density of the electrolyte in the immediate vicinity of the cathode, seemed to be the most reasonable explanation for this non-uniformity. To test this hypothesis the vertical cell arrangement, already described, was constructed; such an apparatus would minimize convection effects. In Figures 14(A), (B), and (C) are shown results obtained in the 35 cm tall vertical column of $CuSO_4$

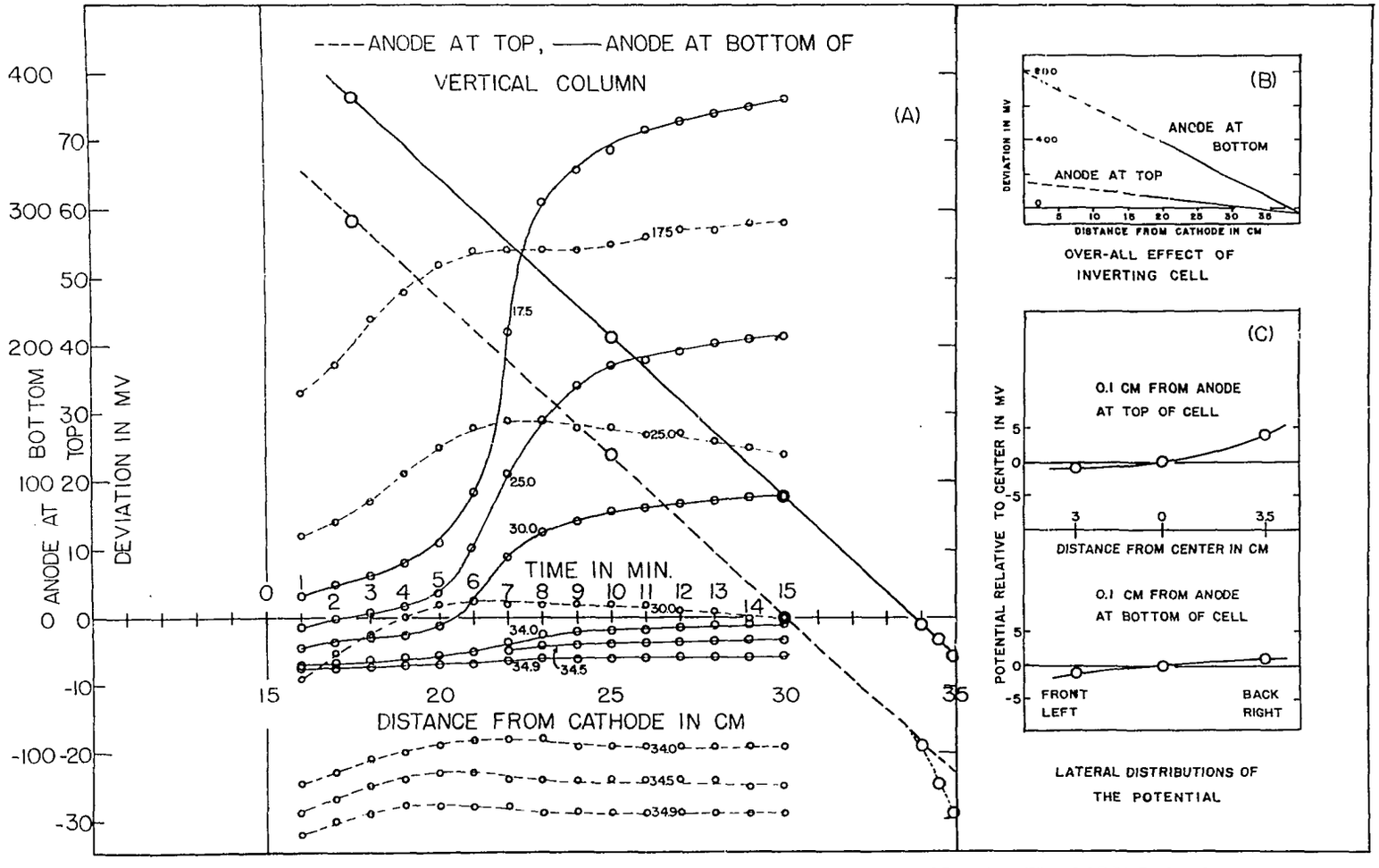

FIGURE 14. DEVIATION DATA & LATERAL POTENTIAL DISTRIBUTIONS FOR BACKED COPPER ELECTRODES IN A 0.0024 N $CuSO_4$ SOLUTION IN THE VERTICAL CELL.

between backed copper electrodes. The deviation-distance data after 15 minutes of electrolysis for the anode half of the column, are represented by the two straight lines of Figure 14(A); the two corresponding sets of deviation-time curves are also shown. [These deviation-distance curves are shown drawn to the same scale in Figure 14(B).] Each of the points represents the average of four runs and a total of 48 runs was required for the two curves.

The potential distributions across a horizontal section of the column were made at 0.1 cm from the anode. These data are shown in Figure 14(C). The probe moved along the arc of a circle whose radius was the length of the probe arm and whose center was at the center of the glass tube which supported the probe.

When the cell was tipped from the vertical by slightly less than three degrees (this would aid natural convection), the potential drop near the higher edge of the cathode at the top of the column was very nearly the same as the potential drop an equal distance from the electrode before tipping. However, near the lower edge of the cathode surface the potential drop was over 200 mv less. Larger tipping angles were not feasible.

In Figure 15 are shown examples of the deviation-time data for several cathodes and solutions at points 0.1 cm from the electrode.

For convenience in picturing the current distributions near the electrodes the "cross-sectional distribution of potential" curves may be considered to be exaggerated equipotential surfaces near the particular electrode. For the figures showing the distribution near the anode the current lines should be considered as approaching the electrode from the top of the figure; for figures depicting distributions near the cathode

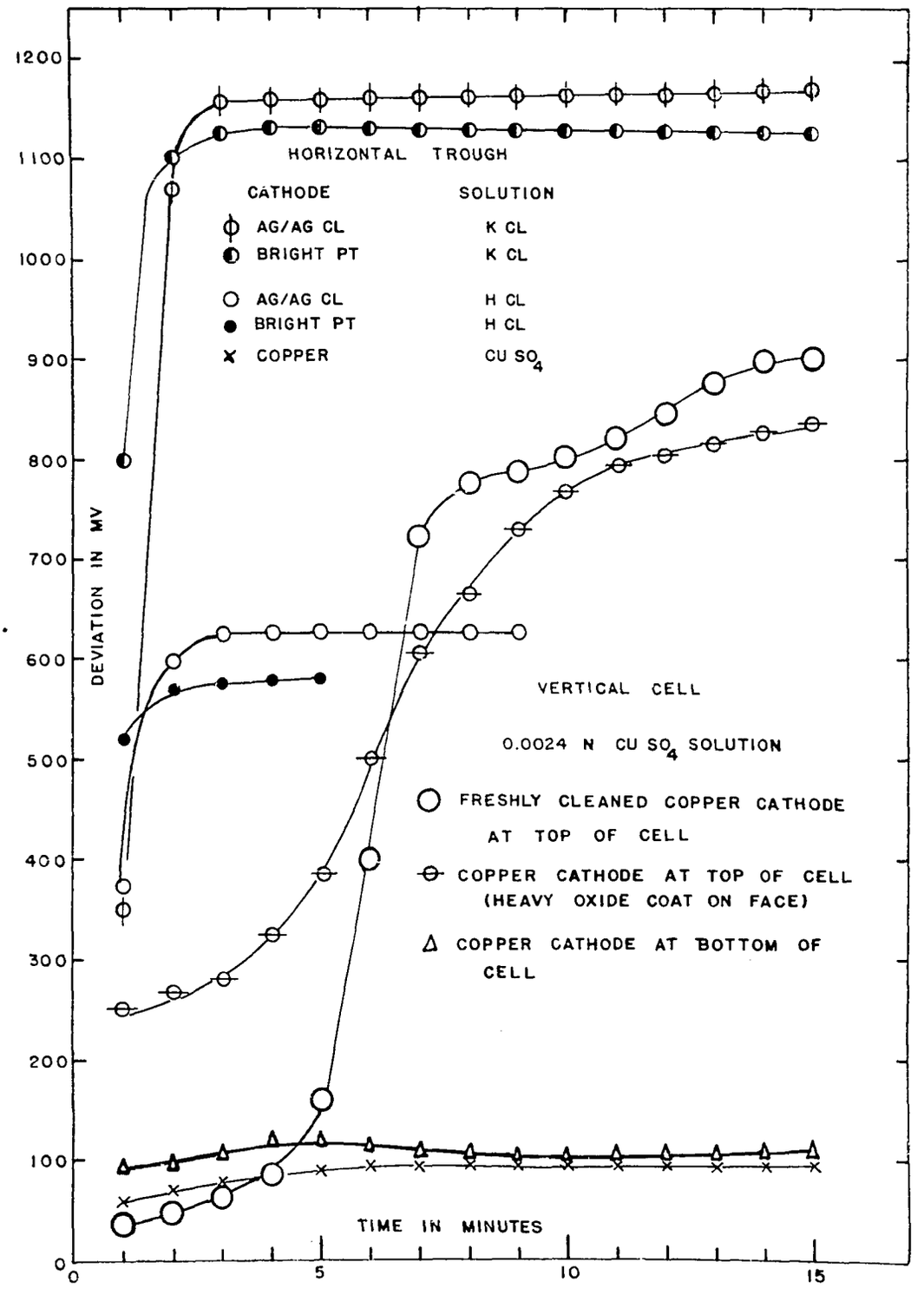

FIGURE 15. EXAMPLES OF DEVIATION–TIME CURVES AT A POINT 0.1 CM FROM THE CATHODE

the current lines should be considered as approaching the electrode from the bottom of the figure.

E.M.F.'s Associated with Probes

The potential difference between the Ag/AgCl probe and the current electrode immersed in KCl was observed both with and without current passing through the column of electrolyte. The same observations were made for this same current electrode and a platinum probe (used by Ferguson[8]) placed at the same position. The e.m.f. of the two probes together immersed in the electrolyte with the current off was also observed.

It was found that the potential of the platinum probe with respect to the solution fluctuated considerably but that, if these fluctuations were accounted for, two relations were observed to hold: (a) The relation $e_{12} + e_{23} = e_{13}$ holds for the three electrodes 1, 2, and 3 in a single solution. (b) The difference in potential between the Ag/AgCl probe and the platinum probe is the same whether or not current is passing through the electrolyte. There was virtually no fluctuation in the potential of the Ag/AgCl probe; this was also true for the new type of copper probes already described.

Changes in Ag/AgCl Electrodes with Electrolysis

The freshly prepared Ag/AgCl electrodes described in Appendix I were used as current electrodes in the 0.0024 N KCl solution. It was observed that after several hours of electrolysis the potential measured at 0.2 cm from the cathode began to increase considerably as is shown in Figure 16. Attending the relatively rapid increase in potential after about 10 hours of electrolysis was a change in the appearance of the

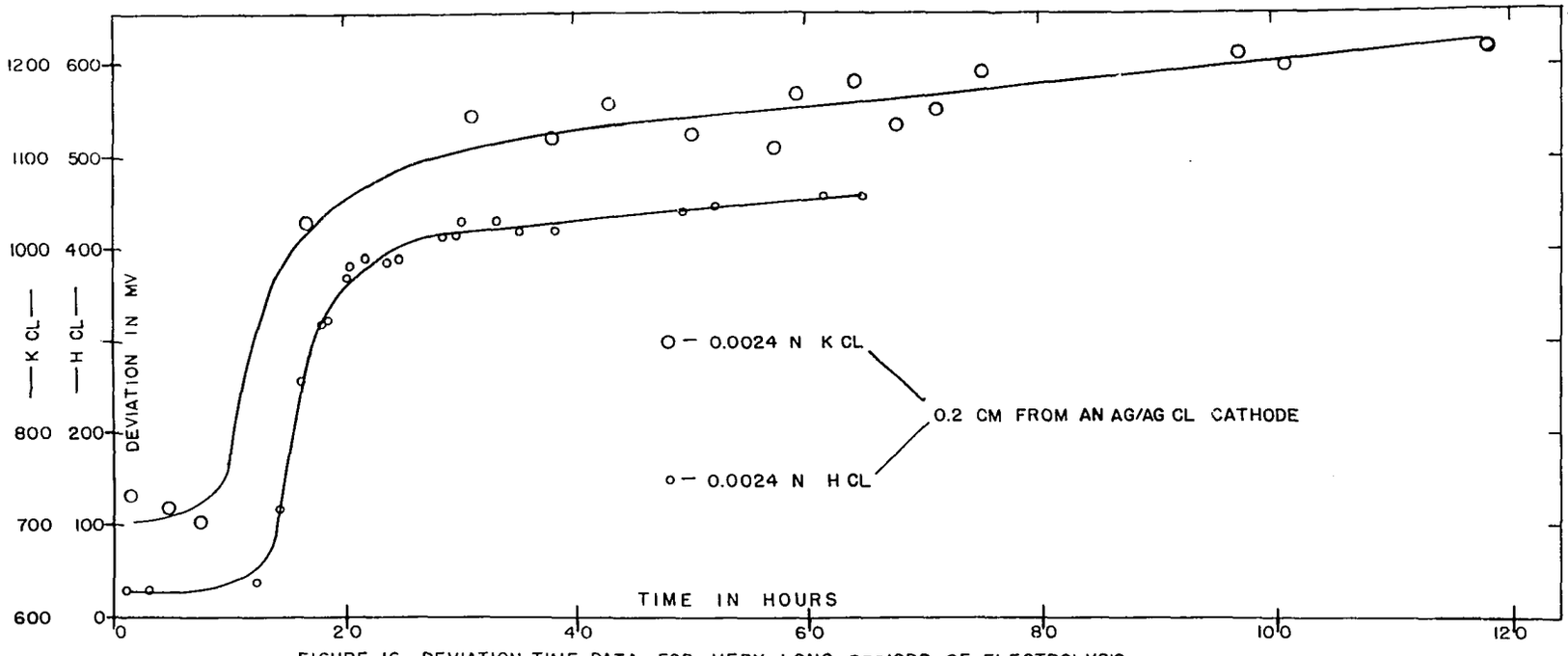

FIGURE 16. DEVIATION-TIME DATA FOR VERY LONG PERIODS OF ELECTROLYSIS.

cathode from the characteristic grayish-black to a creamy-white; the anode remained grayish-black in color. However, the potential measured at 0.1 cm from the anode increased in magnitude evidently because of the increase in the thickness of the AgCl layer.

The KCl curve of Figure 16 does not represent a continuous electrolysis but does represent the total time the electrode served as a cathode while a long series of "runs" was made. Each datum represents the measured potential of the probe with respect to the cathode during the last second of electrolysis of a 20 minute run at a point 0.5 cm from the cathode surface. The electrodes had 15 minute intervals of rest between runs, and they also rested in the electrolyte during the nights. The solution in the trough was replaced with freshly prepared solutions several times over the period of 120 hours.

A very similar situation occurred when 0.0024 N HCl solution was electrolyzed with the Ag/AgCl electrodes. The data are shown by the HCl curve in Figure 16.

Potential Distributions After Electrolysis Ceases

During the work described earlier in this chapter it was found that even 20 minutes after electrolysis ceased there was still considerable potential difference between the probe and the Ag/AgCl cathode. Also it was observed that this potential difference varied with time.

It was believed that this variation in potential might be associated with the drift of a space charge from the electrolyte. For this reason a distribution of the potential along the axis of the trough, after electrolysis ceased, was deemed important. For each point along the axis

the potential between the probe and the cathode decayed in such a manner that the potential appeared to be an exponential function of the time. Typical curves depicting the build-up of this potential during electrolysis and its decay after electrolysis ceased, are shown in Figure 17.

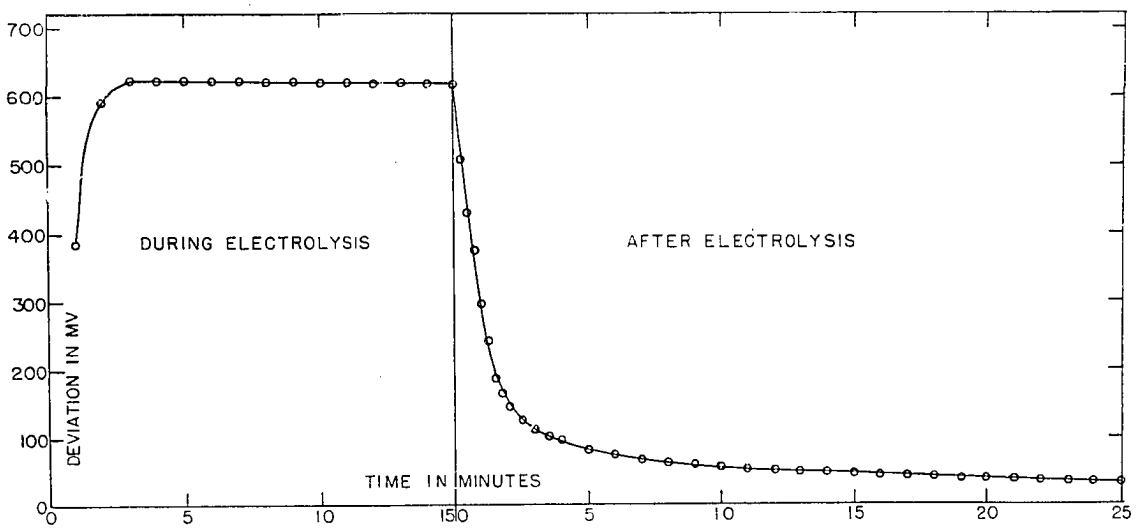

FIGURE 17. A TYPICAL BUILD-UP AND DECAY CURVE OF THE DEVIATION VERY NEAR A CATHODE

There was evident during the first two minutes after electrolysis ceased a slight difference in the decay curves at points along the axis within approximately 4 cm of the cathode. However, since these differences were very small compared to the large changes in the probe to cathode potential during this same time, no conclusions could be drawn from them. To overcome this difficulty the potential at various points along the axis after electrolysis ceased, was measured with respect to the anode. Again only within about 4 cm of the cathode did significant differences in the decay curves occur. A set of these curves is shown in Figure 18. These tests were carried out with unbacked electrodes.

With backed electrodes potential variations like those shown in Figure 18 did not occur. Slight fluctuations did occur at points very close to the cathode. These data again indicate that the current went

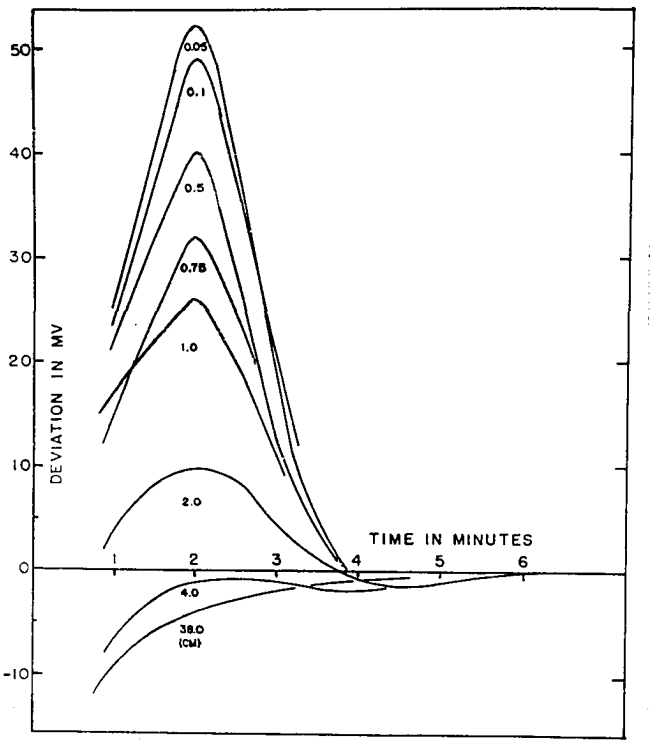

FIGURE 18 DECAY OF THE DEVIATION WITH RESPECT TO THE ANODE AT EACH OF EIGHT DISTANCES FROM AN UNBACKED CATHODE

around the edge of, and to the back of, the electrode, thus causing a non-uniform current distribution in the column of electrolyte. This in turn caused the type of curves shown in Figure 18.

CHAPTER IV

DISCUSSION AND INTERPRETATION OF RESULTS

Factors such as reproducibility of the data obtained from the apparatus, evaporation of solution from the open trough, etc., have been adequately treated by previous workers[1-10] who used essentially the same equipment. Such changes in the apparatus as were made did not affect the reproducibility.

The results will be discussed under four topics which are the effects that produce non-uniform current densities over the electrode surface.

(a) Effect of Coating Backs and Edges of Electrodes with a Non-Conductor.

(b) Non-uniform Deposits on Electrodes after Long Periods of Electrolysis.

(c) Effect of Atmosphere in Contact with Electrode-Electrolyte Junction.

(d) Convection Effects at Electrodes During Electrolysis.

Even though the second topic refers to an effect observed at only a single electrode, it may represent an effect that is very general in nature. Preceding the discussion and interpretation of convection there will be a short review of recent discussions of convection effects. This will aid in the interpretation of the results of this work.

Effect of Coating Backs and Edges of Electrodes With a Non-Conductor

The cross sectional distribution of potential curves of Figure 8 and Figure 9(A) should be compared. It is seen in Figure 8 that the equipotential surfaces are by no means planes as required by the third assumption listed in the Introduction. The average potential gradient in this electrolyte was 6.5 mv/mm which means that the point 3.5 cm to the left of center and 0.5 cm out from the cathode, should correspond very closely in potential to a point at the center against the cathode. In other words the equipotential surface deviates 0.5 cm from a plane at a point 3.5 cm to the left of the axis. In Figure 9(A) it is evident from the lateral distribution, that the prevention of the current from reaching the backs of the electrodes, did improve very much the lateral potential distribution in front of the electrode. In both instances a greater current density on the left side of the electrode is indicated.

Of paramount significance is the concomitant change of the potential distribution along the axis of the trough. Whereas before backing the electrodes the deviation of the potential, at 0.1 cm from the cathode (from an extrapolation of the linear portion of the deviation-distance curve in Figure 7), was of the order of 40 mv; the deviation after backing was only 3 mv. Thus the current diverged laterally upon approaching the unbacked electrode. Surprisingly this divergence was large enough to affect the potential gradient measurably even along the axis of the column.

Prior to this study with backed electrodes, the concave upward curvature of the deviation-distance curve would have been interpreted as a region of negative space charge. To see more clearly how these two

effects at the cathode, a negative space charge and a diverging current, can be confused, consider Figure 19(B) which shows the current distribution in a horizontal plane near the cathode. If Figure 19(B) is compared

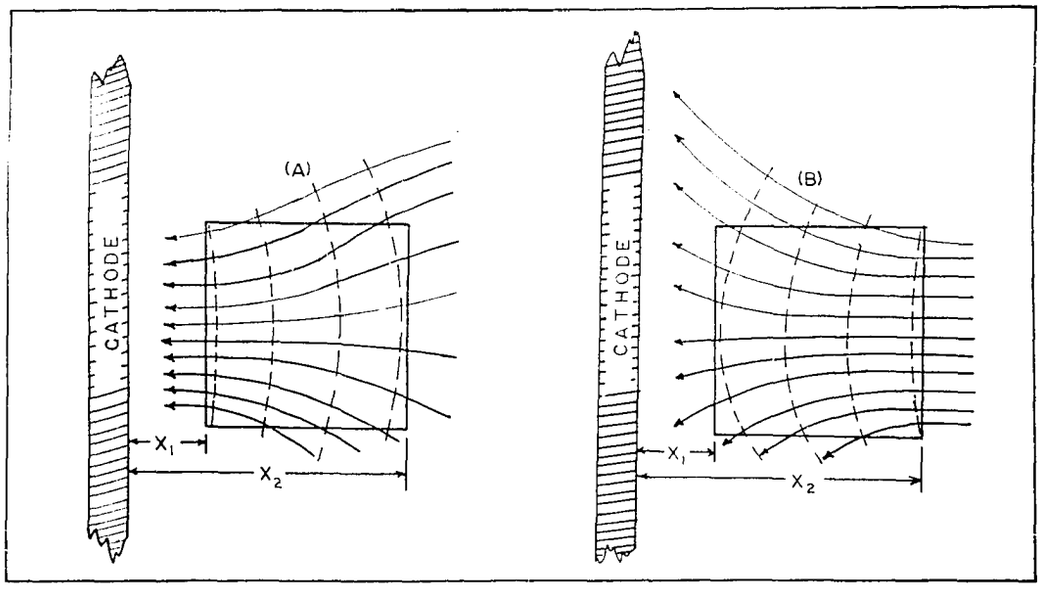

FIGURE 19. EQUIPOTENTIAL SURFACES FOR CONVERGING AND DIVERGING CURRENT FLOW-LINES

to Figure 1(B), it is seen that this current distribution would produce the same potential gradient along the axis of the trough as would a negative space charge in the same region. Thus we see that if the lateral components of the current or field are ignored, this non-uniform potential gradient would reasonably be interpreted as negative space charge.

Therefore near the cathode, a concave upward deviation-distance curve may be caused by a current diverging as it approaches the electrode and a concave downward curve may be interpreted as a current converging as it approaches the cathode. Similarly in approaching the anode, a concave downward deviation-distance curve may imply that the current lines are diverging, and a concave upward curve may imply that the current lines are converging toward the electrode.

These results indicate that the non-uniform potential gradients observed by several workers in the past were, in all probability, due to uneven current distributions rather than to space charge.

Ferguson's electrodes were backed and yet he observed curved deviation-distance curves. This suggests that yet other effects may produce non-uniform current distributions.

Non-Uniform Deposits on Electrode After Long Periods of Electrolysis

Much of the work on space charge was carried out in 0.0024 N solutions of $CuSO_4$ between copper electrodes. Therefore it was decided to examine cross sectional distributions of potential near such copper electrodes rather than to return to the relatively unexplored deviations observed in KCl between Ag/AgCl electrodes.

As mentioned previously it was believed that the copper electrodes, which were on hand, were those used by Reed; the cathode was recognized by the thick deposit of copper on its face. This electrode (this particular piece of copper metal) was of particular importance because it was here that Reed observed not only a concavity upward in the deviation-distance curve but also a bending downward of this curve as this cathode was approached from as far out in the solution of $CuSO_4$ as 2 cm. Previous workers, Rice[9] and Brooking[4], had not observed this bending down. Carson's work, as reported in Dalke's thesis[10] does give the same type of phenomenon but ONLY AFTER LONG PERIODS OF ELECTROLYSIS (between 6 and 12 hours). It is therefore important to note that Reed[1], for his work in $CuSO_4$, always aged the electrodes by passing a current for 12 to 14 hours before the

potential distributions were determined. Rice[9] and Brooking[4] each prepared their electrodes by plating them and then aging them a maximum of only 4 or 5 hours. For his work in a $CuCl_2$ solution Reed plated the copper electrodes.

From the lateral distributions of the potential at two levels shown in Figure 11(B), it is seen that the potential was greatest immediately in front of the regions where the copper deposit was very thin [see white areas in Figure 11(A)]. These distributions show that the current diverged from the light colored regions toward the surrounding dark colored regions. These light colored regions were so situated that the current would converge toward the axis near the cathode. Such a converging current would cause Reed's deviation-distance curve to bend downward at points close to the cathode.

When the electrodes were polished with emery paper and cleaned very thoroughly as Reed had done the effects shown in Figure 11 were still present, therefore it is possible that the actual structure of the crystal faces of the copper may have affected the rate of deposition[11]; also it is known that metals under stress have different electrode potentials[38] from those of unstressed metals. Since Reed's electrodes were unbacked, the current diverged as it approached the cathode and an appreciable fraction of it entered the back of the electrode. This fact, together with the converging of the current toward the axis near the electrode because of the location of the light colored regions, make it possible to explain at least most of the curvature of his deviation-distance curves in $CuSO_4$ in terms of non-uniform current distributions.

Effect of Atmosphere in Contact with Electrode-Electrolyte Junction

The peculiar effect of the current rising toward the top of the horizontal column near the anode was observed in $CuSO_4$ between copper electrodes. This effect, if it had been due to convection, would have been in the wrong direction since the more dense solutions near the anode would have moved downward and consequently decreased the resistance in the lower part of the column. The vertical distribution in Figure 12(B) indicates that there was some diving downward of the current at the anode. However the phenomenon occurring at the top of the anode evidently greatly reduced the result of convection and even caused the current flow lines to rise near the anode. Heat liberated in the anode reaction would also tend to annul the result of convection.

Figure 13(C) shows that the difference in potential between the bottom and the top occurred very shortly after the current was turned on. Two possible effects of the atmosphere were suggested (under experimental results) to account for this phenomenon, a change in the conductivity near the anode at the surface and a change in the anodic reaction near the surface. Since the solution was stirred between runs and allowed to rest for 15 minutes, it seems unlikely that the atmosphere would change the conductivity at the anode and not throughout the entire column of electrolyte (an inverse effect was observed at the cathode).

The results obtained when acid was added, when a glass plate covered the surface, and when the level of the surface of the electrolyte was lowered, all suggest either an acceleration of, or a change in, the anodic reaction at the top of the electrode. (A similar though less pronounced

effect was observed near the backed Ag/AgCl anode in HCl as is shown in Figure 9(B).

Near the anode the deviation-distance curve of Figure 13(B) for points 3.7 cm above the axis of the column of electrolyte, should be concave upward since the current lines are converging toward this region. It is seen that this curve remains straight over a greater portion of the anode half of the column than do the lower deviation-distance curves; however it is concave downward near the anode.

The deviation-distance curve in the vertical cell with the anode at the top of the column of electrolyte [see Figure 14(A)] is very much like this curve. On the other hand with the anode at the bottom, the curve [see Figure 14(A)] remains linear near the anode. Since the reaction at the anode produces a more concentrated solution which has a greater density than that of the bulk solution, this more concentrated solution near the anode at the top, will mix by convection with the bulk solution to some extent and decrease the resistivity near the anode. This would decrease the potential gradient in this region and the deviation-distance curve would be concave downward. In the last case with the anode at the bottom the solution of greater density produced by the reaction would remain very close to the surface of the electrode. The diffusion upward during the 15 minutes of electrolysis would be negligible; thus the deviation-distance curve is linear in the measurable portion of the column near the anode.

Pickett[6](p.42) observed small increases in concentration near the anode in a horizontal column but concluded that they were too small to account for the deviations observed by Reed[1] and Brooking[4]. It must

be remembered, however, that the electrodes used by these workers were not backed. This and the fact that the current lines were converging toward the top of the anode caused the downward concavity of the deviation-distance curve near the anode. An increase in concentration (as indicated in Pickett's[6] work) which is due to convection near the anode will also augment this downward concavity of the deviation-distance curve. A more complete discussion of convection will follow in the next section.

Convection Effects at Electrodes During Electrolysis

In a recent theoretical review of convection and diffusion, Tobias et al[12] describe the modern approach to these topics by making the following statement:

> It is unfortunate that the theory of Prandtl's boundary layer, patterns of velocity distribution, and other aspects of hydrodynamic theory have not been introduced into the field of electrochemistry until recently. Mass, heat, and momentum transfer analogies, and dimensional analysis are valuable tools in the development of modern theories of electrolysis.

It is not the purpose here to detail the theory but to show the factors which produce convection and to correlate this information with the results observed in this work.

In general, three mass transfer processes may occur during electrolysis. They are migration, convection, and diffusion. Migration refers to the transfer of mass through the motion of ions under the influence of an electric field; convection and diffusion are used as commonly defined. A simultaneous treatment of all of these is a difficult problem. Delahay[13](p.46) suggests means of studying diffusion alone:

> Migration need not be considered, since the electrolysis is conducted in the presence of a large excess of supporting electrolyte which carries virtually the totality of the current. Convective

> transfer is avoided under the following conditions: (1) the solution is not stirred, (2) the duration of electrolysis is short, say, less than one minute, (3) the solution contains a large excess of supporting electrolyte and consequently the consumption of the substance reacting at the electrode does not cause an appreciable variation in the density of the solution. These conditions can be fulfilled experimentally. . . .

In another place Delahay[13](p.12) describes the supporting electrolyte.

> Salts of alkali metals, which are difficult to reduce or oxidize, are often used as supporting electrolytes. Since all the ions in the solution carry the current, the contribution of the reducible (oxidizable) ion is negligible in comparison with that of the supporting electrolyte, and migration of the reacting species becomes negligible.

Glasstone[14], assuming the absence of convection and migration through such experimental procedures, determines the limiting current density in electro-deposition. In one case he says,

> . . . the value for the limiting current density was inferred from the point at which the cathode potential rose rapidly. The sudden rise indicated that an alternative cathode process, namely, the evolution of hydrogen, was commencing and that the metal could no longer be deposited at 100 percent current efficiency.

The current which is equivalent to the diffusive rate of a given ion species is called the "limiting diffusion" current for that species. (The "cathode potential" for the purposes of this discussion is the same as the deviation measured at 0.1 cm from the electrode.) It should be noticed that if the initial current density is above the limiting current density then there will be some interval of time before the sharp rise of the deviation takes place; this time interval is dependent upon how much the current density is above the limiting current density[18](p.192).

Several theoretical derivations[12] in which are used the hydrodynamical concepts for natural convective transfer and Ficks' Law for diffusion, arrive at similar expressions for the limiting current density as

a function of the distance from the lower edge of a vertical electrode. In all the theories the limiting current density varies as the one-fourth power of this distance. Some of the theories take migration into account.

Tobias[17], in a criticism of the space charge assumption, says,

> ". . . the current density applied in Schriever's experiments was by no means low; in fact, it was far above the limiting 'diffusion-current' density."

The foregoing remarks, while somewhat lacking in continuity, form the basis for the discussion of some of the experimental results. The following consideration may well introduce the discussion of these results: If the current densities used in both horizontal and vertical columns were far above the limiting current densities (as stated by Tobias), the potential deviations near the cathode (cathode potentials) should rise sharply (as suggested by Glasstone) when the easily reducible ions were removed from the region adjacent to the electrode.

Let us consider the horizontal cell with vertical copper electrodes in $CuSO_4$. At the cathode, Cu^{++} ions would be reduced and deposited while the SO_4^{--} ions would migrate away from the electrode, thus leaving a layer less dense than the bulk solution. A diffusion of Cu^{++} and SO_4^{--} ions from the bulk solution into this less concentrated layer would ensue. It is possible that the lower density near the cathode may have caused a convection, the more dense bulk solution forcing the less dense solution upward along the surface of the electrode. Here, immediately, is a description which is in agreement with the proposed consideration. Convection may have occurred and replenished the easily reducible ion, Cu^{++}, at the cathode. Thus the potential deviations near the cathode would remain small and an appreciable amount of hydrogen would not be reduced.

If such a convective effect does occur, then, since the less dense solution has less conductivity, the potential measured at a given distance from the electrode near the top of the horizontal column should be greater than the potential at the same distance from the cathode but near the bottom of the column. The potentials measured after 15 minutes of electrolysis at these positions [see Figure 12(A)] are in complete qualitative agreement with this picture. Furthermore Figure 13(A) shows that this effect is not present after the first minute of electrolysis but builds up during the first six to eight minutes and remains approximately constant during the remaining time. This, too, is consistent with the convection interpretation.

As suggested in the experimental results, a vertical cell apparatus was constructed in which this convection effect should be eliminated at the cathode if it is placed at the top of the column of electrolyte. With the copper cathode in this position, it is seen from Figure 15 that the potential deviation at 0.1 cm from the cathode is roughly eight to nine times as large as it is when the cathode is at the bottom of the vertical column of electrolyte or is in a vertical position in the horizontal trough. It is further noted that the buildup of the deviation in the first four minutes is nearly the same in all three of these cases (for clean copper cathodes). After four minutes a rapid increase occurs when the cathode is at the top of the vertical column. This may be explained by the fact that the electrolyte next to this cathode is less dense and convection cannot replenish the Cu^{++} ions. For the current to pass the potential must rise until another reduction can occur; in this case it is undoubtedly that of the H^{+} ion as suggested by Glasstone[14]. Further

evidence will be presented in the discussion of the experimental results in Part II concerning this large deviation near the cathode at the top of the vertical cell.

The data obtained when the vertical cell was tilted through only 3° constitute additional evidence that convection did occur. The significantly increased deviation near the higher part of the cathode surface indicates that the less dense higher resistance layer moved up along the under surface of this electrode.

Delahay[13](p.350) suggests that investigations by Laitinen and Kolthoff on plane electrodes of varied design have shown that a horizontal platinum disc surrounded by a cylindrical glass mantle and exposed to the solution on the lower side, is the best electrode arrangement to prevent "convection". The glass mantle limits the "diffusion field". Others[19] have reported on copper deposition in a "convection free" system; the cathode was placed at the top of a vertical column of electrolyte.

It is difficult to believe that such a convection effect can occur in so dilute a solution. The maximum difference in density that could occur in a 0.0024 N solution if all the Cu^{++} and SO_4^{--} ions were swept out of a region adjacent to the electrode surface, has been estimated[15] to be less than two parts in 10,000. Wagner[16] has treated this combination of diffusive and convective effects and suggests that his theory, while suitable for a solution of 0.1 M $CuSO_4$ with 1.0 M H_2SO_4, does not have good experimental verification for a solution of 0.02 M $CuSO_4$ with 1.0 M H_2SO_4. He suggests that this lack of verification may exist because the density differences are not great enough to produce a pronounced convective effect. The $CuSO_4$ concentration in this latter solution is still

10 times that used in the "space charge" work. However it should be noted that in the work of Wagner the supporting electrolyte, 1.0 M H_2SO_4, should lessen the convective effect according to Delahay's third suggestion for eliminating convection.

Wagner tacitly disregards the possibility of a temperature difference between the bulk of the solution and the layer against the electrodes. A temperature rise alone would produce a similar convection effect. The heat of the electrode reaction may cause such a temperature rise. Also since the resistivity of the ion depleted layer is greater, there would be greater electrical heating and, therefore, a further decrease in density. Butler[18](p.196) suggests that Agar and Bowden have shown that the resistance of the diffusion layer gives rise to such an ohmic potential difference.

A comparison of the vertical potential distributions at the Ag/AgCl and copper cathodes in HCl and $CuSO_4$ respectively, indicate that convection was greater in $CuSO_4$ than in HCl. This would be the case if most of the convection was caused by concentration changes in the layer of solution next to the cathode, since the density change in $CuSO_4$ would be greater than that in HCl. Tests were not conclusive in determining whether a concentration change or a temperature change was the more important factor.

The mathematical study of current distributions in electrolytic cells has been pioneered by Kasper[20] who solved LaPlace's equation with appropriate boundary conditions. His work was concerned principally with the geometry of the cell. Similar more recent theoretical investigations have been reported.[21,22]

It is evident that to maintain a uniform lateral distribution of potential across the cathode surface is very difficult in the vertical cell. Even such a small tilt as 3° of the vertical tank produced a difference of potential of 200 mv between the high and low sides of an 8 cm wide cathode. Because of this it was impossible to obtain reproducible mapping data in the cathode region when it was at the top of the vertical column. With the cathode at the lower end of the column of electrolyte the rising of the less dense solution produced equally unstable conditions. For these reasons the deviation-distance curves in Figure 14 were not extended into the cathode region in the vertical cell.

Criticisms of the Space Charge Interpretation

Some of the criticisms of the space charge interpretation have been helpful; some, it is believed, are unjust. The criticisms were directed principally in three letters-to-the-editor by MacInnes, Shedlovsky and Longsworth[23], Gordon[24], and Tobias[17]. In each of the three letters it was inferred that concentration changes must have occurred out as far as there were significant curvatures in the deviation-distance curves. In two independent measurements of the conductivities by Martin[3] and Pickett[6], the concentrations in $CuSO_4$ after 15 minutes of electrolysis were found to be constant throughout the measurable portion of the electrolyte within the precision of their data. Concentration changes which would have produced the observed curvatures in the deviation-distance curves would have been detected easily in their work. Tobias[17] said of these measurements: "The conductivity measurements on which this statement was based must have been rather unreliable". The experimental results in this present investigation are in accord with the results of Martin and Pickett. It has been

shown that at least the greater part of the observed curvature of the deviation-time curves was caused by the diverging of the current flow lines behind the electrodes and by a diving down or a rising of the flow lines near the electrodes. Evidence was given that significant variations in concentration do occur only in a thin layer next to each electrode surface.

The criticism concerning the "erratic behavior" of the electrodes has been shown to be justified. The results of Reed[1] on copper electrodes in $CuSO_4$ did not duplicate those of Rice[9] and Brooking[4]. Also the cathode used by Reed was shown to have regions on its surface which prevented a uniform current density over the electrode. It is, of course, true that Reed could reproduce results with his electrodes. However, it is believed that had he used several copper cathodes and compared the distributions at each with the one he reported he would then undoubtedly have found an "erratic behavior".

Although some of the procedures employed by Reed have been shown to be incorrect, the deviation-distance curve for copper electrodes in $CuSO_4$ has been shown to measure effects which were actually present. It is believed that his curves for other metals and electrolytes also depict the electrical conditions correctly. The real error has been shown to be his assumption of a uniform current density over the electrode, which led to an incorrect interpretation.

A few references should be cited concerning the assumption, or rather the lack of the assumption, that space charge exists. They in part substantiate the results of this work. The "principle of electroneutrality", which states that macroscopic space charges do not exist is commonly

used in several of the theories of electrochemistry of which are theories dealing with electrolytic conductance[37](p.53), convection and diffusion[16] (p.164), activity coefficients (Debeye-Huckel Theory)[25](p.158), [37](p.147) etc. Also MacInnes et al[23] say that the space charge interpretation of Reed and Schriever "if substantiated, would invalidate all work on the transference numbers of electrolytes by the moving boundary method . . . ".

Suggestions for Future Work

More conclusive tests should be designed to determine the cause of convective effects which occur close to the electrodes. Interferometric and Schlieren studies[18](pp.108-112) are suggested as being most appropriate.

An investigation employing thermocouples might produce significant information as to whether there is a temperature increase close to each electrode.

It should be determined which components of the air, if any, catalyze the anodic reaction near the surface of the electrolyte and to what extent they do so. This study should reveal how the anode-electrolyte junction at the surface differs from that down lower on the anode and whether the capillary action or evaporation at the surface affects the anode reaction in that region.

Answers to these questions are of interest and should be sought in future investigations. Cells which can be easily tipped at arbitrary angles and solutions of different kinds and concentrations should be employed in these studies.

CHAPTER V

SUMMARY AND CONCLUSIONS

(PART I)

In comparing the similarity between the proposed mechanisms for conduction in gases and in electrolytes, Professor William Schriever began investigations in 1924 to test the hypothesis that macroscopic space charges might exist in electrolytes as they were known to exist in gases.

Since then but prior to the present investigation, work was done at the University of Oklahoma at different times, in the following order, by Roller, Cameron, Mitchell, Reed, Brooking, Rice, Carson, Martin, Dalke, Reed (Ph.D), and Ferguson. Each of these observers interpreted the data which he obtained as supporting the view that space charges exist well away from the electrode in conducting electrolytes. This required the assumption that no changes in conductivity occurred and that the electric field was everywhere parallel to the axis of the cell.

In the present investigation it was conceived that if the last assumption were valid and "space charges" did exist, then the charges should migrate to the sides of the trough in order to achieve a minimum energy configuration.

This was tested by checking the potential distributions normal to the axis of the trough. These were found not to be constant and to be

of such a form as would result if the current densities were greatest near the edges of the electrodes. This led to the supposition that the current was going around the edges and entering the backs of the electrodes. When the current was prevented from going to the backs of the electrodes, the cross section potential distribution became practically uniform and the potential gradient along the measurable portion of the column on the axis simultaneously became uniform to within the precision of the data. It was then shown that diverging and converging currents could produce the same potential distributions as those that might arise because of space charges in the column.

Next, it was observed that the deviation-distance curve obtained by Reed, curved downward very near the copper cathode whereas earlier workers had shown it continuing upward. A careful determination of the lateral potential distributions close to this cathode showed that certain regions of the cathode used by Reed, did not conduct as well as other regions (after considerable electrolysis) even though this electrode was scrupulously cleaned after the manner used by Reed. These regions were observed visually by noting areas where the cathode deposit was much lighter in color. Furthermore, the regions were arranged such that the current would converge toward the axis upon approaching the cathode surface. Thus Reed's deviation-distance curve was concave downward near the cathode and this was interpreted as a positive space charge by Reed.

A third effect was observed at the copper-air-electrolyte junction at the anode. The current was found to rise to the top of the anode where it was believed that the air may have catalyzed the anode reaction (lowering the effective interface resistance). This was believed true

for three reasons. First, under certain circumstances this effect was suppressed entirely by placing a glass cover on the electrolyte surface and in contact with the electrode; second, it was suppressed by making the electrolyte slightly acid; and third, the effect was not noticed in the vertical cell when the cell was tilted slightly (air was not in contact with the solution near the electrode surface).

A fourth effect, convection, was observed very close to the copper cathode. This effect was revealed by the shapes of the equipotential surfaces near the electrode. Its existence was quite well established by observations in both the horizontal and the vertical column of electrolyte. There also appeared some evidence for convection at a copper anode.

These four observations were sufficient to explain almost the entire observed curvatures in the deviation-distance curve for copper reported by Reed, without resorting to the "space charge" explanation.

A few brief suggestions for future work were included.

CONCLUSIONS

The non-uniform potential distributions, more than 1 mm from the electrodes, in uniform columns of electrolytes during electrolysis, as reported by Reed, by Ferguson, and by earlier workers, were found to be caused by non-uniform current distributions over the surfaces of the electrodes; these non-uniform distributions also extended out into the columns of electrolytes at both ends of the columns.

The chief cause of the non-uniform distribution was the passing of an appreciable fraction of the current around the vertical and bottom edges of the electrodes and then entering (or leaving) the backs of the

electrodes. This caused the current flow-lines in front of each electrode to diverge toward that electrode. This divergence affects the results of Reed and all earlier workers at the University of Oklahoma, but not those of Ferguson.

The second important cause of the non-uniform current distributions was the convection of a thin layer of solution in front of the cathode after a few minutes of electrolysis. This caused the current density to increase with depth near the cathode.

The third cause of the non-uniform current distribution over a copper cathode was the development of a surface layer which offered a non-uniform resistance per unit area to the current. This caused the current densities to be less over those parts of the surface that developed the higher resistances per unit area.

A fourth cause for the non-uniform current distributions was observed at a copper anode. The current density was greatest just below the surface of the $CuSO_4$ solution. It is possible that the "atmosphere" in some way affected the surface of the anode near the top of the electrolyte so as to lower its resistance per unit area, or the atmosphere in some way catalized the anode reaction near the surface of the horizontal column.

It is believed that the convection had two causes. First, the solution next to the cathode became less concentrated during electrolysis, and thus became less dense. Second, this less concentrated solution had less conductivity and thus had increased Joule heating; the resultant rise in temperature caused the solution to become less dense. The second effect possibly was augmented by the additional heat liberated by the

reaction at the cathode surface. At the anode it is believed that the increase in density because of electrolysis did cause the more concentrated (more conductive) solution to sink toward the bottom of the anode, but this effect may have been partially nullified by the expansion caused by the heat of reaction at the electrode surface.

The formation of areas of the copper cathode surface having different resistances per unit area, may have been caused by differences in the crystal structure of different areas of the copper surface.

It is improbable that macroscopic space charges more than 0.5 mm from an electrode, as reported by Reed and Ferguson, do exist; if they do they must be relatively small in magnitude. It is extremely difficult to attain the sufficiently uniform current distribution that would permit the determination of sufficiently precise potential distributions for the space charge calculations. Space charges undoubtedly exist in double layers very close to the electrode surfaces during electrolysis but such space charges are not directly observable by the methods used by Reed and Ferguson.

PART II

THE ANALYSIS OF ACTIVATION OVERPOTENTIAL INTO EXPONENTIALLY DECAYING COMPONENTS

CHAPTER VI

INTRODUCTION

When a metal is introduced into an electrolyte, the potential difference which arises across the electrode-solution interface is not measurable by an externally applied potential measuring device because in making contacts with both the electrode and the solution, two new junctions are produced, each of which also contributes a potential difference. In practice the potential difference at a single metal-solution interface is studied by measuring the potential difference of the terminals of a complete electrochemical cell composed of a metal, M_1, in a solution, S_1, a metal, M_2, in solution, S_2, and the two solutions in contact through a KCl bridge. The metal of which the potential difference measuring apparatus is composed does not contribute to the net e.m.f. of the cell. It is assumed that the S_1S_2 liquid junction potential can be reduced to a negligible value by the KCl bridge between the two solutions. The normal hydrogen electrode is chosen as one of the half-cells (one metal in contact with a solution), and by convention it is postulated that the contribution

of this hydrogen half-cell to the total e.m.f. of the cell is zero at all temperatures. The measured value of the e.m.f. of this complete cell is referred to as "the electrode potential" of the other metal-solution junction. If this measurement is carried out with no current crossing the interface, the processes occuring at the interface then are considered to be thermodynamically reversible and the single "electrode potential" is e_r, the net e.m.f. of this special cell.

When a current exists across this electrode-solution interface, normally it is found that the electrode potential changes from this reversible value, and the complex phenomenon associated with it is termed "polarization". (To prevent the confusion of this with polarization of dielectrics the term polarization should be preceded by "electrolytic" or "dielectric" as determined by the case in question).[25]

The more specific term, overpotential (overvoltage), is used to describe this change in the electrode potential. When a current density i exists at this interface and the electrode potential is measured to be e_i, then the overpotential, η_i, is defined to be,

$$2. \qquad \eta_i = e_i - e_r .$$

Some authors permit this term to include changes in the electrode potential due to all causes while other authors prefer to include only departures from the reversible potential, e_r, which are due to electrochemical reactions occuring at the electrode interface.[25,13,18] In the following discussion η_i will be used to represent deviations from the reversible potential due to all causes; the specific possible causes will be itemized. Since in this work reference electrodes other than the hydrogen electrode

were used, it should be noted that the overpotential can be determined by any reference electrode, the electrode-solution potential of which does not vary under the conditions of measurement.

Three types of overpotential have been described. (a) In some electrode processes oxide or other films may form on the electrode surface and give rise to a resistance. If this resistance is of magnitude r, then the value of the overpotential due to this cause will be Ir where I is the current at the electrode. Overpotential due to this cause is called ohmic overpotential. During electrolysis a pseudo-overpotential may arise if a Luggin capillary tip, used for the measurement, is placed at some distance from the electrode surface since the ohmic potential drop in the solution will be included in the measured value. Kortum and Bockris suggest that this overpotential is appreciable only for high current densities or low concentrations.[25] Ohmic overpotential is represented by η_r. (b) According to the Hittorf scheme of conduction in electrolytes it is to be expected that concentration changes will occur in the immediate vicinity of an electrode during electrolysis. If, for example, one considers the processes at a cathode where positive ions are being deposited, it is clear that the solution immediately adjacent the electrode will become less concentrated. If the concentration in this region is c_e and that in the bulk of the solution is c_b, and if only small departures from equilibrium occur, the thermodynamic equations are still approximately applicable. Then the overpotential caused by these concentrations changes is given by,

$$3. \qquad \eta = (RT/zF) \ln (c_e/c_b)$$

for a system in which the ions, to which the electrodes are reversible, have a valency z, R is the gas constant per mole, T the temperature in

degrees K, and F is the value of the Faraday. This kind of overpotential is called concentration overpotential and it occurs when electrolysis proceeds at an appreciable rate. It is represented by η_c. (c) The third type of overpotential arises because of action occuring during electrolytic deposition of ions with the evolution of gases. It can usually be calculated from the observed total overpotential by making allowance for the ohmic and concentration overpotentials. It is especially large in electrolytic processes associated with the evolution of hydrogen and oxygen. Bockris[18](p.156) states,

> . . . this overpotential appears to have its origin in some slow process along the reactions involved in the deposition of ions and formation of the final product.

This slow process may be accelerated by a change in the electrode overpotential. Because of the association of a slow process with a high energy of activation or a high energy barrier, in reaction kinetics the term activation overpotential has become associated with it and it is represented by η_a. Sometimes this overpotential is subdivided into two categories, "transition overpotential" and "reaction (chemical) overpotential"; the former is used if the rate controlling step is the crossing of an energy barrier between the solution and the electrode, and the latter if it is a chemical reaction such as the combination of two hydrogen atoms to form a hydrogen molecule.[25]

The measured total overpotential in general is thus the sum of these three types. Kortum and Bockris[25] have described ways of differentiating them experimentally.

> To examine the ohmic, concentration, or activation overpotential separately it is necessary to reduce the other types of overpotential to negligible values. True ohmic overpotential can generally

be recognized easily, since it is usually very much larger (particularly at high current densities) than other types of overpotential. Concentration overpotential can be studied if the absence of resistive films upon the electrode is ensured and an electrode is chosen at which the activation overpotential is negligible (eg., a mercury electrode in an aqueous mercurous nitrate solution). The activation overpotential can be examined in the absence of resistive films, if the concentration overpotential is diminished to negligible proportions by rapid agitation of the electrolyte in the vicinity of the electrode so that the diffusion of ions to the electrode surface is increased and c_e becomes practically equal to c_b.

Kortum and Bockris state that an immediate distinction between these three types of overpotential can be made experimentally by observing their rates of decay. Ohmic overpotential decays instantaneously, concentration overpotential decays slowly and in a complex way, whereas activation overpotential decays exponentially. These characteristics are of particular importance in the present work.

Bockris[18](p.156) suggests that activation overpotential "presents problems of the greatest modern interest" and that the overpotential associated with the evolution of hydrogen at the cathode has become the most commonly observed case of activation overpotential for modern investigators; it will be the main topic in this discussion.

Bockris[18](p.159) indicates several approaches to the study of activation overpotential. These are itemized as follows:

(a) The measurement of the dependence of the reaction rate (i.e., the current) upon overpotential.

(b) The measurement of the capacitance of the electrode-solution interface at various frequencies.

(c) The measurement of the relation between the electric charge and the overpotential during the charging of the double layer.

(d) The measurement of the decay of overpotential after electrolysis ceases.

(e) The measurement of the effect of light (photochemical effect) on overpotential.

The following factors have significant effects on the reaction rate: The temperature, the concentration of hydrogen ions (pH), the concentration of "neutral salts", the nature of the solvent, the nature of the electrode, and the pressure. The "neutral salts" do not participate in the electrode reaction though they may carry an appreciable fraction of the current.

The ultimate goals of the analysis of overpotential are to determine the successive intermediate reactions that are involved in the over-all process at an electrode, and to determine which of these intermediate reactions is the rate-determining reaction. As an example we may consider the liberation of hydrogen at a cathode and the resulting "hydrogen overpotential". The over-all process may be represented by the equation:

4. $2H^+ + 2e^- \longrightarrow H_2$.

The most commonly suggested intermediate reactions involved in this process are given by the equations:

5. (a) $H_3O^+ + e^- \longrightarrow M - H + H_2O$ (discharge)

(b) $M - H + M - H \longrightarrow 2M + H_2$ (desorption)

(c) $H_3O^+ + M - H + e^- \longrightarrow M + H_2 + H_2O$ (desorption)

where M - H represents an electrically neutral hydrogen atom adsorbed on the metal of the electrode. The hydrogen gas would be liberated by either of the two pairs of successive reactions (a) and (b), or (a) and (c).

Observers are divided primarily on the question as to which of the above reactions is the rate-determining reaction in the over-all process. The two principal choices are the "slow discharge" process, 5(a), and the "slow combination" process, 5(b). A few observers choose a combination of (a) and (b) or a combination of (b) and (c) as the rate-determining reaction. Bockris[26](p.133) is of the opinion that "there seems no need to consider that more than one of the stages governs overpotential . . . ".

The supporters of the slow-discharge theories of overpotential generally make the basic assumption that the relation between overpotential and the current density is accurately given by the relation,

6. $$\eta = a - b \log i$$

where η is the overpotential and i the current density (a and b are constants).[27] This relation was discovered empirically by Tafel in 1905. It can be derived[18](p.167) from the following assumptions:

(a) The velocity of the rate-determining reaction in the foreward direction is much greater than in the reverse direction.

(b) The particles undergoing this reaction have some minimum (activation) energy.

(c) All such particles have a Maxwellian distribution of energies.

(d) The energy of activation of the reaction is affected by the field at the cathode-solution interface by an amount proportional to the metal-solution potential difference (the overpotential).

Then the current, which is a measure of the rate of the reaction, can be expressed as,

7. $$i = A \exp \left(- \frac{U + \alpha \eta F}{RT} \right)$$

where U is the thermal part of the energy of activation and α is the constant of proportionality. A is a "collision factor" characteristic of the mechanism of the reaction. This equation can be changed readily to the form of equation 6. Several variations, some with additions, have been applied to this derivation in attempts to make it fit the experimental data better.

Studies in the decay of overpotential after electrolysis ceases have been somewhat fruitful in leading to explanations of the processes which occur at the cathode in the production of this hydrogen overpotential. Bowden and Rideal[28], Armstrong and Butler[29], Hickling and Salt[30], Ferguson et al[31], Schuldiner and White[32], and Bryant and Coates[33], among others, have sought to gain information on these processes through the study of the decay of overpotential. The general conclusion of these groups is that no theory, so far proposed, is adequate to explain the results for all the systems of electrodes and electrolytes which produce hydrogen overpotential.

Gurney was able to obtain the Tafel relation by assuming it to be a result of the transfer of electrons from the electrode to the hydrogen ions in solution. Extending these concepts to conditions immediately after the interruption of the current Armstrong and Butler[29] arrived at the relation,

8. $$\eta = a' + b' \log t$$

which should describe the variation of overpotential with time, t, after electrolysis ceases. They arrive at this relation by integrating the equation,

9. $$d\eta/dt = i/B$$

where i is the time rate of transfer of electrons across the double layer and B is its capacitance. The assumptions are that this current discharges the double layer and that the potential difference across the layer can still (even during decay) be expressed in terms of the overpotential by the relation (6). In their work with mercury surfaces, the relation (8) was shown to hold quite well. However on platinum a more complicated behavior was observed. Apparently, because of its success in explaining the decay of overpotential on mercury, the relation (8) has gained acceptance; at least many recent observers choose to plot η as a function of log t in displaying their data.

Of considerable interest to this present work is the statement by several authors that, during the decay, there appears to be more than one process occuring in connection with hydrogen overpotential. Hickling and Salt[30] conclude that: "Two processes proceed in the decay independent of one another". Ferguson[31(c)] states the following after many observations of the decay of overpotential.

> All hydrogen decay curves are divided into two sections; the first part decays exceedingly rapidly and its magnitude is a function of both current density and electrode material; the second part decays relatively slowly and its magnitude is not a function of current density.

Bryant and Coates[33] in summarizing their study of concentration polarization (overpotential) in dilute (0.1 N) HCl say,

> The curves showing the time decay of polarization on interruption of the polarizing current indicate a rather sharp transition between two types of electrode processes . . . .

Bowden and Rideal[28], using current densities of from 10^{-8} to 10^{-3} amp/cm^2, did not observe the initial rapid drop of potential that some of the other workers found at higher current densities. From this

Ferguson[31(d)] concluded that, with an increase in current density, there may become operative a new process in the discharge of hydrogen ions at the cathode. He and most of the other workers usually used current densities greater than those of Bowden and Rideal.

Schuldiner and White[32] attempted a separation of the electrode potential associated with the Helmholtz double layer from that associated with the diffuse (Guoy) section of the Stern double layer. In this separation they claim to have measured the capacitance of the Helmholtz double layer.

The Problem

During the determination of the Deviation-Time data described in Part I it was believed advisable to study the decay of the potential difference between each electrode and the probe after the electrolysis ceased in order to ascertain whether or not such data would reveal the rate of disappearance of the space charge which was then believed to exist. These decay data, when plotted on ordinary coordinate paper, yielded curves which looked suspiciously like the decay curve for a mixture of a long-lived and a relatively short-lived radio-active substance. A study of the data plotted on semi-log paper showed that, after the first two minutes, the first curve could be represented accurately by two straight lines having radically different slopes. Thus it appeared that this decay process, after the first two minutes, was in reality two processes each decaying as an exponential function of the time.

Since the deviations measured in Part I are actually "overpotentials", from each of which has been subtracted the ohmic-overpotential

caused by the rI drop through the solution, it was evident that the procedure described in the preceding paragraph was a new and improved method for studying overpotential phenomena.

It was believed that a study, in which the new method was employed, would assist in finding answers to the three questions:

(a) What is the form of the function which represents the decay of an overpotential after electrolysis ceases?

(b) What intermediate reactions are involved in hydrogen overpotential?

(c) Which intermediate reaction is the rate-determining reaction during the liberation of hydrogen?

CHAPTER VII

APPARATUS

Little need be said concerning the apparatus for it was the same as that used in Part I.

The electrometer would not indicate accurately the rapid fall of overpotential during the first few seconds (this time varied with the magnitude of the overpotential) of decay since the period of vibration of the needle was approximately 30 seconds. It appeared that during the first half-minute, in the cases where the overpotential was high (say 500 mv or more) and decaying very rapidly, the deflections of the electrometer might lag behind the actual potential difference by as much as 50 mv. This inaccuracy proved to cause little difficulty, however, because of the method used to interpret the data.

The electrodes were those described in Part I. The decay curves were observed for several conditions of the various electrode surfaces.

CHAPTER VIII

PROCEDURE AND RESULTS

The decay of overpotential was first studied at the unbacked Ag/AgCl cathode that is described in Part I after it had participated in approximately 30 hours of electrolysis of KCl. After an overnight interval of no electrolysis, if electrolysis of KCl was carried out for a 15 minute period and then the current turned off, the overpotential of this cathode was found to decay very rapidly at first and then to decay relatively very slowly. Even after 20 minutes of decay there was considerable potential difference between the probe and this electrode in addition to that which existed before the electrolysis began, i.e., the overpotential had not disappeared. The manner in which this decay took place was investigated and it seemed natural to ascertain whether the decay was an exponential function of the time such as,

$$\eta = \eta_0 \exp(-kt) \qquad 10.$$

where η_0 is the overpotential just after electrolysis ceases and k is a constant that measures the rate of decay. (The writer was then unaware of the relation, equation 8, $\eta = a' + b' \log t$.) When the logarithm of the overpotential was plotted as a function of the time, (see Curve A of Figure 20), the decay became linear for times greater than approximately 10 minutes, and it remained linear for times as long as 60 minutes.

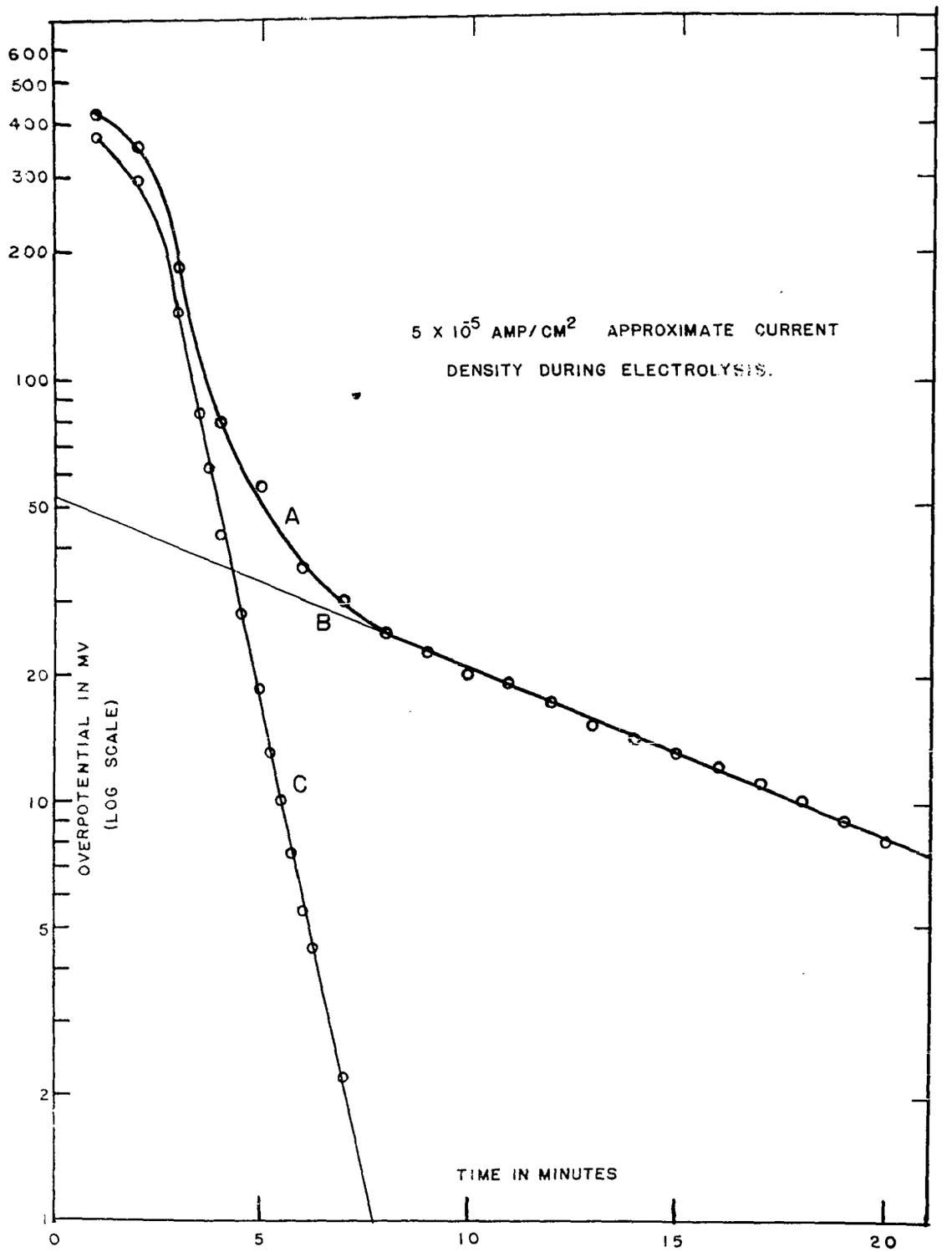

FIGURE 26 DECAY OF OVERPOTENTIAL WITH AN UNBACKED AG/AG CL CATHODE IN A 0.0024 N K CL SOLUTION

If one assumes that this straight portion represents a single reaction which began to decay as soon as the electrolysis ceased, then one may extrapolate this straight part of the curve back to zero time, as is shown by Curve B. If one then subtracts the potential at various times along this line from the corresponding potential on Curve A, these differences, when similarly plotted, yield the Curve C. This curve was linear between approximately two minutes and ten minutes, i.e., down to η = 1 mv. This indicated that a second exponentially decaying reaction also took place after the second minute.

After the Ag/AgCl electrodes were backed with Krylon, as described in Part I, the decay of the overpotential of the cathode in KCl was again observed in exactly the same manner as before. The data are shown by Curve A of Figure 21(A). This curve remained linear after times greater than approximately 10 minutes; this portion, extrapolated back to zero time is shown by Curve (1). The differences between the ordinates of Curve A and the corresponding ones of Curve (1) are shown as a function of the time by Curve (2). The linear portion of Curve (2) was extrapolated back to zero time, as shown. Then the differences between ordinates of the non-linear part of (2) and the extrapolated linear part of (2) are shown as a function of the time by Curve (3). Thus the overpotential of this backed electrode was resolved into three exponentially decaying components.

For some of the systems studied the potential did not return to the same value that existed before electrolysis. Sometimes the potential became constant at a value somewhat higher and on other occasions it fell below the former value. It was necessary to find rather accurately the assymptote of the decay curve in order to obtain an exact separation of

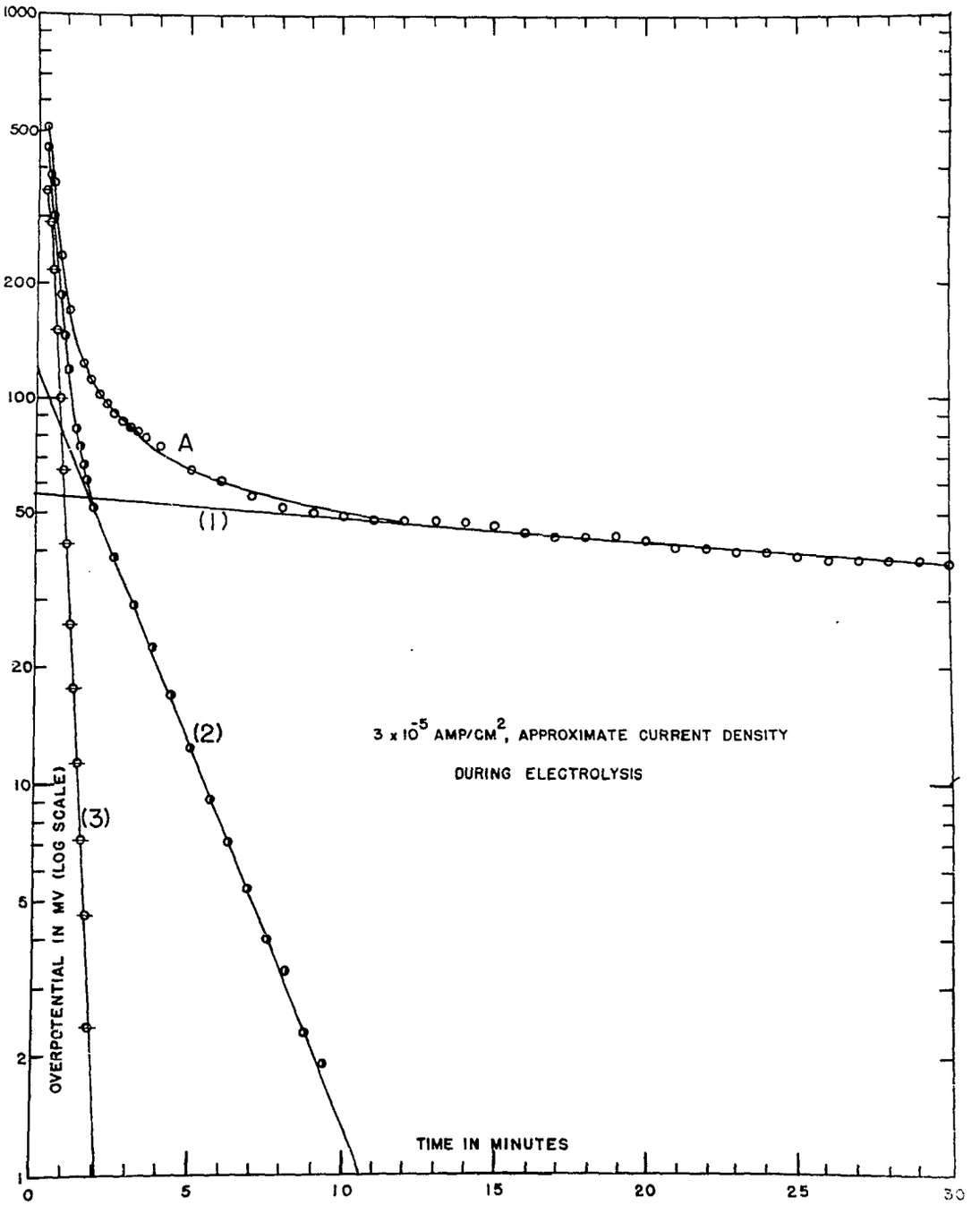

FIGURE 21(A). THE DECAY OF OVERPOTENTIAL WITH A BACKED AG/AG CL CATHODE IN A 0.0024 N K CL SOLUTION

the three processes. Two methods were used to accomplish this. First, the decay curve could be plotted for a considerable length of time (approximately 30 minutes) until an assymptote corresponding to this constant value of potential was indicated. Second, the logarithm of the overpotential could be plotted by use of semi-log paper as a function of the time and, if the straight portion began to curve for large values of the time, a few millivolts could be added to or subtracted from all values of η until the curve was linear after 10 to 12 minutes. In most cases such a correction was not necessary, that is, the measured potential difference returned to its value prior to the electrolysis.

As well as can be determined from the data of Curve A, Figure 21(A) Curves (1), (2), and (3) together represent these data during the entire process of decay. The fact that these observed decay data can be so well represented by the three straight lines indicates that the whole process of decay of this overpotential is, in reality, a combination of three exponentially decaying processes.

For convenience in discussing these three exponentially decaying processes let us label the corresponding overpotentials η_1, η_2, and η_3 in the order in which they are obtained by the method of analysis. The total overpotential at anytime t during the decay will then be:

$$\eta = \eta_1 + \eta_2 + \eta_3$$

and in view of equation 10 we can write,

$$11. \quad \eta = \eta_{01} \exp(-k_1 t) + \eta_{02} \exp(-k_2 t) + \eta_{03} \exp(-k_3 t).$$

To aid in visualizing the relative magnitudes of the three overpotentials, η_1, η_2, and η_3, they are shown plotted on ordinary

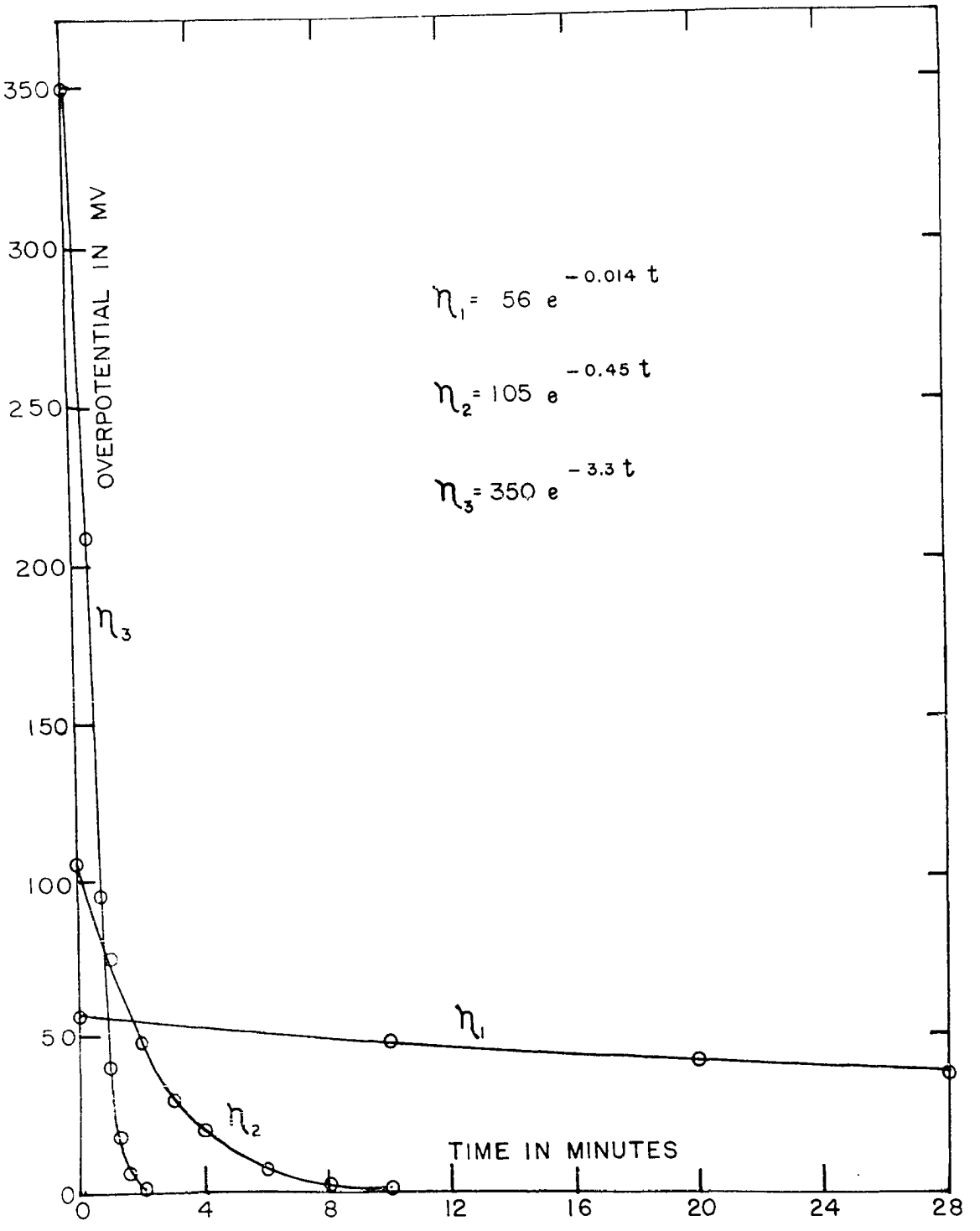

FIGURE 21(B). THE DECAY OF OVERPOTENTIAL WITH A BACKED AG/AG CL CATHODE IN A 0.0024 N KCL SOLUTION

coordinate paper in Figure 21(B). These are the same data shown by the straight lines in Figure 21(A). In this case the ratio of the decay constants $k_1:k_2:k_3$ is equal to 1:32:230.

Apparently these same three processes as determined by the decay constants were observed for various current densities, for various durations of electrolysis, for several electrode materials, for several solutions, and for the various ages of electrodes. The results will be presented, and later an interpretation of them will be made.

Effect of Current Density

Only the Ag/AgCl (backed) cathode in KCl was studied under a variety of current densities. The values of η_1, η_2, and η_3, after 15 seconds of decay, are shown as a function of electrolysis current density in Figure 22. It is seen that the component η_3 increased rapidly at current densities above 2×10^{-5} amp/cm^2 and quickly comprised the major part of the total overpotential. The component η_2 varied comparatively little, and η_1 was virtually independent of the current density.

For each of the current densities the overpotential during electrolysis was observed. In Figure 23 the curve for KCl shows the data for the backed Ag/AgCl cathode after 15 minutes of electrolysis. At 2×10^{-5} amp/cm^2 the overpotential began to rise rapidly and it increased to an apparent saturation value at approximately 4×10^{-5} amp/cm^2.

Decay curves at Ag/AgCl electrodes in HCl were not obtained. However, the striking similarity between the curves for HCl and KCl in both Figure 16, Part I, and Figure 23 indicates that similar relations would have been found for HCl. Also data obtained with other electrodes and solutions reveal the whole process of decay to be made up of three exponentially decaying reactions.

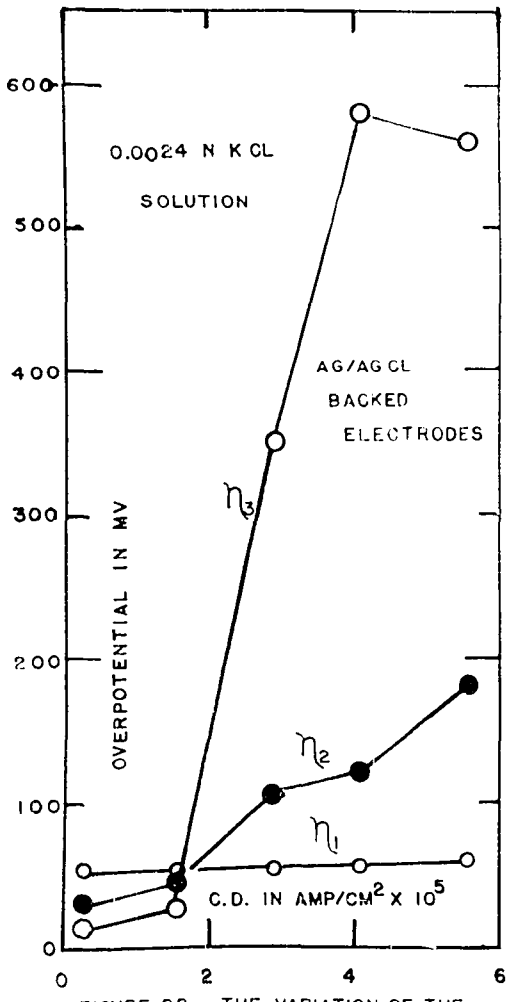

FIGURE 22. THE VARIATION OF THE OVERPOTENTIAL WITH CURRENT DENSITY AFTER 15 SECONDS OF DECAY.

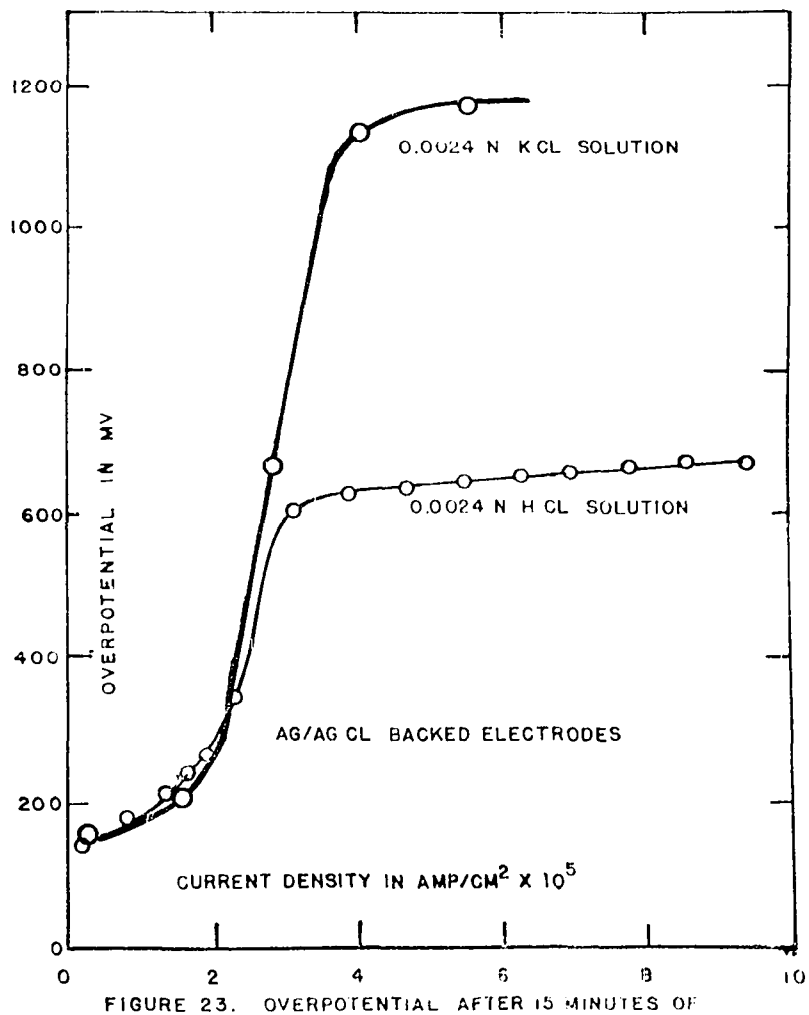

FIGURE 23. OVERPOTENTIAL AFTER 15 MINUTES OF ELECTROLYSIS AS A FUNCTION OF THE CURRENT DENSITY.

Effect of Duration of Electrolysis

It is seen in Table I that the values of the decay constants k_1, k_2, and k_3, show no consistent variation with the duration of the electrolysis preceding the decay. At current densities near 5×10^{-5} amp/cm^2 the values of k_2 and k_3 for all electrode materials and solutions, vary by less than a factor of two. The table includes data for a variety of times for the duration of electrolysis.

In Figure 24 and in Table I are shown the decay of the three components of cathode overpotential at the top of a vertical column of 0.0024 N $CuSO_4$ solution. Whereas after 5, 10, and 15 minutes of electrolysis η_1 and η_2 each increase in the approximate ratio 1:2:4, η_3 rises in the ratio 1:3:9. (Only the data which are important to the extrapolations of the linear portions are included in Figure 24.)

Effects of Age of Electrodes

A few decay curves were obtained for the unbacked Ag/AgCl cathode before it made the change from a grayish-black to the creamy-white, i.e., before the steep potential rise shown in Figure 16, Part I, had occurred for both solutions of KCl and HCl. Only two decay processes were observed which, from their rates, were identified as the k_2 and k_3 processes.

A second instance for which only <u>two</u> decay processes were observed was for a copper cathode that had been used for several hours and also left exposed to the air for two weeks. It had become covered with a heavy reddish-brown coat characteristic of cuprous oxide. In this instance the more rapid decay was in accord with a k_3 process whereas the other decay constant was slightly less than the values found for k_2 for various other electrodes.

TABLE I

OVERPOTENTIAL COMPONENTS AND DECAY CONSTANTS

Electrodes	Solution	Current Density	Duration of Electrolysis	No. of Runs Avg'd.	Decay Constants			Overpotential Components			Overpotential During Last Sec of Electrolysis
K-cathode A-anode	0.0024 N	amp/cm^2 x 10^5	minutes		minutes^{-1} k_1	k_2	k_3	millivolts η_1	η_2	η_3	millivolts η
Ag/AgCl K	KCl	0.28	15.0	1	0.039	0.35	1.5	54 *	34 *	16 *	153
"	"	1.56	"	1	0.023	0.40	2.0	51 *	47 *	25 *	207
"	"	2.86	"	1	0.014	0.45	3.3	56 *	105 *	350 *	665
"	"	4.08	"	1	0.006	0.44	2.7	54 *	120 *	639 *	1133
"	"	5.55	"	1	0.004	0.63	3.0	61 *	180 *	560 *	1170
Ag/AgCl K	HCl	5	15.0	6	0.027	0.53	2.9	80 *	180 *	280 *	630
Pt K	KCl	5.0	1.0	1	0.015	0.38	3.7	115	58	180	400
"	"	4.5	15.0	1	0.021	0.38	2.8	208	53	850	1130
Pt K	HCl	5.9	0.5	1	0.071	0.32	2.6	57	59	175	350
"	"	5.2	5.0	1	0.070	0.37	2.3	93	98	340	586

TABLE I (cont.)

Electrodes	Solution	Current Density	Duration of Electrolysis	No. of Runs Avg'd.	Decay Constants			Overpotential Components			Overpotential During Last Sec of Electrolysis
K-cathode A-anode	0.0024 N	amp/cm^2 x 10^5	minutes		minutes^{-1}			millivolts			millivolts
					k_1	k_2	k_3	η_1	η_2	η_3	η
Cu K	$CuSO_4$	6.9	5.0	1	0.055	0.50	3.8	12	12	70	140
"	"	6.4	10.0	1	0.053	0.40	2.5	23	25	230	788
"	"	6.2	15.0	1	0.052	0.40	2.6	45	49	600	904
Cu K [1]	$CuSO_4$	5.0	15.0	2	-----	0.19	2.5	---	72	280	840
Ag/AgCl K [2]	KCl	5	15.0	6	-----	0.37	1.5	---	83	470	730
Ag/AgCl K [2]	HCl	5	15.0	1	-----	0.33	2.0	---	37	140	---
Pt A [3]	HCl	7.0	10.0	1	-----	0.30	3.4	---	-70	-400	-470
Pt A [4]	"	5.5	10.0	1	-----	0.27	2.9	---	-310	-520	-1090

* 15 seconds after electrolysis ceased.
1 Cu exposed to air for about 2 weeks after considerable electrolysis as cathode.
2 Ag/AgCl cathode before large potential increase noted in Figure 16, Part I.
3 Pt acted as anode 10.0 minutes after several hours as cathode.
4 Pt acted as anode 20.0 minutes after several hours as cathode.

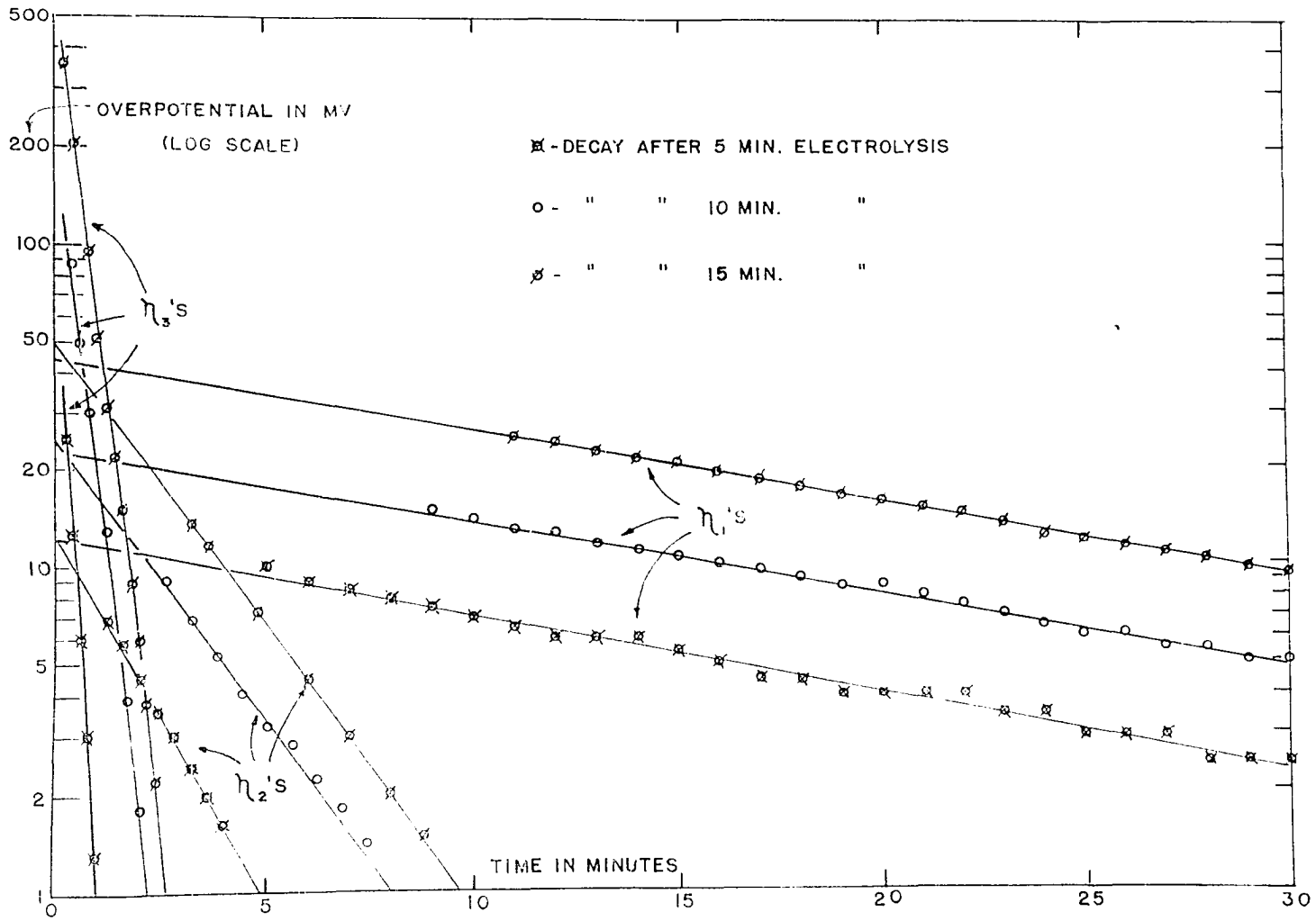

FIGURE 24. DECAY OF THE COMPONENTS OF CATHODE OVERPOTENTIAL AT THE TOP OF A VERTICAL COLUMN OF 0.0024 N $CuSO_4$ SOLUTION.

Effect of Agitating the Solution

When the solution was stirred near the Ag/AgCl cathode in solutions of KCl throughout the 15 minute period of electrolysis only the η_1 and η_2 processes were observed during the decay and their magnitudes were much reduced.

When electrolysis was performed without agitation, and the cathode surface was quickly wiped with a glass wool swab immediately after the 15 minutes of electrolysis ceased, again only the η_1 and η_2 processes were observed in the decay. On the other hand, if the entire body (approximately 2.5 liter) of the solution was stirred immediately after electrolysis ceased, the decay of the potential was erratic, evidently due to the continued motion of the solution. In the former case when the cathode was swabbed immediately after electrolysis ceases, η_1 and η_2 were reduced roughly by 5 and 50 per cent respectively, and η_3 was removed completely.

The data upon which these results are based were obtained with the following procedure. Five runs were made, runs 1, 3, and 5 without stirring, and runs 2 and 4 with the stirring. Each of the two sets of runs was averaged point by point and then comparisons of the two sets of averages were made.

Effect of Concentration

The three decay processes were observed at Ag/AgCl cathodes in various concentrations of HCl as shown in Table II. It is seen that no consistent variations in the decay constants occurred. However, there was a pronounced effect on the overpotentials, η_1 and η_3; these decreased with increasing concentration.

TABLE II

EFFECT OF CONCENTRATIONS ON THE COMPONENTS OF OVERPOTENTIAL

(Ag/AgCl Electrode; Current Density - 5.0×10^{-5} amp/cm^2; Duration of Electrolysis- 5 min.)

Normality and Solution	Number of Runs Averaged	Decay Constants			Overpotential Components			Overpotential During Last Sec of Electrolysis
		minutes^{-1}			millivolts			millivolts
		k_1	k_2	k_3	η_1	η_2	η_3	η
0.0024 N HCl	2	0.091	0.49	2.8	89	80	600	620
0.01 N HCl	2	0.110	0.46	2.6	88	110	440	540
0.1 N HCl	1	0.090	0.42	2.4	18	97	340	450
0.5 N HCl	2	0.090	0.32	2.7	17	78	180	365
0.5 N HCl + 0.1 N HCl	2	0.098	0.40	2.9	14	71	200	395

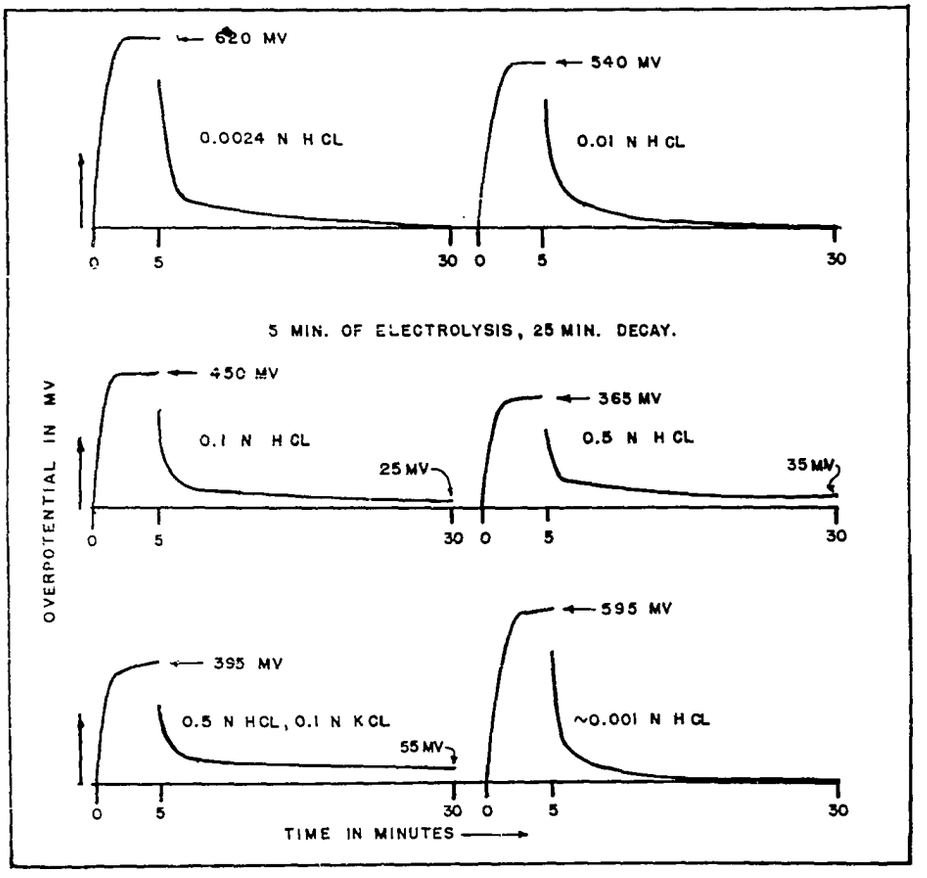

FIGURE 25. BUILD-UP & DECAY OF OVERPOTENTIAL AT AN AG/AG CL CATHODE FOR SEVERAL CONCENTRATIONS OF HCL

A peculiar effect was noted with regard to the relatively constant value which the overpotential in the higher concentrations of HCl approached as the decay proceeded (see Figure 25). When this value was subtracted from the observed overpotentials in the decay, the curve of these differences was resolvable into the same three decay processes observed in less concentrated solutions. It is seen in the figure that this constant value increased with concentration, and it was observed that stirring did not remove it. This apparently constant overpotential was not produced by a change of the probe-to-solution e.m.f.; two observations showed this. First, when the concentration was increased to 0.5 N, the level of the solution was raised to a region on the cathode surface where extensive electrolysis had not taken place. The potential between the probe and cathode was then very near zero, just as it was at the lower concentrations. When the solution level was lowered, the probe to cathode potential jumped immediately to approximately 50 mv. Second, when left to decay overnight, this apparently constant potential difference, even in the 0.5 N HCl, dropped to zero, but when electrolysis was resumed, the "constant" potential difference again began to appear in the decays and it increased again to approximately 50 mv.

The last build-up and decay curve of Figure 25 was taken after 45 minutes of electrolysis in a 0.001 N HCl solution. It is seen that even with this longer electrolysis the constant potential found in the decay curves at the higher concentrations was again absent just as was previously found to be the case at the lower concentrations.

Decay Phenomena at the Anode

The decay of anode overpotential was measured only at platinum in HCl; the data are shown in Figure 26. The electrode had previously been used as a cathode for several hours. After 10 minutes of electrolysis with this electrode as an anode its overpotential decayed to zero within 20 minutes. An analysis of the decay curve yielded two processes;

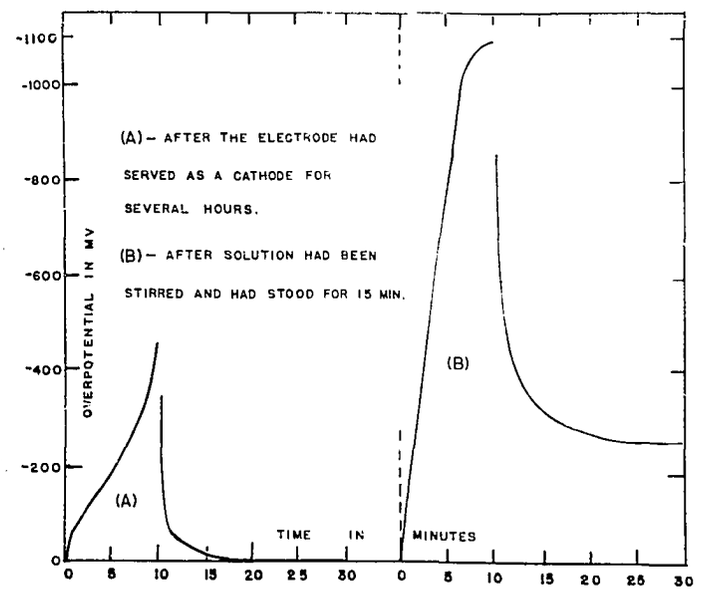

FIGURE 26. BUILD-UP & DECAY OF OVERPOTENTIAL AT A PLATINUM ANODE IN H CL.

the overpotential and the decay constants are given in Table I. The solution was stirred and allowed to stand undisturbed for 15 minutes. Then during an additional 10 minutes of electrolysis with this same electrode as an anode the overpotential attained a much greater value than in the previous run and it decayed, not to zero, but to a steady value of "250 mv"; this curve is also shown in Figure 26. When this 250 mv was subtracted from the observed overpotentials, the resulting curve was analyzed into the same two processes (essentially same k's) that were found for the previous run. The overpotentials and the decay constants are given in Table I.

CHAPTER IX

DISCUSSION AND INTERPRETATION OF RESULTS

The fact that the decay of overpotential can be represented as the sum of three exponential functions of the time suggests that some type of capacitor analogy would better describe the observed decay than does the "log t" relation suggested by Armstrong and Butler[29]. Schuldiner and White[32] do consider that the Helmholtz and the diffuse double layers act as capacitors in series, each with a resistance in parallel through which it discharges after electrolysis ceases.

Bowden and Rideal[28] arrive at the following conclusion from their previously mentioned work on the decay of overpotential.

> . . . the electrode potential is due to the presence of electrical doublets on its surface, the electric moment of these doublets being given by a proton and an electron separated from each other by a distance equal to the diameter of the hydrogen atom.

After Frumkin, Agar[34], in an interpretation of overpotential measurements, describes the total metal-solution potential difference " ϕ ", as made up of two parts, " ϕ_h" across the Helmholtz double layer and " ϕ_g" across the Guoy diffuse double layer. These three qualitative descriptions, among similar ones, suggest the build-up and decay of double layers.

It appears certain that the cathode phenomena discussed in the last chapter are caused by (hydrogen) activation overpotential. This is

believed true for three reasons. First, results were obtained in all cases, that were very similar to those observed in HCl where hydrogen was the only ion which would react at the cathodes. Second, during the decay any ohmic overpotential would have disappeared immediately. And third, since the decay was neither "erratic" nor "complex" concentration overpotential was not indicated. These reasons, in addition to the fact that many of these data compare favorably with those reported in electrochemical literature concerning hydrogen overpotential, led to the assumption that the observed data already described are the result of hydrogen overpotential. As an example, a particular decay curve reported by Ferguson[31c](p.231) was transferred to a plot of the potential as a function of the time and the curve was extended somewhat in order to determine the potential with which the decay curve was assymptotic. Then when the logarithm of the potential was plotted as a function of the time and the analyzing procedure of the previous chapter was applied, two exponentially decaying processes were observed.

If the hydrogen ion alone was responsible for the overpotential during electrolysis, then the three (probably four at greater concentrations) distinct processes should somehow be associated with hydrogen in different adsorbed states on the electrode surface. The fact that three distinct processes occurred during the decay suggests the possibility that the same processes also occurred during electrolysis.

In the General Discussions of the Faraday Society, Butler[35](p.130) made the following relevant statement:

> I should like to advocate, as I have been doing for the last fifteen years, that there is not just one mechanism of overvoltage, but several . . . I think the modes of adsorption need better

> definition . . . I should also like to see a study of the adsorption of hydrogen in a second layer i.e. when the first layer is completed; and the properties of hydrogen held in this way.

Very recently Becker[42] in a study of adsorbed atoms, ions, and molecules (abbreviated adatoms, adions, and admols, respectively) has made the following distinction between adsorbed states. If the valence electron of the atom in question is still associated with its nucleus when the atom is adsorbed it is called an adatom, whereas if the valence electron is attracted more strongly by the atoms of the electrode, it is termed an adion. He suggests further that these may be distinguished by the electrical fields or potentials they produce. An admol is defined as an aggregate of two or more atoms adsorbed on a metal surface in such a way that the attractive forces of the atoms for each other are greater than the attractive forces of the atoms for the metal. He also states that electric fields associated with a layer of adions will be larger than that for a layer of adatoms.

In view of these suggestions, let us consider what types of adsorptions we may expect for the hydrogen ions and atoms associated with hydrogen overpotential. It is commonly believed that the hydrogen ion in solution is hydrated with one molecule of water; the formula is written as H_3O^+. On the electrode the state of hydrogen most often suggested is that of the chemadsorbed atom. Also the hydrogen molecule may be lightly adsorbed before leaving the electrode as a gas. Though a general distinction is made between physical and chemical adsorption, still, as implied in the statement by Butler, there may be different modes of adsorption of hydrogen atoms, ions, or molecules even within the general classification of say, chemadsorption. The degree of association of the

valence electron with the metal of the electrode, as suggested by Becker[42], appears to be a convenient way of describing different modes of adsorption. For example, a hydrogen atom sharing its electron with two metal atoms would represent a different adsorption state from that of a hydrogen atom sharing its electron with only one metal atom.

The foregoing considerations permit us to make an interpretation of the observed decay curves in terms of transitions between the following proposed adsorption states:

12. Adion $\longrightarrow$ $(e^- + M) - - - H_3O^+$

Adion $\longrightarrow$ $(e^- + M) - - H^+$

Adatom $\longrightarrow$ $M - H$

(Audubert[43] and others have studied the transitions between the first two in interpreting hydrogen overpotential.) The electron e^- is written specifically in order to emphasize the double-layer nature of the adsorption; the different designations of bonds imply different adsorption energies as well as different separations of the charges in the various double layers. These states are illustrated schematically in Figure 28(D).

After Audubert, if we compare the potential energies of the H^+ and H_3O^+ ions as independent functions of the perpendicular distance from the electrode, they should appear something like the curves in Figure 27. This gives us a picture of the relative positions of these ions in these adsorbed states but there is no attempt to represent the actual potentials and distances quantitatively.

Although in some solutions positive ions other than H_3O^+ and H^+ were present, still these two <u>alone</u> are believed important in this interpretation principally because the same three processes occurred in HCl

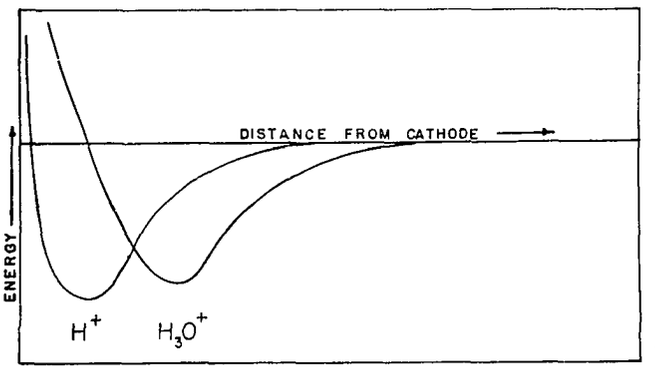

FIGURE 27. THE POTENTIAL ENERGIES OF THE H^+ AND H_3O^+ IONS NEAR AN ELECTRODE.

where these were supposedly the only positive ions [unless we postulate doubly hydrated ions which are not generally accepted, though they more likely occur in dilute solutions[37(p.94)]]. Other adatom states, it is believed, would not produce the large overpotentials, η_2 and η_3.

If these three states of adsorption exist simultaneously there would exist in the steady state before electrolysis, transitions back and forth between these states, the net transfer being zero between any two of the adsorbed states. During electrolysis the transitions would occur primarily in the forward direction as follows:

13. (3) $(e^- + M) - - - H_3O^+ \xrightarrow{w_3} (e^- + M) - - H^+ + H_2O$

(2) $(e^- + M) - - H^+ \xrightarrow{w_2} M - H$

(1) $M - H + M - H \xrightarrow{w_1} 2M + H_2$

where w_3, w_2, and w_1 are the energies of activation of the three respective processes. (The reactions are numbered to correspond to the three observed decay processes.) These three reactions are illustrated in Figure 28(A).

If η_i represents the potential due to the ith of these layers we can express it as

14. $\eta_i = (4\pi/\epsilon)(q_i/A_i)\ \delta_i = (4\pi/\epsilon)\ \sigma_i\ \delta_i$

where q_i is the total charge in the ith layer determined by the number of

ions in that layer, δ_i is the thickness of the layer, A_i is the area of the ith layer, σ_i is the charge density for the ith layer, and ϵ is the dielectric constant.

The foregoing descriptions will facilitate the interpretation of the experimental results.

Effect of Current Density

The distinct manner in which the three components of the overpotential vary with current density is of particular interest because of the reports of the four groups, Hickling and Salt[30], Ferguson et al[31], Bryant and Coates[33], and Schuldiner and White[32]; each group mentions two types of decay and calls attention to the way that the two types vary with current density. Although Bryant and Coates presumably were measuring concentration overpotential they questioned whether the new process that

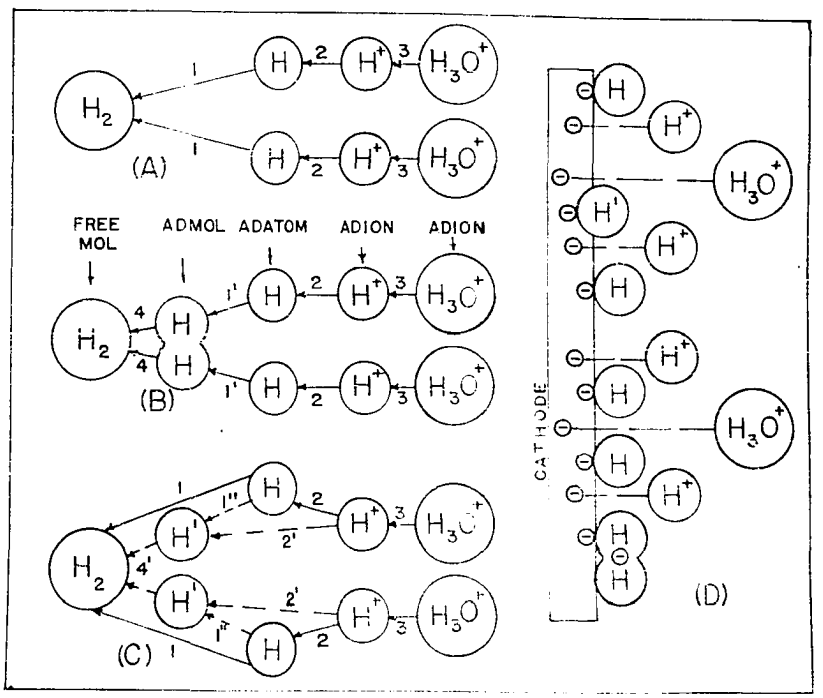

FIGURE 28. SUGGESTED PROCESSES IN THE EVOLUTION OF HYDROGEN OVERPOTENTIAL

appeared was true concentration overpotential. They showed that the effect was associated with the condition of the electrode.

Though Ferguson[31c](p.233) gives tables of values for the "initial" and "residual" components in the decay of overpotential with several electrodes it was not possible to determine from his publications how he obtained these values. It is of particular interest at this point to note that the "initial" overpotential, for all the cases reported, increased with current density while the "residual" overpotential showed little variation.

In Figure 23 it is seen that at a current density of about 2.5×10^{-5} amp/cm^2 the overpotential, measured during electrolysis, began to rise very rapidly and at this same current density, Figure 22, η_3 became the predominant component in the decaying overpotential. As reported by the observers cited above, here is a component of the overpotential which varies considerably with current density. The other two components, η_1 and η_2 of Figure 22, are seen to be relatively insensitive to changes in the current density.

It is inferred that, during electrolysis at this "transition current density", the layers of adatoms, H, and of adions, H^+, are practically filled, and that the current is supplying adatoms and adions respectively as fast as they leave these layers by way of reactions (1) and (2) of equation 13. Then when the current density is increased, the layer of H_3O^+ adions begins to fill and the potential rises sharply. (Notice the quotation from Butler[35] on the second page of this chapter.) It will be shown that the indications are that δ_3, the distance the H_3O^+ layer is from the cathode, is large; thus the potential difference η_3 will be

larger than η_2 and η_1 for a given charge per unit area, σ, and, in fact, η_3 could be larger even for a smaller σ.

It is important to observe in Figure 22 that at the smaller current densities the η_3 process does not cease but does become relatively small. In accord with the proposed reaction scheme it appears reasonable to suppose that, even at low current densities, the ions must pass through this adsorption state. Thus when electrolysis ceases, some will be present in this state and the subsequent observable decay of η_3 will occur. In addition this may account for the fact that the decay curves of Bowden and Rideal did not show the initial rapid decay reported by others at higher current densities, since η_3 could have been present but would have been very small and therefore undetectable by their methods.

The approach to a saturation value illustrated particularly well in Figure 23 for HCl, indicates that the three layers of adsorbed particles are all practically filled to their steady-state densities. Thus no further rise in overpotential should be expected. Other observers[26] have noted this saturation on various electrode surfaces.

Effect of Duration of Electrolysis

If this hydrogen overpotential is actually caused by the three adsorbed layers, then electrolysis for short intervals of time should not result in large overpotentials until the H^+ and H_3O^+ layers begin to fill appreciably. This idea is borne out nicely in the case of a platinum cathode in KCl. After one minute of electrolysis η_2 was observed to be 58 mv and after 15 minutes of electrolysis η_2 remained 53 mv (see Table I). This indicates that an early saturation of the second layer

took place. The potential difference across the first layer doubled in this 14 minute period, possibly because of the increase in the number of adsorption sites, whereas η_3 of the third layer increased by a factor five.

If we assume that the current is supplying H^+ ions to the second layer at a rate greater than that at which they leave this layer, then if given sufficient time all of the H^+ adion sites would be taken. Consequently the ions would be held in the H_3O^+ adion layer and the overpotential associated with this layer would increase.

In the vertical cell with the copper cathode at the top, the reduction of hydrogen took place although the solution was $CuSO_4$ because the current density was greater than the limiting diffusion current density for the Cu^{++} ions (See Part I). The decay of the three components of the overpotential after 5, 10, and 15 minutes of electrolysis, shown in Figure 24, bore this out. Again after longer times of electrolysis, when the layers closer to the electrodes were more nearly full, the third layer filled and the potential rose sharply.

Effects of Electrode Material and Solution

Bonhoeffer[36] has shown experimentally that the combination of hydrogen atoms adsorbed on metals that exhibit large overpotentials, occurs much more slowly than when adsorbed on metals exhibiting small overpotentials. This has been one of the reasons most commonly held for choosing process (1) Equation 13, ("slow combination") as the rate determining step in the over-all reaction at the cathode.

The data of Table I suggest an answer as to which is the rate determining reaction and whether it is the same for metals exhibiting both

high and low overpotentials at all current densities. It is to be noted that, for the Ag/AgCl cathode in solutions of HCl and KCl, $k_1(HCl) > k_1(KCl)$ and concomitantly that $\eta_3(HCl) < \eta_3(KCl)$. Also consider the following observed experimented facts:

$$k_1(Pt;KCl) < k_1(Cu:CuSO_4) < k_1(Pt;HCl)$$

and

$$\eta_3(Pt;KCl) > \eta_3(Cu;CuSO_4) > \eta_3(Pt;HCl).$$

It is inferred from these data that, when the decay constant k_1 is small, more ions are held in the H_3O^+ adion layer and consequently the total overpotential η, predominately made up of η_3, is large. It appears consistent then to interpret process (1) as the rate-determining step. This may be true for current densities up to those which cause the layers to be full of adsorbed ions or atoms. Thus the results of Bonhoeffer[36], that reaction (1) is catalized by the electrode metal, and that other positive ions in the solution affect this rate, are of interest.

In a summary of one of his papers describing the decay of overpotential Ferguson[31a] observed.

> The rate of transition from one type of overvoltage to the other varies greatly between different electrode materials and also between anode and cathode for the same material.

As mentioned previously Ferguson[31c] refers to an "initial" and a "residual" overpotential in the decay. If his method of separation of these components distinguishes only two such components then the variations of the η_2 overpotential (omitted by him) with electrode material, solution, etc., observed in this present work, would appear as a variation in the rate of transition from the "initial" (η_3) overpotential to the "residual" (η_1) overpotential.

Effects of Aging the Electrodes

If the cathode surface were coated with an oxide which would react with the hydrogen rather than permit adatoms of hydrogen to form on the electrode, it is of interest whether the corresponding process (1) equation 13 would be absent in the decay and whether the rates of the other processes would be affected.

As described in conjunction with Figure 16, Part I, the Ag/AgCl electrodes were grayish-black before the large potential build-up occurred in both HCl and KCl. This color is more characteristic of silver oxide or peroxide than of AgCl. After the large build-up occurred, the electrodes became white and this white material remaining on the silver electrode was insoluble, which is indicative of AgCl. A comparison of these phenomena with a well-known process[18](p.213) suggests that the darker deposit may be an oxide. The method of measuring the amount of oxide present on a metal surface involves cathodic reduction of the oxide; the reduction is complete when the rapid rise of the potential at the metal cathode occurs. Before the Ag/AgCl electrode turned white only two decay processes, η_2 and η_3, were observed! Instead of forming an adatom double layer the "oxide" was reduced by the following reaction:

15. $$Ag_2O + 2e^- + 2H^+ \longrightarrow 2Ag + H_2O.$$

A similar phenomenon occurred at a Cu electrode which had a heavy coat of oxide on its surface. Here, too, process (1) was not observed. These facts give strong evidence that decay process (1) is the combination of adsorbed hydrogen atoms to form molecules. Although there may have been very small amounts of oxide on the well-cleaned cathodes, this would have been removed quickly by the electrolysis.

As mentioned in the Introduction of Part II a commonly suggested reaction between the adion H_3O^+ and the adatom H is the following:

16. $$H_3O^+ + M-H + e^- \longrightarrow M + H_2 + H_2O.$$

If this were the mechanism, or even partially so, for the removal of the H_3O^+ adions from their second ionic layer, then in the foregoing cases in which the adatom layer was removed, the above reaction could not occur and the rate k_3 should be changed considerably. On the other hand if the reaction time is determined by the energy for the removal of a water of hydration, then k_3 should be altered much less by the removal of the adatom layer. It was observed that neither k_3 nor k_2 was affected appreciably by the oxide coat.

When the oxide was present the adatom layer was not formed and the rate determining reaction was a different one. Therefore, it would be expected that the total overpotential would be changed also. This was observed!

Effect of Agitating the Solution

According to the over-all reaction scheme already proposed and the description of the adsorbed layers, the H_3O^+ adion layer decays most rapidly, the H^+ adion layer decays at the intermediate rate, and the adatom layer decays at the slowest rate. The distances of these layers from the cathode decrease in the order mentioned. The layer with the greatest separation might be removed by stirring!

Shortly after the discovery of the three processes but before any structure for the adsorbed layers had been assigned, agitation of the solution and swabbing the cathode both during and immediately after electrolysis were carried out. As outlined in the results, consistently the

most rapidly decaying process (η_3) was removed.

In swabbing the Ag/AgCl cathode immediately after electrolysis ceased all of η_3, and about 50 percent of η_2, but very little of η_1 were removed. These facts are consistent with the proposed description of the three layers at the cathode surface.

It has been the practice[25](p.399) to stir the solution near the cathode while making overpotential measurements in order to remove the concentration overpotential and thus to measure only the activation overpotential. The results described above demonstrate the reduction of the activation overpotential with stirring during electrolysis, and this raises a serious question as to the advisibility of stirring in order to remove concentration overpotential.

Effect of Concentration

According to Kortum and Bockris[25](p.423) the activation overpotential should decrease with increasing concentration. Both this and the predicted ranges of concentration at which the changes should occur, agree very well with the data presented in this work. We see in Table II that between 0.0024 N and 0.01 N HCl there is a definite regular decrease in the overpotential with increasing concentration. The data show that η_3 decreases most, that η_1 decreases considerably, and that η_2 varies relatively little.

Attending this decrease in the magnitude of the total overpotential is the occurrence of a fourth decay process, a fourth component of the overpotential. Apparently another very strongly adsorbed layer exists ("another mode of adsorption" in Butler's words) since the associated

potential was completely unaffected by stirring and the potential took eight to ten hours to decay. Exact measurements of the decay constant for this process may be difficult since it is not easy to keep all the factors constant over the long time intervals.

Two additional reaction schemes are suggested in Figures 28(B) and 28(C) to account for this fourth component of the overpotential. Figure 28(B) divides reaction (1) into two consecutive reactions and suggests that another potential might be observed, which is associated with adsorbed molecules of hydrogen (admols). Figure 28(C) indicates another type of adatom adsorption (M-H') and permits two possible side reactions 2' and 1''. After the manner of Becker[42] we could possibly distinguish M-H and M-H' by assuming the hydrogen atom for the first case is associated with only one metal atom whereas the hydrogen atom for the latter case is associated with two atoms of the metal.

The decrease of the total overpotential with an increase in concentration and the observed attendant increase in the potential associated with a fourth reaction, suggests that this new process is a side reaction rather than a consecutive reaction. If this extremely slow fourth reaction were consecutive, as shown in Figure 28(B), there would occur a filling of the adion and adatom states and the overpotential would increase. On the other hand if increasing the concentration provides another side route for the discharge of the adatom and adion layers, the overpotential would be less. The latter was observed and therefore this fourth process must be a side reaction.

It should be observed further from the data in Table II and in Figure 25 that for the lowest concentration (0.1 N HCl) at which the fourth

slow decay process occurred, the initial value of η_1 dropped significantly. It appears reasonable that many of the adsorption sites on the electrode surface, originally occupied by the adatom (M-H), may now be occupied by atoms existing in another type of adsorption (M-H') which is stronger.

It is possible that this fourth component of the overpotential exists even at the lower concentrations since its magnitude may be so small that it cannot be distinguished with certainty. However it appears from the few available data that a certain minimum concentration is required before this fourth component comes into being.

Anode Overpotential

Though it is difficult to say whether or not the overpotential observed at the anode was oxygen overpotential there is certainly evident a remarkable similarity between the curves observed at the cathode and at the anode; similarities have been observed elsewhere between oxygen and hydrogen overpotential[18](p.185).

The anode curves of Figure 26 may be given the following tentative explanation. During the first 10 minutes all the hydrogen on the Pt anode surface, placed there by considerable cathodic polarization, was not used up. Therefore only two processes, undoubtedly very similar to (2) and (3) at the cathode, occurred. This electrolysis produced no adsorbed atoms of oxygen or chlorine on the platinum. However, during the next 10 minutes of electrolysis the hydrogen was used up, oxygen or chlorine atoms were adsorbed, the over-all rate of the anode reaction was decreased, more ions appeared in the two adion states, and therefore the anode overpotential

increased to a much greater value. In addition during the decay, there appeared a third process which could not be stirred out and the overpotential of which was apparently constant. This would be characteristic of adsorbed oxygen atoms for they are held very tenaciously by platinum[18](p.187).

General Discussion and Interpretation

The tri-double layer hypothesis for hydrogen overpotential has been shown consistent with several experimental results in the foregoing discussions. However, most generally three apparently independently decaying potentials would not be observed since, according to this proposed decay scheme, the discharging of some of the layers charges other layers. The following discussion demonstrates how these processes may appear to be independent.

It is seen in equation 14 that the greater the thickness δ, of a layer, the greater the potential for a given σ. Therefore, as suggested earlier, the adion layer H_3O^+ may produce the largest potential even though its charge density may be the same or even very much smaller than the others.

The adatom layer, in particular, may follow closely the microscopic irregularities of the electrode surface while in addition many of the dipoles that make up this layer may be oriented at angles other than 90° to the general plane of the electrode surface. These two possibilities would permit a much greater total charge, q_1, for a given observed potential η_1. For the second and third layers these effects should be somewhat smaller.

The experimental results indicate that the inequality,

17. $$\delta_3 >> \delta_2 > \delta_1$$

is true, while in addition it has just been suggested that:

18. $A_1 >> A_2 > A_3$.

Thus the inequalities,

19. $q_1 >> q_2 >> q_3$

may be so great that the discharge of the H_3O^+ layer into the H^+ layer does not appreciably affect the overpotential of the latter. A similar condition could exist for the inequality $q_2 << q_1$.

The number of ions leaving the H_3O^+ adion layer in a given time may be considerably fewer than the number leaving the H^+ adion layer during the same interval. Still the fall of the overpotential, η_3 may be, as was observed, greater than the fall of η_2 during the same interval of time. In such a case the decays would <u>appear</u> to proceed independently.

In his book, Electrode Processes, Butler[18](p.185) states the following concerning the present (1951) state of hydrogen overpotential theory.

> It appears to be established that upon metals of high overpotential, such as Hg, Pb, etc., the mechanism in aqueous acid solution consists in the slow discharge of protons onto adsorption sites on the cathode surface. On metals of low overpotential, such as platinum, the rate determining reaction appears to be the combination of hydrogen atoms, at least at low c.d.'s.

The present work illustrates how the above conclusions could be drawn, possibly erroneously. For example, at metals of high overpotential, or in the cases of high current densities, the rate determining reaction could <u>still</u> be the slow combination of adatoms even though the overpotential component η_3 here is very large. In other words, while the large overpotential is produced primarily because of a large η_3, the over-all rate of the reaction is still controlled by the rate of combination of

adsorbed hydrogen atoms on the electrode surface. A detailed study of the many experimental and theoretical results upon which Butler's conclusions were based would have to be made before the foregoing suggestion could be established.

Reproducibility

Exact reproducibility of the individual overpotentials and of some of the decay constants was not achieved. For example, k_1 for the Ag/AgCl cathode in HCl as recorded in Table II, is considerably different from the value in Table I. This is illustrative of the variation of the "rate determining reaction" even under apparently the same conditions. The two cathodes were prepared by the same procedure and, visually, they appeared identical.

The sum of the extrapolated values of η_1, η_2, and η_3 at zero time did not always agree with the value of the overpotential at the end of the electrolysis. When the sum of the three components was smaller, the difference could be explained by the loss of the ohmic overpotential as soon as the current ceased. However, when Ag/AgCl electrodes were used, the sum of the components extrapolated to zero time was always greater than the overpotential at the end of the electrolysis. The overpotential after electrolysis ceased seemed to remain constant for a short time before the rapid decay began. As mentioned earlier the quadrant electrometer could not follow these changes during the first 15 seconds and thus the exact variation of potential during the first 15 seconds of the decay was unknown. Also it is observed in Figure 21(A) that the value of η_3 immediately after electrolysis ceased (determined by extrapolation) is very sensitive

to changes in the slope, k_3. A very small change in k_3 will cause η_{03} to change greatly. Since the total overpotential after 15 minutes of electrolysis is predominately composed of η_3 this inaccuracy could produce a large mistake in the total overpotential if it is determined by adding the values of the three components obtained by extrapolation to zero time. For these reasons, in Table I, the values of η_1, η_2 and η_3 for Ag/AgCl electrodes at t = 15 sec were recorded.

Suggestions for Future Work

I. It will be of interest to determine the relation between the decay rates determined here experimentally and those calculated from the equation of Eyring[39,40] for the "activated complex",

$$23. \qquad k = (RT/Nh) \exp[(\Delta S_a/R) - (\Delta Ha/RT)]$$

where R, N, and h are Boltsman's constant, Avogadro's number and Plank's constant, respectively, T is the absolute temperature, and ΔS_a and ΔH_a are respectively the entropy and the heat of activation. In the theory he assumes that the reacting components spend a time (which is determined statistically) in an activated state prior to the formation of the product. The variation with temperature and the value of the heat of activation should be of interest; the latter would be of particular value in arriving at a more certain determination of the process that is occuring.

II. Instrumentation was a handicap in the present work. An electrometer with a much more rapid response is needed for future work. This would permit the determination of the overpotential accurately in the first few seconds of decay. Several observers have recorded the decay potential as early as 10^{-5} sec after electrolysis ceases.

The cell for polarizing the electrode should be so designed as to prevent convection as well as other phenomena which might produce a non-uniform current density.

III. Better designed methods of stirring the electrolyte and swabbing the electrode should be devised and these should be used in the study of overpotentials at various surfaces.

IV. Electrical circuitry should be arranged so that a known constant current can be supplied to the cell. With such an apparatus a careful check of the variation of each component of the overpotential with current density should be made. This would test the Tafel relation for each component providing the entire current passes through each double layer.

V. Many interpretations of overpotential measurements have been made on the basis of studies of the total overpotential under different conditions. A study should be made of the effect of light on the total overpotential[25](p.419) and also its effect on the magnitudes and the rates of decay of the components η_1, η_2, and η_3. (The suggested study of the effect of light is merely an example.)

VI. A more precise investigation of the effect of the removal of the adatom layer by use of oxidized cathodes, on the decay rates, k_2 and k_3, would make it possible to determine how dependent or independent these processes actually are.

VII. The foregoing analysis of the decay of overpotential should be applied for metals having both high and low overpotentials.

VIII. Additional measurements of the decay of anode overpotential are necessary; it is important to use some solution such as KOH which

would produce "oxygen overpotential".

IX. The information obtained concerning anode overpotential indicates that it would be possible to determine at what potential oxygen begins to be adsorbed in anodic polarization. This would be evidenced by the appearance of a very slowly decaying process.

X. The use of a solvent other than water should help determine whether the most rapid decay represents the decay of a hydronium layer. This might provide a simple means of determining solvation energies.

CHAPTER X

SUMMARY AND CONCLUSIONS

(PART II)

During the determination of the Deviation-Time data described in Part I it was believed advisable to study the decay of the potential difference between each electrode and the probe after electrolysis ceased, in order to ascertain whether or not such data would reveal the rate of disappearance of space charge which was then believed to exist. An examination of these decay curves showed that each could be analyzed into three exponentially decaying potential differences. Since the potential differences near the electrodes were in reality overpotentials, this was thus a new and improved method for studying overpotential phenomena.

Investigations were carried out in solutions of HCl and KCl at Pt and Ag/AgCl cathodes and in solutions of $CuSO_4$ at a Cu cathode placed at the top of the vertical column of electrolyte.

This study, in which a new method for analyzing the decay of overpotential into exponentially decaying components was employed, made possible the determination of answers to the three questions:

1. What is the form of the function which represents the decay of overpotential after electrolysis ceases?

2. What intermediate reactions are involved in hydrogen overpotential?

3. Which intermediate reaction is the rate determining reaction during the liberation of hydrogen?

The total overpotential η at any time t after electrolysis ceased it was found could be expressed as,

$$\eta = \eta_{01} \exp(-k_1 t) + \eta_{02} \exp(-k_2 t) + \eta_{03} \exp(-k_3 t),$$

where η_{01}, η_{02}, and η_{03} represent the initial values of the components and k_1, k_2, and k_3 represent the respective decay constants.

Observations of these three processes for various current densities, for various durations of electrolysis, for several electrode materials, for several solutions, and for various ages of electrodes, indicated that the intermediate reactions involved in the reduction of hydrogen and associated with hydrogen overpotential were as follows:

$$(e^- + M) - - - H_3O^+ \longrightarrow (e^- + M) - - H^+ + H_2O$$

$$(e^- + M) - - H^+ \longrightarrow M - H$$

$$M - H + M - H \longrightarrow 2M + H_2$$

where $(e^- + M) - - - H_3O^+$, $(e^- + M) - - H^+$, and M - H represent adsorbed hydronium (adion), adsorbed hydrogen ion (adion) and adsorbed hydrogen atom (adatom) states, respectively. The electron e^- is written specifically in order to emphasize the double-layer nature of the adsorption; the different bonds imply different adsorption energies as well as different separations of the charges in the various double layers. The observed potentials η_3, η_2, and η_1 were associated respectively with the three double layers, H_3O^+ - electrode, H^+ - electrode, and H - electrode.

Swabbing the cathode immediately after electrolysis ceased removed all of the hydronium layer, about fifty percent of the hydrogen ion layer,

and very little of the adsorbed hydrogen atom layer. As the current density was increased more ions were observed in the two adion layers. When the cathode had a heavy oxide coat the adatom layer did not form. The hydronium adion layer which had a relatively small charge per unit area after short periods of electrolysis ($<$ 1 minute), apparently reached saturation after longer intervals (5 to 10 minutes) of electrolysis. These and other experimental results were found consistent with the proposed intermediate reactions.

A fourth process, believed to be associated with another more strongly adsorbed state of the hydrogen atom, was observed in relatively concentrated solutions of HCl at an Ag/AgCl cathode.

CONCLUSIONS

The cathode overpotentials which existed after 15 minutes of electrolysis of dilute HCl and KCl solutions between "Ag/AgCl electrodes, of HCl between bright Pt electrodes, and of $CuSO_4$ solution in a vertical column between Cu electrodes with the cathode at the top, are hydrogen (activation) overpotentials; there is no significant ohmic or concentration overpotential.

It was found possible to analyze each of these cathode activation overpotentials into three exponentially decaying components that disappear respectively in approximately 2.5, 11, and 20 or more minutes.

The causes of these overpotentials, at least after electrolysis ceases, are the adsorbed states of the hydronium ion, the hydrogen ion, and the hydrogen atom. The total overpotential is a hydrogen activation overpotential.

The fastest decaying component of the overpotential disappears as the H_3O^+ adion layer becomes a layer of H^+ adions.

The component that disappears next does so when the layer of H^+ adions becomes a layer of H adatoms.

The last component disappears slowly by the passage of the H adatoms into H_2 molecules.

Of these three processes the last determines the current density, i.e. the rate at which the charge can pass to the electrode; thus the H-adatoms $\longrightarrow$ H_2-molecules is the rate determining process.

The layer of H_3O^+ adions is weakly adsorbed and exists farthest from the electrode surface. The layer of H adatoms is most strongly adsorbed and exists closest to the electrode surface. The layer of H^+ adions has an intermediate degree of adsorption and exists between the other two adsorbed layers.

The decay of anode overpotential is also composed of three exponentially decaying components.

Vigorous stirring of the solution next to the cathode removes a part of the activation overpotential. Thus the practice of stirring to remove concentration overpotentials is unwise.

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APPENDIX I

PREPARATION OF ELECTRODES AND SOLUTIONS

The Ag/AgCl Exploring Electrode (or Probe)

The exploring electrode, or probe, for use in chloride solutions, see Figure 2(C), was prepared by sealing a size 28 B.&S. gauge silver wire into a glass tube of small bore. The tube, having been previously tapered near one end and the silver wire inserted, was sealed off at the narrowest place by fusing the wire in two. (Only a short length of silver wire was used; a similar gauge copper wire was soldered to it for a lead up through the probe to the outside.) Next at about 1 cm from the tip the tube was bent through 90°. The tip was then ground carefully with fine emery paper until the end of the exposed silver wire was flush with the end of the surrounding glass tube. After washing the tip in dilute HNO_3 and rinsing, it was ready for the plating of the chloride which was accomplished by placing the tip in a chloride solution as an anode. Neither the current density nor the type of chloride solution seemed critical. With a nearly saturated KCl solution the deposit was dark as viewed under a low power microscope whereas with HCl the deposit was white. The self potentials of the probes, prepared in these two solutions, appeared to be the same within about a millivolt as indicated by measuring the potential difference between each and one of the current electrodes. The potential of this

probe remained remarkably constant, as expected, since the maximum current drawn by the electrometer was about 10^{-10} amp/cm^2 and the reaction at the plated tip should be nearly reversible at this current density.

The Ag/AgCl Current Electrodes

The procedures found in electrochemical literature for preparing Ag/AgCl electrodes varied considerably. Thus a series of tests at several current densities was made in order to determine which would produce the best adhering surface of AgCl on Ag. A nearly saturated solution of KCl was chosen because this was found to be commonly used. A piece of silver foil 2 inch by 2 inch was cemented to a lucite surface 8 cm by 12 cm. Next a window opening slightly less than 2 inch by 2 inch was cut in a lucite block, 8 cm by 8 cm square and 1 inch in thickness. This was placed over the foil and sealed to the lucite back around the edges of the foil. The silver foil was exposed only through the window. Previously a small strip of silver had been spot welded at the top edge of the silver foil and was led out between the two pieces of lucite. When this was placed in the plating solution opposite a large platinum sheet, it was supposed that the current density was nearly uniform over the silver foil. After three trials where current densities of 1.0, 0.5, and 0.1 ma/cm^2 were used, it was found that the last of the three had produced a uniform deposit which adhered well. The other two deposits were spotted and flaky.

After this information had been obtained the silver electrodes described in the text were prepared for plating at a current density of 0.1 ma/cm^2 by the following procedure.

(a) The electrodes were cleaned with naphtha to remove oil, grease, etc.

(b) Each electrode was scoured with repeated applications of a cleansing powder until the entire surface would wet with water.

(c) The electrodes were then washed in dilute HNO_3 and rinsed with distilled water.

(d) After a second washing in HNO_3 and a thorough rinsing in doubly distilled water, the electrodes were placed immediately into a dilute solution of NH_3OH and electrolyzed as cathodes for a few minutes.

(e) The electrodes were thoroughly rinsed and lowered into the plating bath, a nearly saturated solution of KCl. For the cases where these two electrodes were to be used respectively as cathode and anode over a period of time long enough to get sufficient data for plotting a potential distribution, the electrodes were plated as anodes for approximately 90 hours at the chosen current density of 0.1 ma/cm^2. During these long runs a slimy deposit formed on the platinum cathodes; this was removed and cleaned two or three times. The solution became basic with the evolution of hydrogen at the platinum cathodes; therefore at two or three intervals the plating solution was neutralized with HCl.

Electrodes prepared in the foregoing manner received a dark grayish-black fine-textured surface which adhered well to the silver plate.

The Copper Electrodes

(a) For the Horizontal Trough

The copper electrode surfaces, flattened as much as possible on a belt sander, were then ground down to within 0.002 in. of being plane by using coarse emery paper. The copper sheets were then annealed and soldered into the brass holders. Next with emery as fine as #600 grit the surfaces were polished.

The unfinished back surface and the edges of each electrode were sprayed with four separate applications of acrylic plastic (Krylon); each application was allowed to dry independently.

The polished surfaces were rubbed thoroughly with very fine grain emery paper along with applications of cleansing powder. This procedure was continued until each entire surface would remain wet. They were then

rinsed in distilled water and placed immediately (without being allowed to dry) into a copper plating solution. The solution consisted of 125 grams of crystallized copper sulphate ($CuSO_4 \cdot 5\ H_2O$), 50 grams of concentrated sulphuric acid and sufficient distilled water to make one liter. The electrodes were plated for five hours with a current density of 1 ma/cm^2. A reduction in current during the last hour gave the surface a finer texture. The plated electrodes were rinsed in distilled water and quickly transferred to the horizontal trough.

It was found that equally good results were obtained without plating; thus for most of the investigation the electrodes were cleaned with scouring powder, rinsed and placed in the trough. When any copper oxide streaks appeared during cleaning, they were removed with dilute HNO_3.

(b) For the Vertical Cell

Since the lucite separators for these electrodes prevented an even cleaning after assembly, the electrodes were cleaned very thoroughly before the assembly of the apparatus. It was found that if the excess water was blown off the electrode face by a jet of air immediately after cleaning as above, a visible oxide coating would not be formed during assembly of the apparatus. Such a slight coating as was found was removed with dilute HNO_3 and rinsed away after the assembly, and the apparatus was immediately placed into the vertical tank.

The backs and edges of these electrodes and the copper plated cap screws were coated with Krylon.

The Solutions

For each electrolyte a 0.24 N stock solution was prepared and

this solution was diluted to make the 0.0024 N solution for the trough by taking 10 ml of the concentrated solution and adding doubly distilled water to make a liter of dilute solution. It required about 2600 ml for the horizontal trough and approximately 5100 ml for the vertical tank. Each time the cells were filled, three and six liters, respectively, of dilute solution were made.

For the 0.24 N $CuSO_4$, 29.966 grams of crystalized copper sulphate ($CuSO_4 \cdot 5\ H_2O$) were added to doubly distilled water to make one liter. Since drying in an oven showed practically no loss of weight (0.03% for a sample of KCl crystals) 17.89 gm of Baker's reagent grade KCl were added to water to make one liter of 0.24 N solution. The stock solution of 0.24 N HCl was prepared by diluting 19.9 ml or 36-38% reagent grade HCl (sp.gr., 1.18) with doubly distilled water to one liter of solution.

The value 0.0024 may not describe the normality to as many significant figures as recorded particularly in the case of HCl where the percentage is uncertain. However since each preparation of the 0.0024 N solution was prepared from the same 0.24 N stock solution (for a given electrolyte) the normalities are reproducible to as many figures as recorded. Furthermore the results of this work have been shown not to be critically dependent upon the concentration of the electrolyte.