MEASUREMENT OF STREAMING POTENTIALS

by

Glen Kay Korpi

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Signature of Professor in
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ABSTRACT

The method of measuring streaming potentials used by previous investigators at the M.I.T. Richards Mineral Engineering Laboratory was studied and evaluated. It was found that extraneous potentials, originating at the electrodes, interfered with streaming potential measurements in an unpredictable manner. A new measurement technique was developed which utilized an electronic recorder coupled to a Vibrating Reed Electrometer, thereby permitting accurate streaming potential measurements even in the presence of electrode polarization. The new technique is described in detail and an example of the recorded data is included.

The zero point of charge of crystalline hematite was determined and was found to lie in the vicinity of pH 6.8.

Thesis Supervisor: Professor P. L. de Bruyn

Title: Associate Professor of Mineral Engineering

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ACKNOWLEDGEMENTS

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Finally, the author acknowledges the important part played by his wife, Margaret, in the successful completion of this dissertation.

INTRODUCTION

Several investigators(1,2,3,4,5) have recently utilized electrokinetic techniques for the purpose of elucidating the structure of the double layer at solid-solution interfaces. There are several methods available for obtaining electrokinetic data and the one which has received most attention at the M.I.T. Richards Mineral Engineering Laboratory was that of measuring streaming potentials. Fuerstenau(6) constructed an apparatus which was used to study the quartz surface. Later Modi(7), who studied the corundum system and Li(8), who correlated streaming potential and adsorption data on quartz, both utilized Fuerstenau's apparatus with minor alterations. All these investigators observed an anomalous potential during the measurements, and attributed it to extreme polarization of the platinum electrodes. Consequently, a correction method was developed by Fuerstenau which was supposed to have eliminated the effect of the extraneous potentials on the actual streaming potentials. Before adopting the correction method of Fuerstenau, Modi spent considerable effort in an attempt to isolate or remove the cause of the strange electrical effects, but was unable to reach any conclusion other than that the effect was associated with the electrodes and was probably polarization. In his study, Modi also found that in electrolytes of high concentration, the correction method did not work for the platinum electrodes, but that Ag-AgCl electrodes helped to aleviate the situation.

Considerable difficulty due to extreme electrode polarization, was encountered by the author in a recent attempt to extend the streaming potential techniques to another oxide mineral system. It became evident that before streaming potential measurements could be initiated on a new oxide system, the effect of the unexplained polarization phenomena on streaming potential measurements must be eliminated, and it is, therefore, the purpose of this thesis to develop a method which will permit accurate measurement of streaming potentials in the presence of electrode polarization.

Outline of Research

The following outline briefly describes the steps taken which permitted this research project to be completed.

(1) Measurement of streaming potentials according to the method of previous investigators.

(2) Examination of data.

(3) Development and application of a new method for obtaining streaming potentials in the presence of polarized electrodes.

(4) Measurement of the zero point of charge for crystalline hematite utilizing the new method.

MATERIALS

Hematite

Pure crystalline hematite was difficult to obtain, and therefore the following five different samples were scrutinized for the most desirable characteristics.

(1) Elba crystalline, obtained from Ward's Natural Science Establishment, Inc.

(2) Michigan Specular, personal specimens, Champion Mine, Champion, Michigan.

(3) Michigan needle, Ward's.

(4) Michigan micaceous, personal specimens, New Richmond Pit, Palmer, Michigan.

(5) Labrador specular, obtained from the U. S. Steel Corporation.

The samples were examined microscopically and subjected to separation treatment in a Franz Isodynamic Separator. In samples (1) and (2), magnetite was locked with hematite at 150 mesh and since the desired size was - 35 + 48 mesh, these two samples were discarded. Samples (3) and (4) contained only small amounts of magnetite which was liberated and easily removed by the Franz Separator. The silica, held to a minimum by hand picking, was removed to a great extent by repeated passes through the Franz Separator. The final products appeared pure under microscopic examination and were assayed. The results of the assay are given in Table 1.

TABLE I

Sample	% Fe_2O_3	% FeO	% SiO_2	Total %
1. Michigan Needle Hematite	96.52	0.07	1.64	98.23
2. Michigan Micaceous Hematite	99.59	0.05	0.05	99.69
5. Labrador Specular Hematite	99.77	.05	.09	99.77

Although there was virtually no quartz in the needle hematite when observed microscopically, the assay reported 1.64 % SiO_2. The intimate association of quartz with hematite in this sample made it unsuitable for experimentation. Sample (4) could not be used because the micaceous hematite had a tendency to abrade during handling. Subsequently, the sample (5) obtained from the U. S. Steel Corporation and which was a gravity concentrate from a sugary type iron ore in Labrador, was examined. The material received was - 14 mesh and included completely liberated quartz and a small amount of locked magnetite, both of which could be removed satisfactorily by treatment with a Carpco magnetic separator.

The following consecutive steps were used in the preparation of this material as a plug in the streaming cell:

(1) Sized to - 35 + 48 mesh.

(2) Washed in boiling water to facilitate removal of slime coatings.

(3) Repeated separation or cleaning of the above size fraction with a Carpco magnetic separator until no quartz was visible under a low power microscope. The magnetite was removed by discarding any material which was attracted by low intensity magnetization.

(4) Step (2) was repeated and then the hematite was rinsed with hot KOH-alcohol solution to remove organic contaminants.

(5) Rinsed with distilled water and extracted with concentrated nitric acid for three hours in a Soxhlet extractor.*

(6) Extracted with water for 3 days with two changes of water in the Soxhlet.

(7) Material stored under conductivity water in small glass flasks.

Quartz

A number of grams of ground quartz were obtained from an unsized fraction which had been ground previously by H. C. Li. The quartz was sized to - 35 + 48 mesh and then boiled in concentrated hydrochloric acid for three hours. Steps (6) and (7) shown in the discussion of hematite above were repeated using quartz in place of hematite. The quartz was originally obtained as selected crystals from Brazil.

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* The Soxhlet extractor appears to be an ideal way to wash small quantities of ground materials or fine precipitates. Not only is the amount of conductivity water used for washing purposes reduced, but the material is continuously exposed to hot re-distilled water of high purity.

Reagents and Water

Double-distilled water (conductivity water) was prepared in a block-tin still in the Department of Chemistry. Only water with a specific conductance less than 6 x 10^{-6} ohms^{-1} cm^{-1} was used. This water was kept in four-liter pyrex bottles and dispensed by nitrogen pressure.

Acid and base solutions were made from tenth normal Acculute Standard Volumetric Solutions (Anachemica Chemicals, Ltd., Champlain, New York). Solutions made from these reagents have been checked by Parks(9) and were found to be as accurate as the titrating procedures would permit.

Prepurified nitrogen was used for controlling pressure while streaming, and was further purified by passing it through Caroxite, glass wool and water. Saturating the nitrogen with water vapor helped to eliminate evaporation of the solution in the streaming potential apparatus.

EXPERIMENTAL TECHNIQUES AND APPARATUS

Electrical Circuit and pH Measurements

The circuitry and mechanical detail of the streaming potential apparatus, which was used in the start of this study was essentially the same as was used by Li(8). This system was tested by obtaining a linear relationship between streaming potential (E) and pressure (P) as obtained by previous investigators.(6,7) This relationship was found for hematite in 10^{-4}M KNO_3 solution

The circuit was changed later and the schematic diagram shown in Figure 1 was used for both pH and streaming potentials. The L & N K2 Potentiometer was used to calibrate the scale on the Brown Electronic Recorder through a voltage divider between the amplifier and recorder, and it was then disconnected from the streaming potential measuring circuit. The potentiometer was used to measure the EMF between a glass and calomel electrode for determination of pH using the Electrometer as a null indicator. Note that this circuit did not employ "back EMF"* for measuring streaming potentials greater than the range of the potentiometer (1.6 V). Only flow potentials less than 500 mv. could be measured with this system, as this is half of the full scale deflection of the electrometer. Since the EMF was of opposite

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* "Back EMF" refers to the additional EMF (usually dry cells) needed to extend the working range of the potentiometer when the compensation method of measuring potentials is used.

polarity, each half of the scale was used for flow in opposite directions. This situation caused no difficulties. In fact, very good data was obtained at low pressures (0 to 6 cm. Hg) with small streaming potentials (0 to 50 mv, ± 0.5 mv).

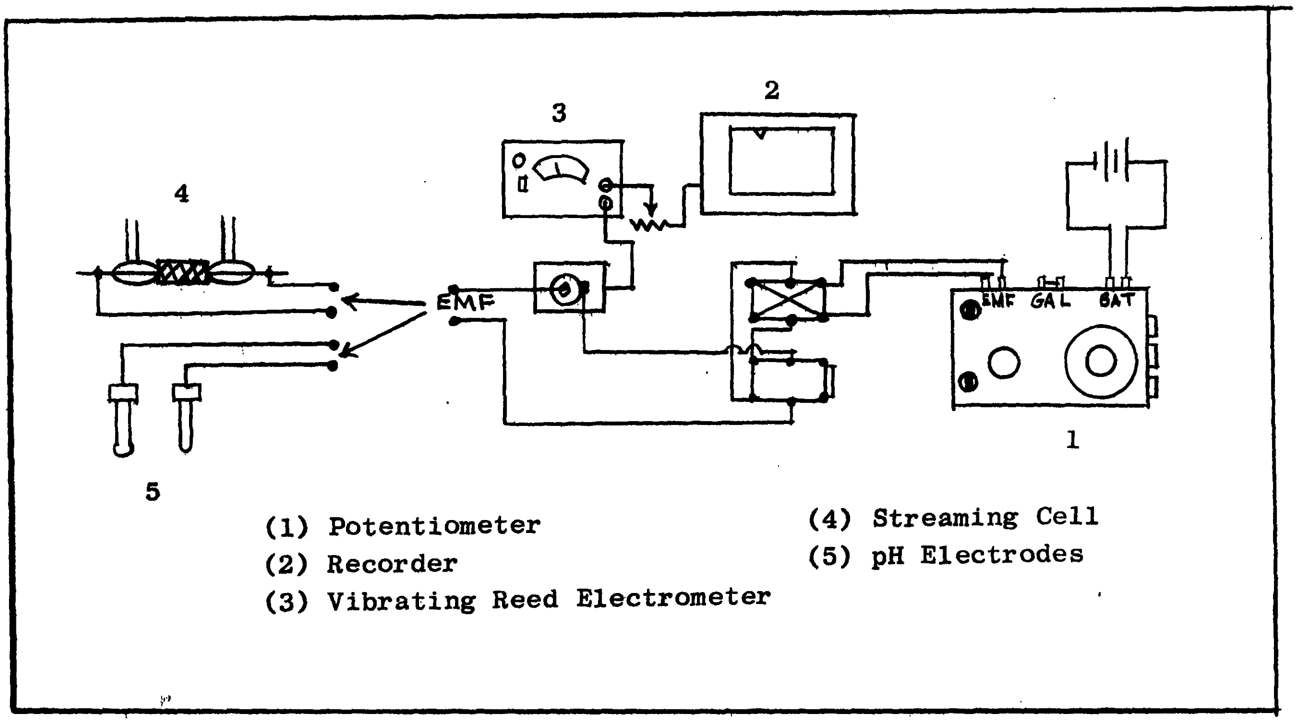

FIGURE 1 ELECTRICAL CIRCUIT FOR STREAMING POTENTIAL APPARATUS AND pH MEASUREMENT

Pressure Control

A cartesian manostat was used to control the pressure of nitrogen which in turn controlled the pressure across the streaming cell. This device made it possible to control the nitrogen pressure to within 0.1 mm. Hg. With a constant pressure across the cell, a number of runs could be made with flow being reversed at will. This type of experiment permitted a simple check of the streaming potential data by directly comparing the potentials for flow in opposite directions. They should, of course, be equal.

Resistance Measurement

Measurement of high plug resistances (i.e. resistances greater than 1 mehohm) proved to be difficult due to the polarized electrodes. The DC bridge method of balancing a potential through the plug against a known resistance and potential source was not accurate because the changing polarization potential in the plug contributed an unknown EMF to the circuit and duplicate results could not be obtained. In order that resistance measurements could be made with an AC impedance-bridge with a measurement limit of 1 megohm, a new streaming potential cell was constructed with a greater diameter and a shorter distance between the electrodes. The cell was approximately 3.8 cm. long and 2.5 cm. in diameter. The new cell had a resistance below 1 megohm, with the quartz plug and 10^{-5} M KNO_3 and all resistance measurements were made with an impedance bridge-oscilliscope type circuit described in Appendix II.

Streaming Potential Measurements

Method I

The usual technique used to obtain the streaming potential will be briefly discussed and will be referred to as Method I. Electrolyte solutions were flowed through the plug water under a known pressure which was changing slowly, due to the difference in the head of liquid in the reservoirs, as the streaming operation progressed. Potentials were read from a Leeds and Northrup K2 potentiometer at indefinite intervals until the flow of solution was to be stopped. Immediately prior to stopping the flow, the pressure was recorded and the potentiometer circuit balanced. The time at which the flow was stopped was recorded and a "no-flow" potential measurement was made exactly 60 seconds later. This procedure was repeated for a slightly higher pressure with a flow in the opposite direction. The "no-flow" potentials were applied as a correction to the measured "flow" potentials. The system which had been developed by previous investigators(6,7) for the use of the "no-flow" correction factor was as follows: if the polarities of the streaming potential and no-flow potentials were similar, these potentials were subtracted and if the polarities were opposite, the potentials were added. This method of calculation gave a straight line relationship between E and P for solutions of low concentrations, (see Figure 2) but produced anomolous curves when the solution concentrations were of 10^{-3}M and greater. If the E vs. P curve was observed to pass through the origin, the data obtained in this study were considered to be valid.

Method II

In order to eliminate the arbitrariness of the potential correction according to Method I after the flow of liquid through the plug was stopped, an electronic recorder was coupled to the Vibrating Reed Electrometer so that a continuous record of the potentials in the plug could be made.

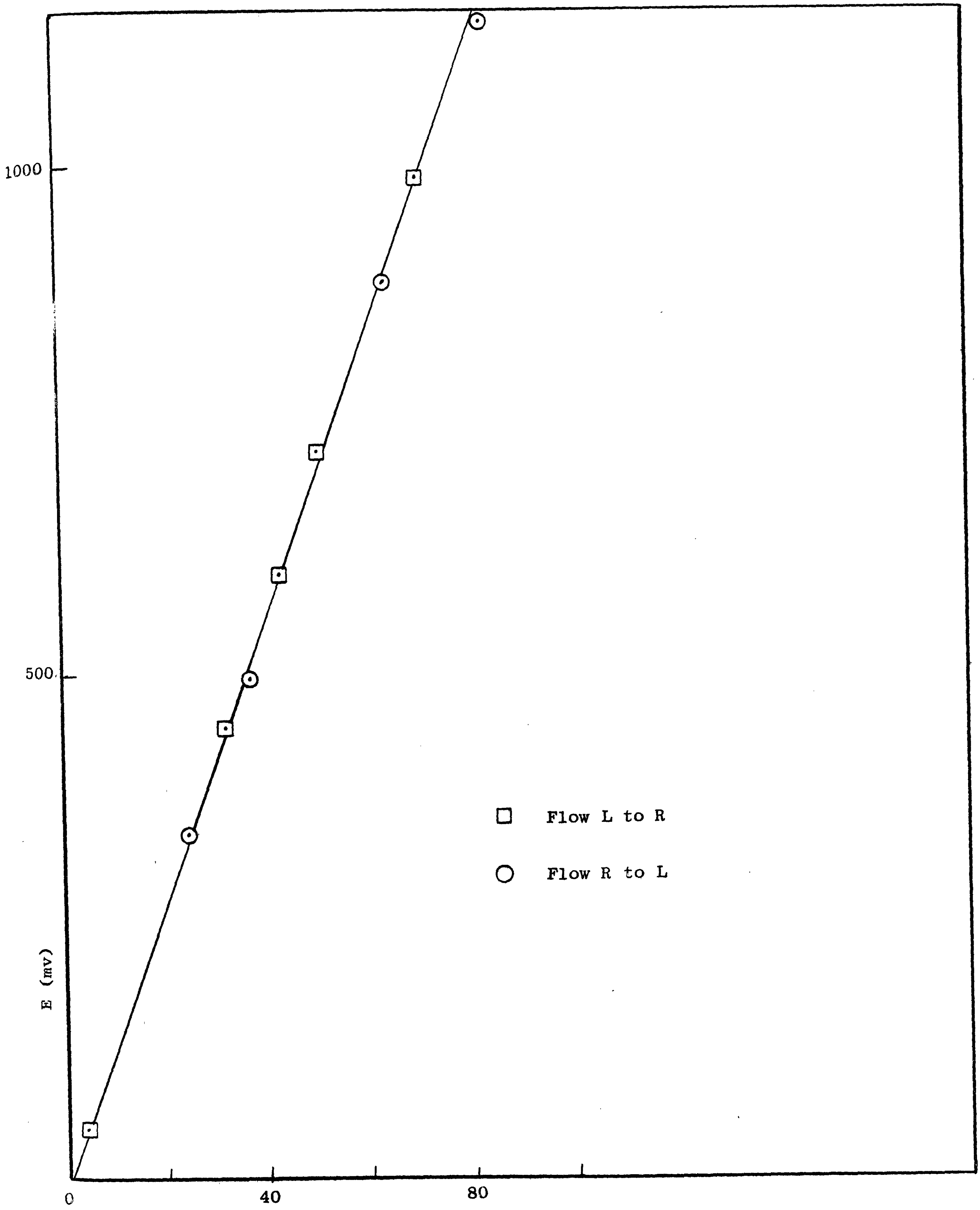

FIGURE 2 E VS. P FOR HEMATITE IN 10^{-5} M KNO_3

An example of these recordings is given in Figure 3 and 18. Figure 18 is included in the Appendix showing the actual form in which the data has been obtained. With reference to Figure 3 at time, t = 0, the solution starts flowing from right to left through the plug. At B the flow is stopped. The potential E_B is the sum of the true streaming potential and a polarization potential E_P.* The potential E_C at C is considered to be the polarization potential immediately after flow was stopped. It is assumed therefore that the algebraic difference $(E_B - E_C)$ is the true streaming potential. This method for determining the streaming potential will be known as Method II. The CD portion of the curve represents the change in E_P during no-flow conditions. Method I when used for determining the true streaming potential will obviously give an erroneous value $(E_B - E_G)$ where G refers to a point on the linear region CD, one minute after the flow was stopped. At D, approximately two minutes from C, the solution was flowed from left to right through the plug. Points B' and C' are analogous to points B and C except that the pressure had been decreased. The extended curve C'H indicated that the no-flow potential is of considerable magnitude and continues long after the flow is stopped.

Analogy to a Spring

The streaming potential system may be compared to a weight loaded spring. See Figure 4. While streaming, the spring is loaded with at least

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* No attempt has been made to define the extraneous potential in exact terms. The reference to polarization indicates that the mechanism of the "no-flow" potential is probably related to polarization.

two weights, A and B. Let A be the actual streaming potential at the pressure which the experiment is being performed, and let B be the sum of the polarization potential and any other similar potential which could possibly be developed at a platinum-water interface. Suppose the weight, B, does not remain constant, but slowly gains or looses mass much as water evaporating from or

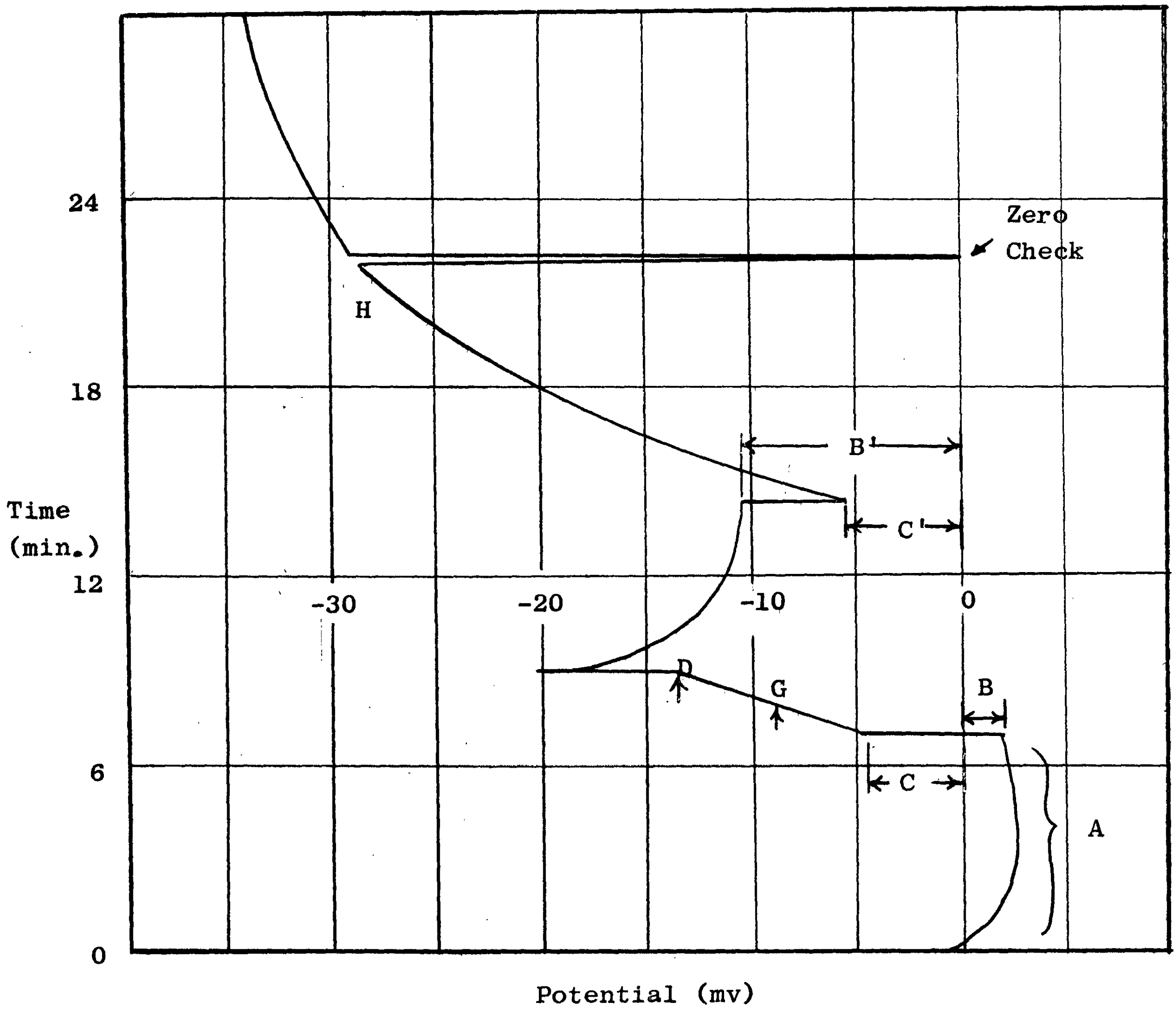


FIGURE 3 STREAMING POTENTIAL VS. TIME

condensing into a container. Therefore the pen which is attached to the spring will be tracing out a curve as time goes on, and it is possible to obtain at any time the total weight of A and B. Now if A is removed (example by stopping the flow so that there is no longer a streaming potential), the spring will move to a new position, and it would be possible to determine the magnitude of A by subtracting the final weight from the initial weight, which had been recorded by the spring's pen. The possible source of error is found when one considers by how much the weight B changes once the weight A had been removed and the spring was trying to attain a new equilibrium position. If the spring moves to the equilibrium position rapidly, and if the weight

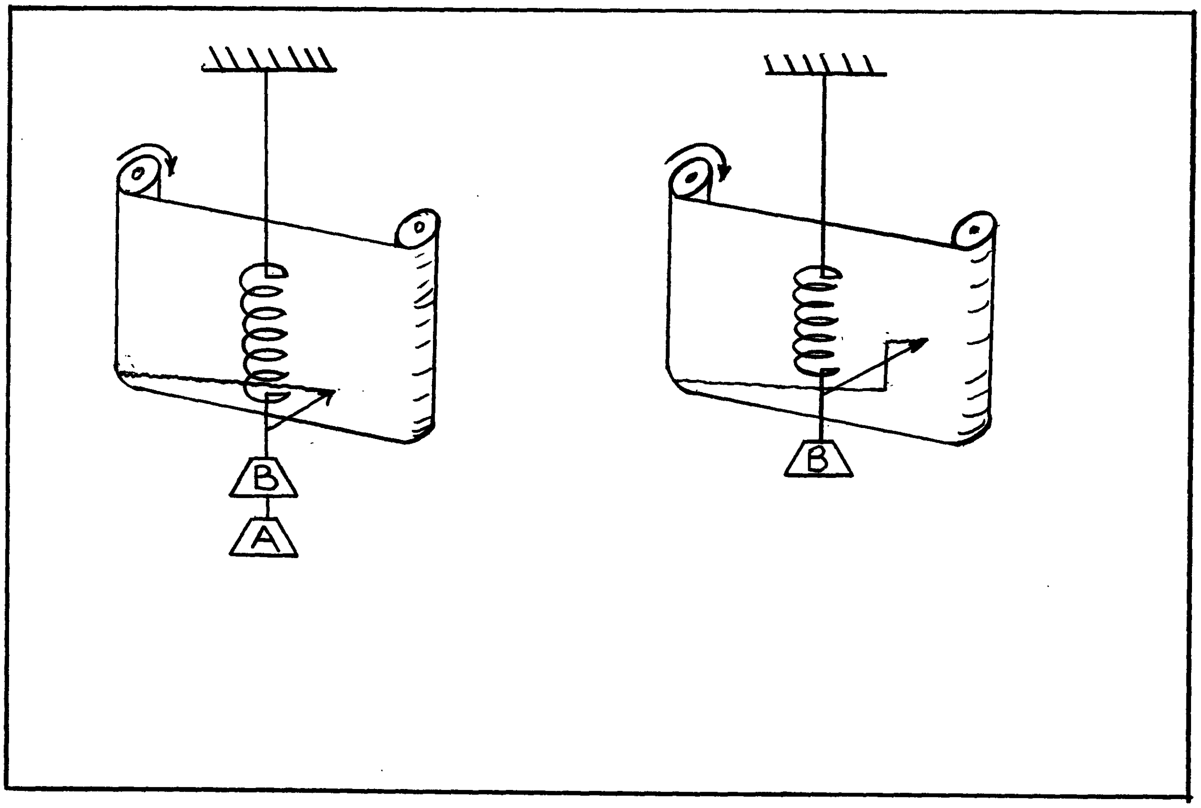


FIGURE 4 EXAMPLE SHOWING HOW STREAMING POTENTIAL DATA IS INTERPRETED

B is changing weight slowly, then it can be understood that the error involved is small.

The comparison between the weight loaded spring and the recording potentiometer is evident. The source of error in the actual system is the response speed of the recorder pen which limits the amount that the polarization potential may change while the recorder is balancing. One other possible error which must be considered is that of a streaming potential of the electrodes themselves. This effect has been investigated by G. Zucker (10) and was the primary subject of his Doctor's dissertation. This particular subject will be discussed later.

Source of No-Flow Potentials

The following steps were taken to isolate the source of the no-flow potential:

(1) Elimination of current leakage in the apparatus by adapting the circuit used by Kraus et al (11) for the continuous measurement of pH.

(2) Comparison of recorder data and direct measurement of potentials by means of a Knick DC Amplifier and microammeter instead of the electrometer.

(3) Elimination of possible polarization of the surface of material in the plug by making measurements on quartz.

The DC amplifier and microammeter were connected directly to the platinum electrodes and solution was flowed in both directions. During and after the flowing, the meter readings were read aloud by one operator and recorded by another at 10 second intervals. The meter reading, which were proportional to the potential difference across the electrodes, were plotted against time.

Ag-AgCl Electrodes

Two Ag-AgCl electrodes of identical geometry were made by plating rectangular sheets of platinum with AgCl according to Janz and Taniguchi(12). These electrodes were placed in the streaming potential apparatus as shown in Figure 5, which shows one arm of the cell assembly. The potential difference across these electrodes in solutions of a finite chloride concentration was recorded for various pressures and a subsequent test was made with the platinum disc electrodes, permitting a comparison of electrode response as well as a comparison of streaming potential data.

Measurement of ZPC of Hematite by Method II

Method II was used to determine the zero point of charge for crystalline hematite in 10^{-4} M KNO_3, with KOH and HNO_3 being used for pH control.

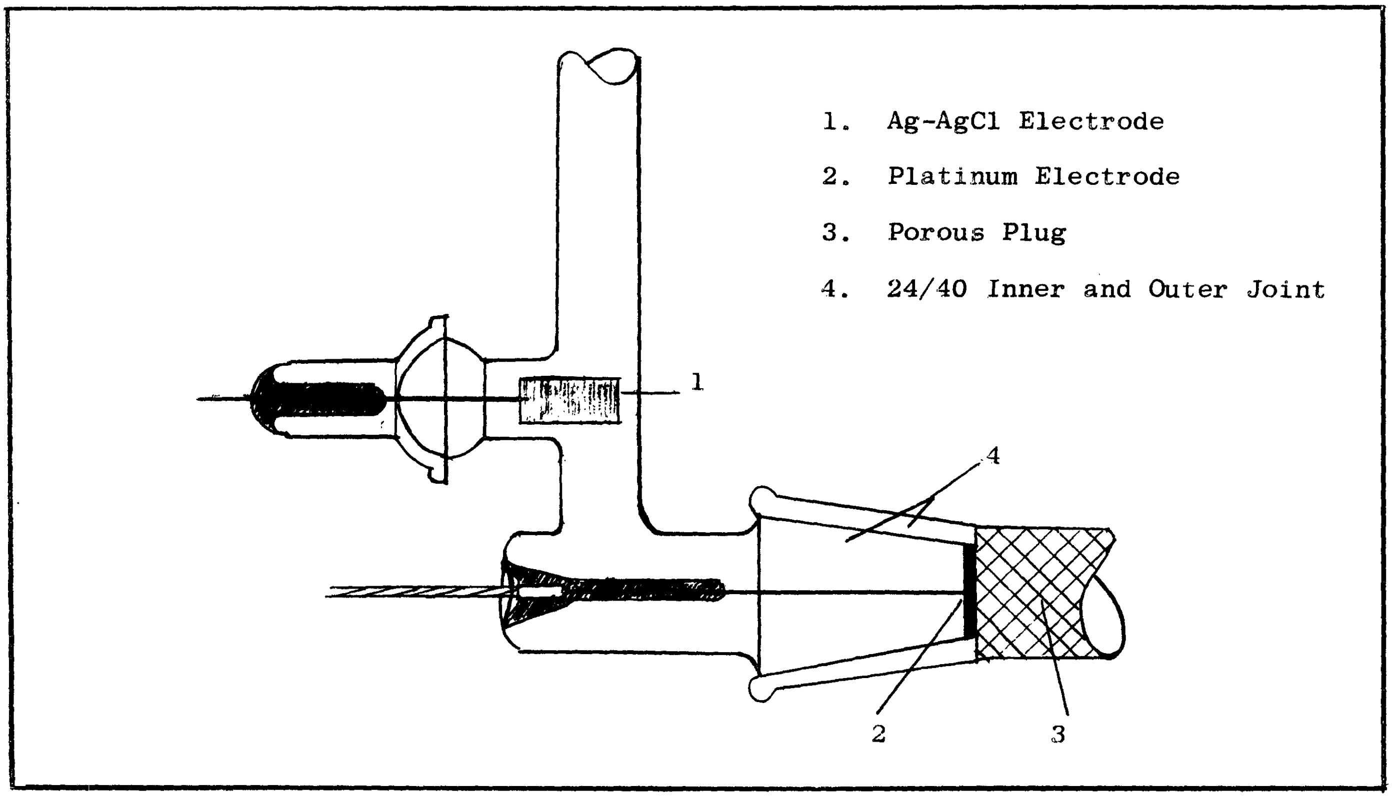


FIGURE 5 ELECTRODE ASSEMBLY

EXPERIMENTAL RESULTS AND DISCUSSION

Electrical Circuit

The new circuit was a great improvement over the old. The primary advantage was the convenience in measuring both streaming potentials and pH, but there was another advantage. Whereas previously, the high resistance part of the circuit went through the potentiometer and various switches, the new circuit needed only one high resistance shielded lead; from one side of the streaming cell to the center post (high resistance terminal) of the Vibrating Reed Head. This meant that previous effects of stray currents which necessitated elaborate shielding and grounding, were no longer possible because the only part of the high resistance circuit not incorporated into the Vibrating Reed, was that wire between the cell and Head. Standardization was accomplished by substituting a Weston Standard Cell for the unknown and changing the internal resistances of the K2 potentiometer.

Measurement of Plug Resistance

The plug resistance of the new cell was measured as a function of electrolyte concentration and the results are shown in Figure 6 where plug resistance is plotted against - log concentration of KCl. From these data, it can be seen that the resistance is below 1 megohm at concentrations greater than 10^{-5}M.

Measurement of resistance with the Impedance bridge was quite successful. Although when a measurement of standard resistance in a decade box was measured there was some discrepancy the error was small (2%).

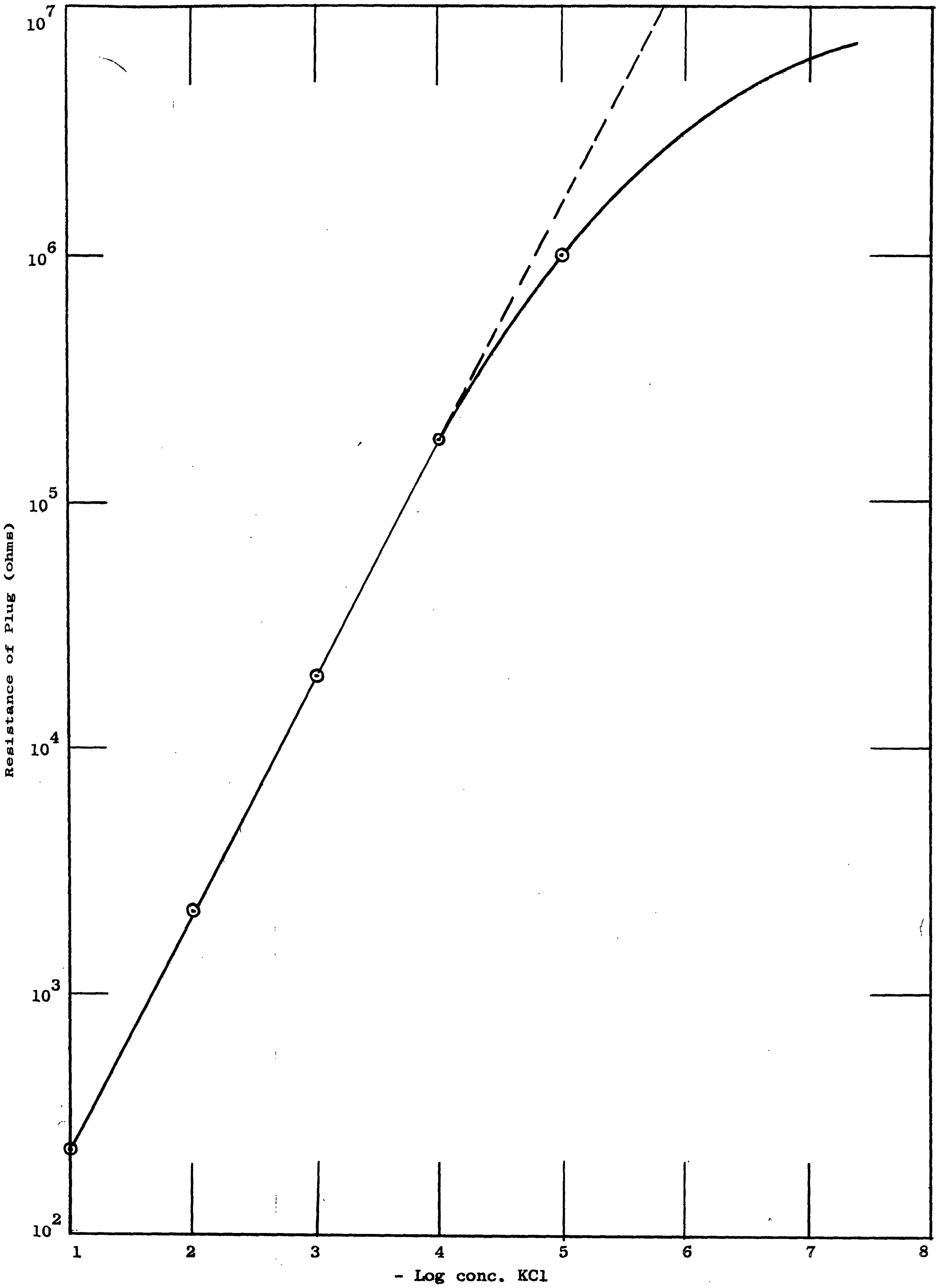


FIGURE 6 PLUG RESISTANCE VS. ELECTROLYTE CONCENTRATION

Resistance of the electrolyte in the plug is used in calculating the zeta potential where the surface conductance of the mineral is appreciable. The contribution of the surface conductance to the conductance of the electrolyte in the plug is normally compensated by the use of a cell constant, as can be seen by the discussion in Appendix I. If the total conductance of the mineral does not contribute an appreciable portion to the total conductance at the concentration at which streaming potentials are being measured, the actual specific conductance of the solution may be used in calculating zeta potentials. As the concentration of the electrolyte in the plug increases, surface conductance of a dielectric solid becomes less dominant and finally contributes a negligible fraction of the total conductance of the system. It was believed that the maximum point in the zeta-potentials versus log concentration would be an indication where the surface and bulk conductance (in the case of conductors or semi-conducting materials) begin to diminish in importance. With reference to Figure 6, it can be seen that the concentration of KCl where the surface and bulk conductance of the hematite in the plug contributes to the total conductance is approximately 5×10^{-4} M. Therefore, zetz potential measurements for hematite should be made at concentrations 10^{-4} M or greater. It is interesting to note that in Figure 10 the concentration where the zeta potential for quartz begins to reach a maximum is 10^{-4} M. This would seem to indicate that the surface and bulk conductance of hematite are no greater than that of quartz in solution of 10^{-4} M or greater.

Streaming Potential Measurements

Method I: Method I was used with apparent success for determining streaming potentials of both quartz and hematite in solutions of low concentrations. Data, when plotted as E vs. P gave a straight line (See Figure 2) and zeta-potentials for quartz were the same as those reported by previous investigators. (See Figure 10). As long as the E and P data produced the straight line which is predicted from theory, no doubt was cast on the validity of the streaming potential data.

When E vs. P data for streaming from right to left began to disagree with data for opposite flow, some explanation was needed. One test, started at very low pressures, produced the interesting curves shown in Figure 7. The streaming potentials at low pressures behaved erratically but the symmetrical change of potentials with increase in pressure suggested possible polarization of the platinum disc electrodes. At higher concentrations (greater than 10^{-3} M) results were worthless as far as calculation of zeta potentials were concerned because of the diverging nature of the E vs. P data. (See Figure 8). The concentration limit mentioned above, is near that mentioned by Modi,(13) when he attempted streaming potential measurements on corundum, and it is most probable that the anomolous effects observed in this work are the same as those observed by Modi. Disagreement of data for flow in opposite directions has also been observed by Mular(14)

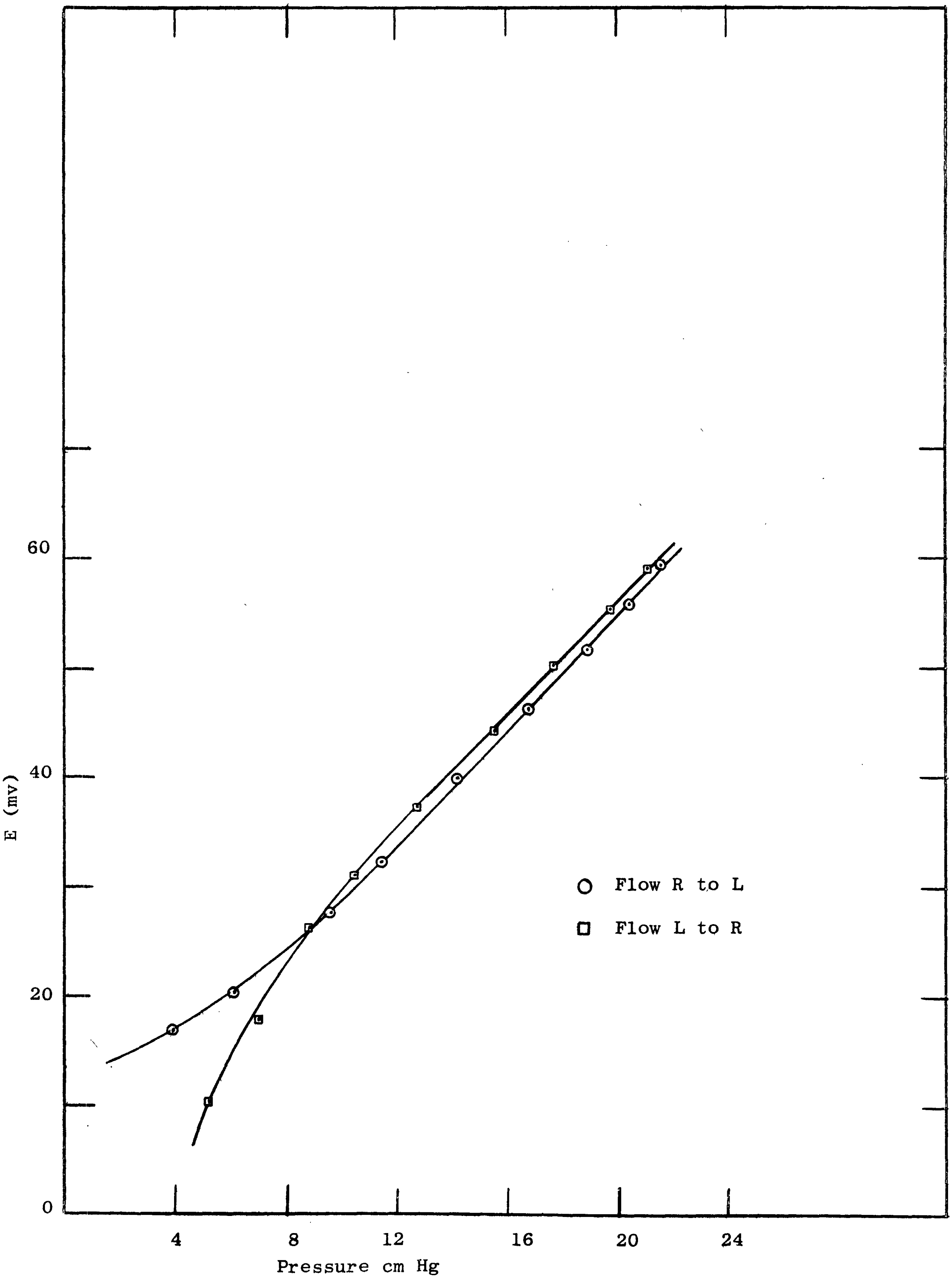


FIGURE 7 E VS. P FOR HEMATITE IN 10^{-3} M KNO_3

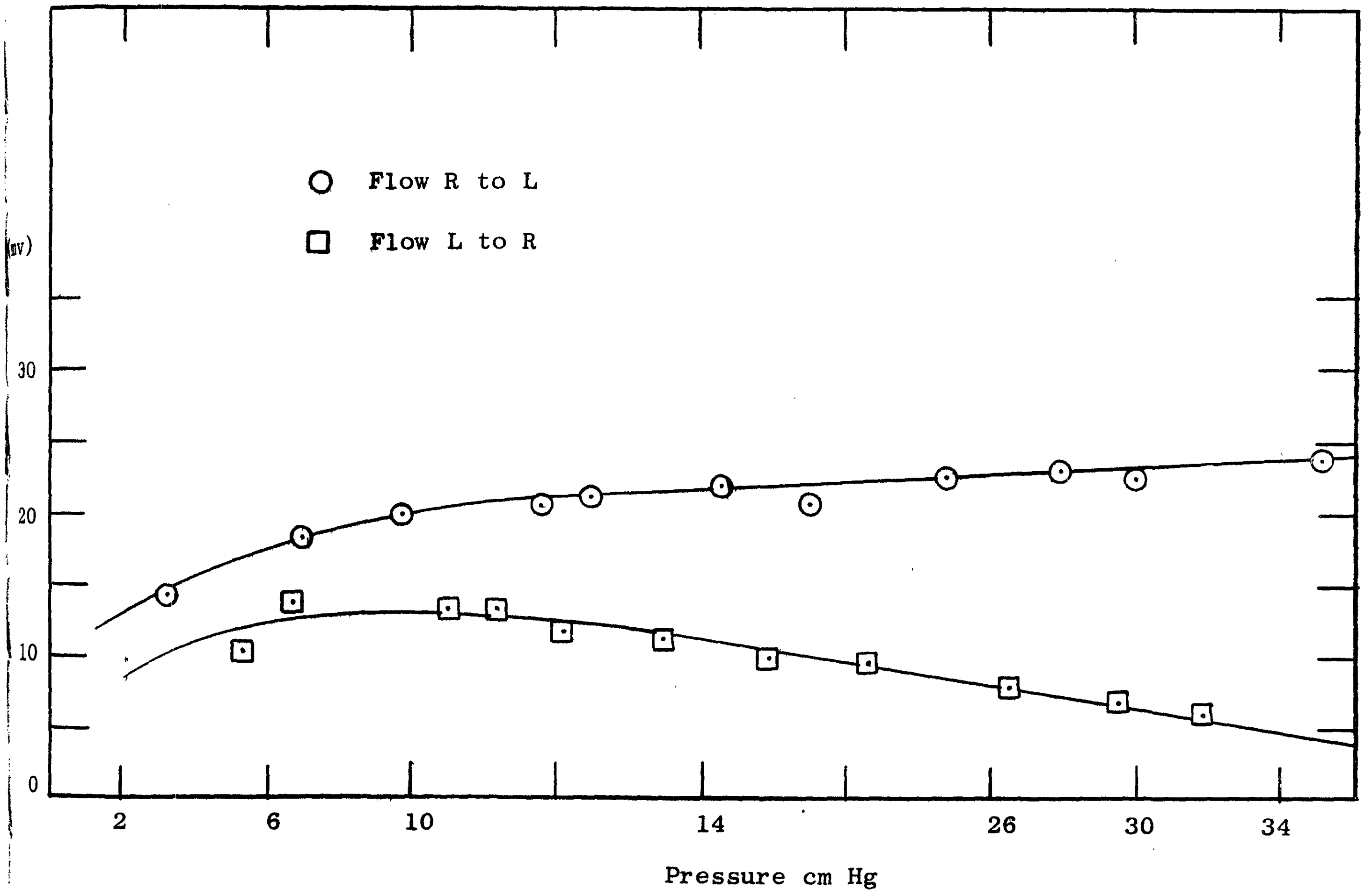


FIGURE 8 ANOMALOUS E VS. P RELATIONSHIP FOR HEMATITE IN 10^{-2} M KNO_3

who used platinum disc electrodes for investigating the manganese dioxide system in a streaming potential apparatus built on Fuerstenau's design. Mular also suggested that the irregularities were due to electrode polarization.

Method II: In connection with these devious results, it was noticed that when the flow was stopped there was an immediate deflection of the needle in the Vibrating Reed Electrometer followed by a slow drift to some other value. There was some concern about the significance attached to the unsteady movement of the Electrometer's potential indicating needle, and an attempt was made to obtain additional information by observing the movement of the needle by eye and then rapidly writing down the numerical readings. After a number of unsuccessful attempts, an Electronic Recorder was coupled to the Vibrating Reed Amplifier which permitted continuous recording of both streaming or "flow potentials" and "no-flow" potentials.

With Method I, no reasonable streaming potential data could be obtained at concentrations greater than 10^{-3} M, but with Method II, E vs. P data appeared to be valid, as the data gave a single straight line passing through the origin. Many tests have been made with Method II and the potentials for opposite directions of flow were equal for the same pressure.

The streaming potential data obtained by Method II for hematite in 10^{-2} M KNO, are plotted in Figure 9 against pressure (P) in cm. Hg. These results were taken from an extended recording (much like that of Figure 18) of which a part is shown in Figure 3. Note that when the actual streaming potential is taken according to Method II a single straight line (A) is

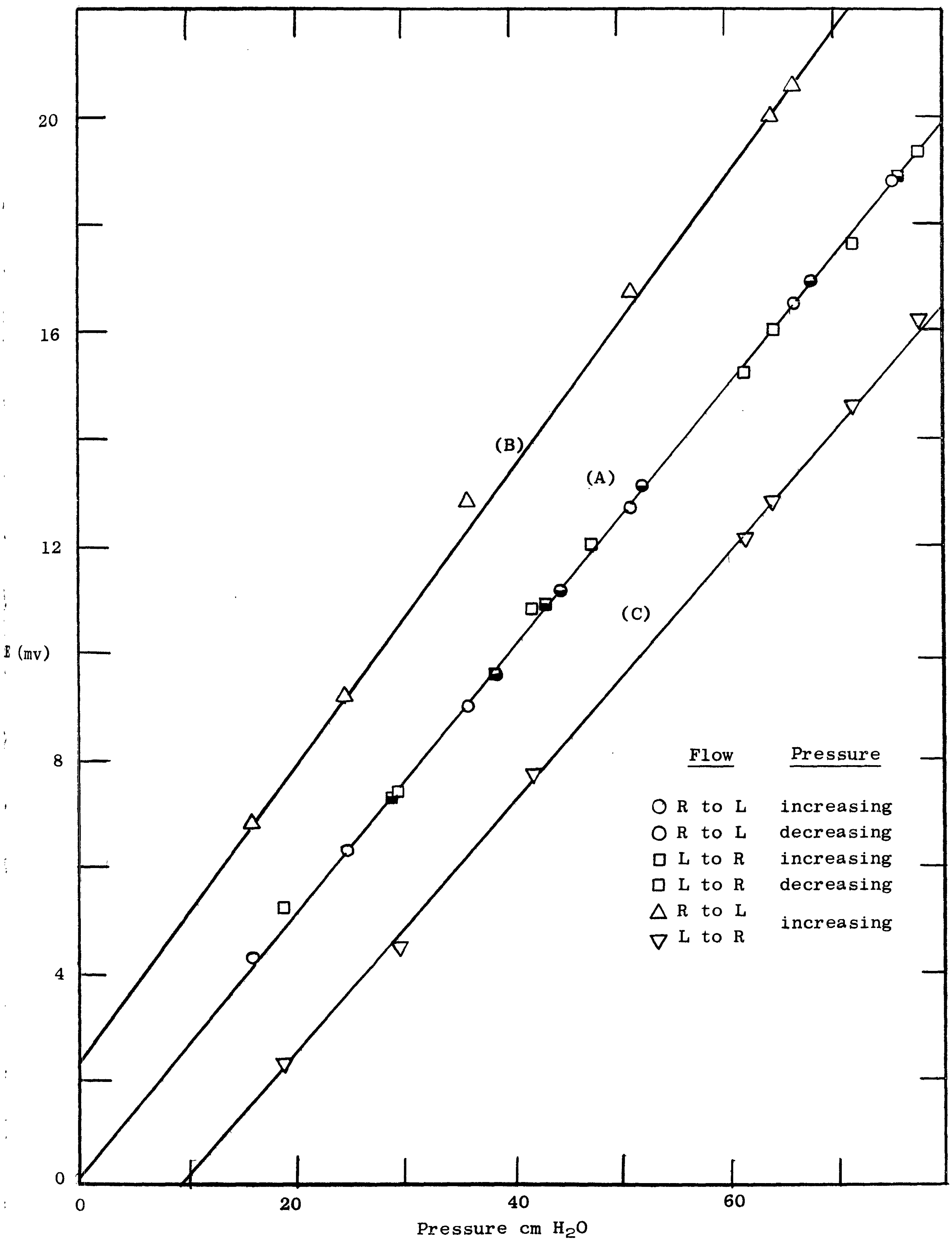


FIGURE 9 E VS. P FOR HEMATITE FOR DATA OBTAINED BY METHOD I AND METHOD II DURING THE SAME TEST

obtained. But when the streaming potential is determined by Method I, two separate lines (B and C) are obtained, one for each direction of flow. This separation of curves has been observed by the writer in previous tests (see Figure 9) as well as by other investigators(7,14) who used Method I to obtain streaming potentials. The single line (A) does not pass through the origin and although the error is small (± 0.2 mv.) larger discrepancies have been observed in other tests. The author is of the opinion that these errors were due to a lag in the response of the recorder pen when a rapidly changing potential was introduced. Consequently, the recorder was equipped with a faster pen response motor. This enabled a more accurate recording of the rapid change in the potential when the flow through the plug was stopped. It has been shown (Figure 3) that this change in potential will be considered as the actual streaming potential.

A series of measurements were made to determine the zeta-potential of quartz in various concentrations of $NaNO_3$ by Method II. The same series of measurements were made by Method I and the results are given graphically in Figure 10 as zeta potential vs. concentration along with measurements made by Li for the same system. The results obtained by Method I agreed with the data given by Li, but for concentrations greater than 10^{-4} M, the results obtained by Method II do not agree with either Li or Method I.

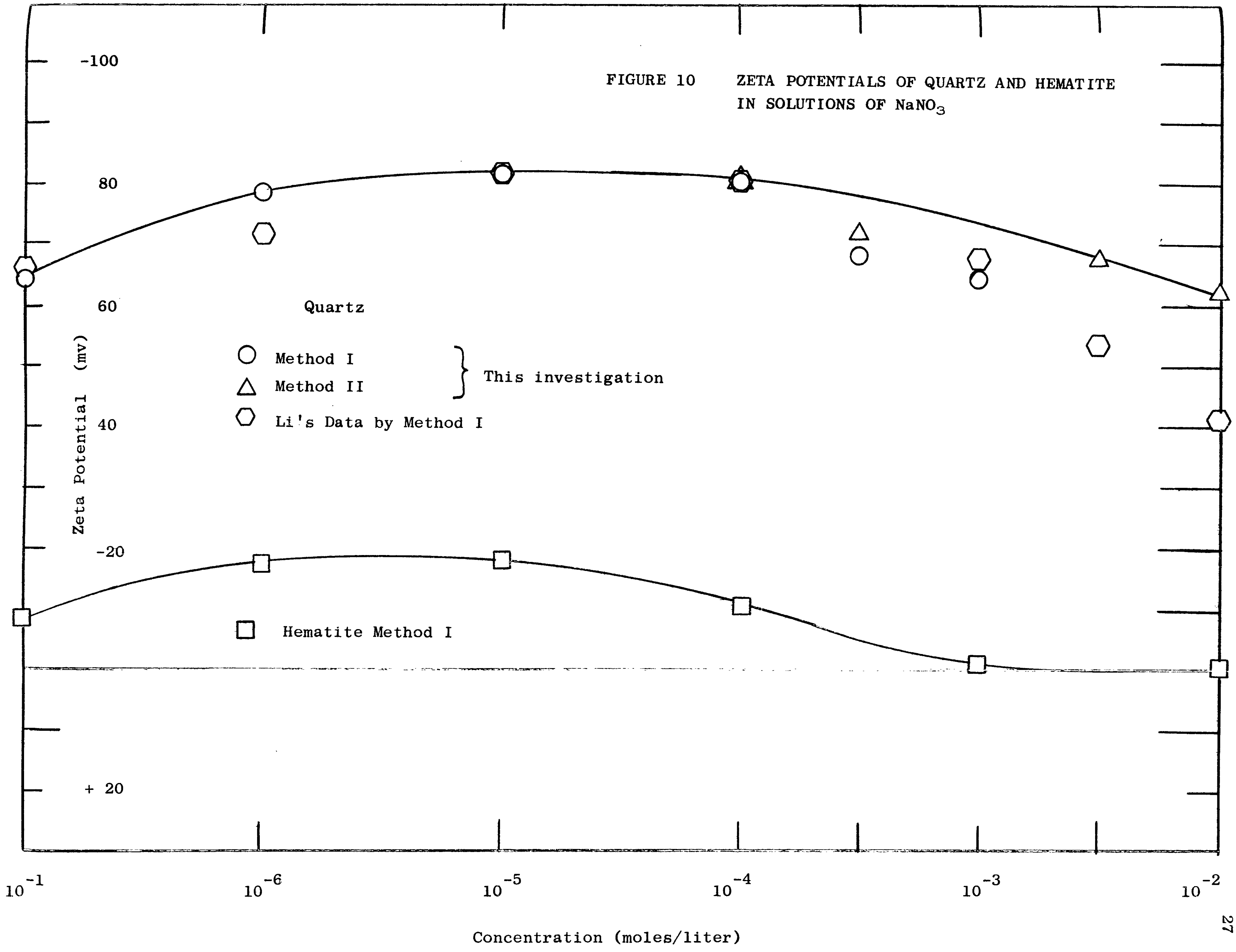


FIGURE 10 ZETA POTENTIALS OF QUARTZ AND HEMATITE IN SOLUTIONS OF $NaNO_3$

No Flow Potentials

After changing the electrical circuit (see page 8) and using quartz in the plug, several streaming potential measurements were made. The results were essentially qualitative and were obtained by comparing data previously obtained to data obtained after the changes had been made. There was no difference between the type of recording patterns obtained.

The data obtained with the Knick amplifier and microammeter are given in Figure 11 as millivolts vs. time. The shape of the potential vs. time curve for flow in both directions, was directly comparable to the shape of the potential vs. time curves obtained by Method II (see Figure 3). Thus, it could be ascertained that the polarization potential could not be attributed to a current leakage in the electrical measuring circuit.

After quartz was put into the plug and the electrical circuit simplified with all possible current leaks eliminated, sodium nitrate solution (10^{-3} M) was flowed through the plug for a preliminary look at recorded streaming potential data. The results were excellent. The recorded potential pattern obtained is shown in Figure 12. However, when the concentration was increased above 10^{-3} M, the familiar type of pattern shown in Figure 3 appeared again. It was then decided to make a detailed investigation of the streaming potential on quartz while changing the solution composition from pure conductivity water to a 10^{-2} M $NaNO_3$ solution while making a continuous recording of the potential versus time changes. The ideal pattern shown in Figure 12 where no potential was

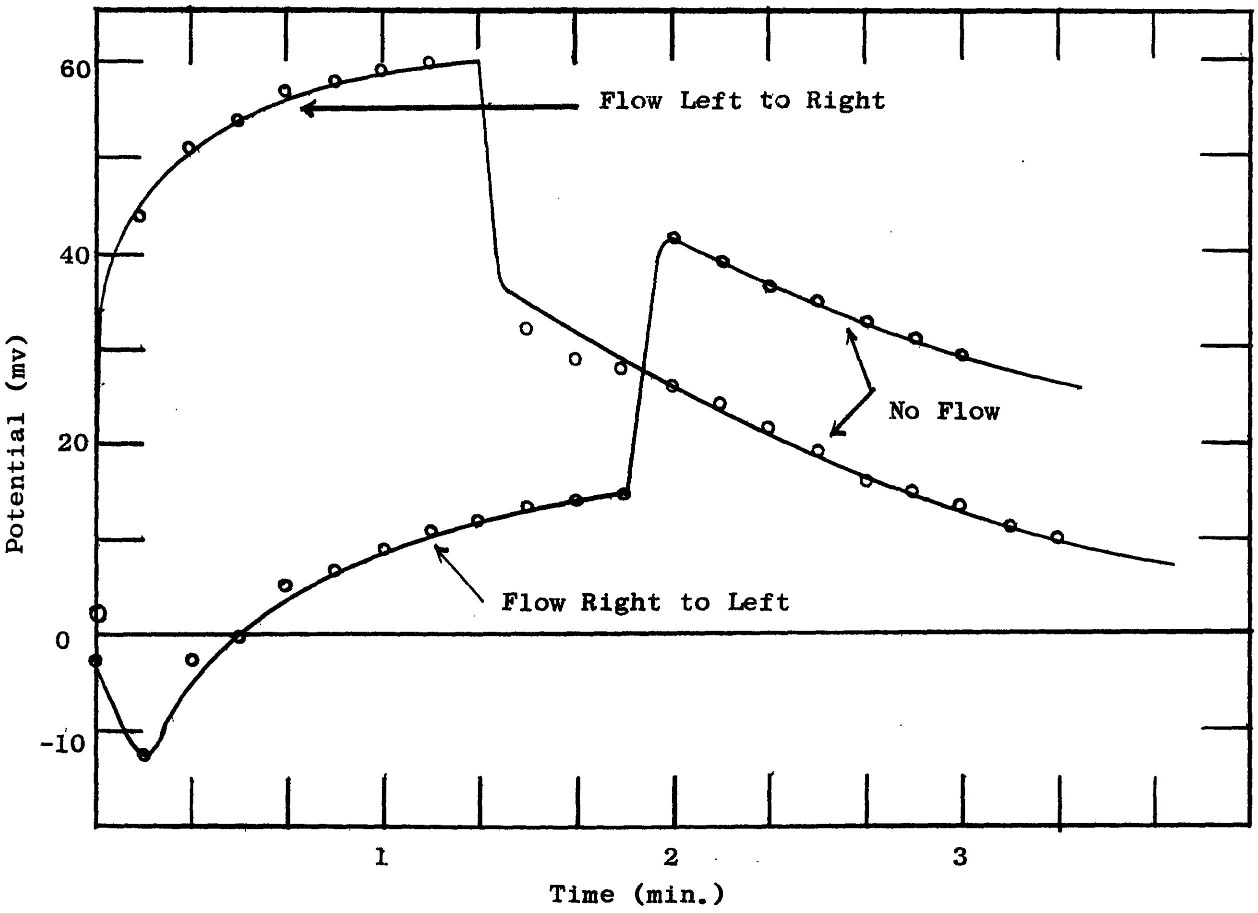
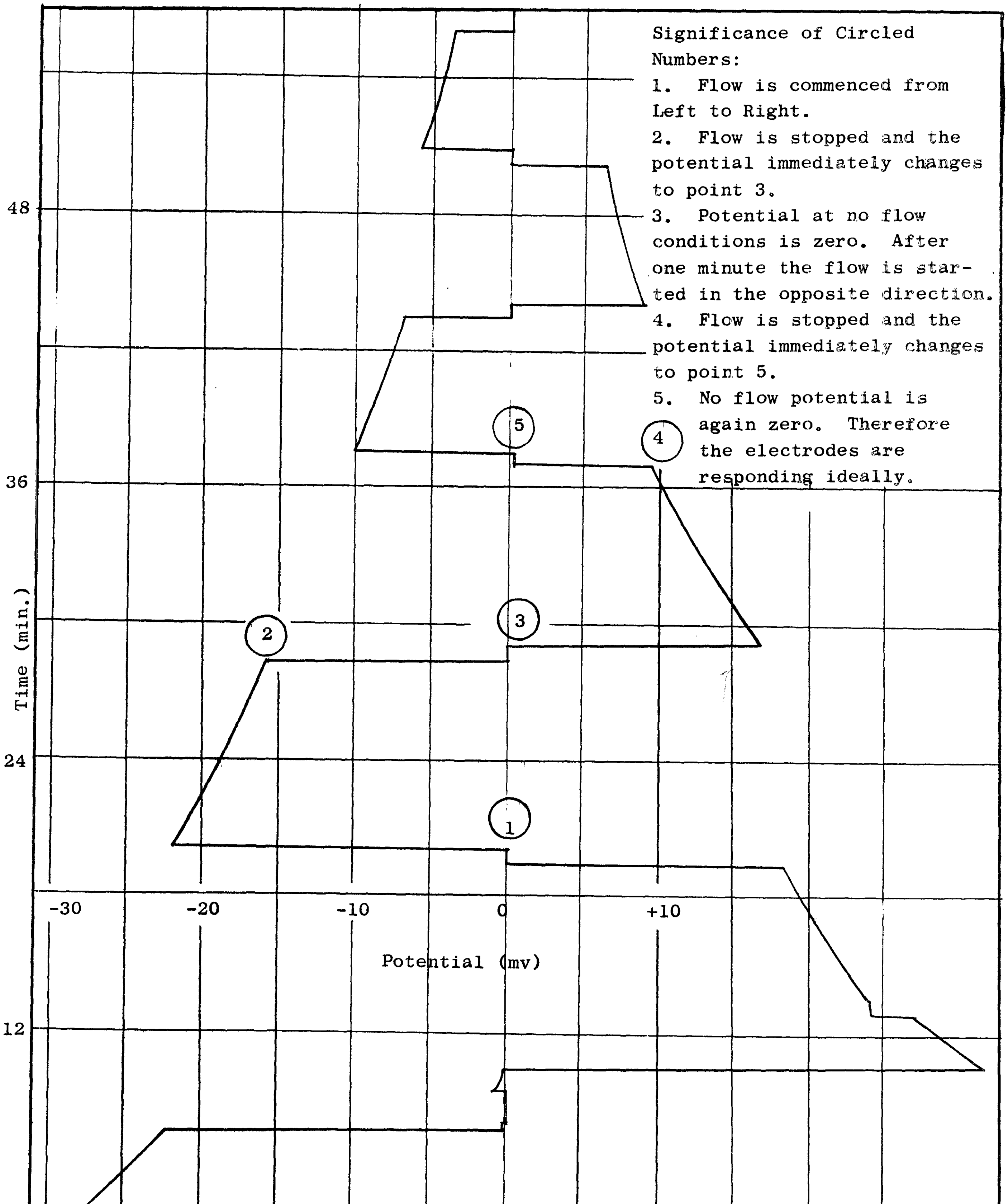


FIGURE 11 POTENTIAL VS. TIME AS MEASURED WITH A DC AMPLIFIER

developed during no-flow, was never observed in this test, nor was it observed again throughout this investigation. The calculated zeta potential vs. log concentration curve for this run was shown in Figure 10.

Figure 10 shows that data obtained by Method II during the same run deviates at concentrations greater than 10^{-4} M. This was as expected since at low concentrations the streaming potential was large compared to any correction which would be applied according to Method I, and the effect of polarization was negligible. But at concentrations greater than 10^{-3} M, the



Significance of Circled Numbers:

1. Flow is commenced from Left to Right.
2. Flow is stopped and the potential immediately changes to point 3.
3. Potential at no flow conditions is zero. After one minute the flow is started in the opposite direction.
4. Flow is stopped and the potential immediately changes to point 5.
5. No flow potential is again zero. Therefore the electrodes are responding ideally.

FIGURE 12 STREAMING POTENTIAL VS. TIME AT DECREASING PRESSURE FOR QUARTZ IN 10^{-3} M $NaNO_3$

streaming potentials were very small and the polarization potentials became controlling, leading to such data as illustrated in Figure 9 when determined by Method I.

Examination and Evaluation of Experimental Techniques

The streaming potential recorder data for both quartz and hematite systems has been carefully examined on several occasions, and the results will be discussed below. If the curves in Figure 13 are referred to, it can be seen that the polarization may be directly connected with flow conditions* by considering the following: If it can be assumed that actual streaming potentials are established in relatively short times (1 to 2 seconds max.) then any change in potential between the electrodes could be assumed to be due to polarization. If the total or flow potential does not change with time, the sum of the streaming potential and polarization potential remains constant. Now when the flow is stopped, the potential immediately changes, and then slowly continues to change towards a mysterious equilibrium value. If the polarization potential was not associated with flow, it would be reasonable to expect that the no-flow potential would reamin fairly constant. However, the no-flow potential does change. The fact that the polarization potential may become constant during flow, but then does not remain constant once the flow is stopped, definitely indicates that the polarization effect may be connected in some manner to the flow. What the relationship is, between the polarization potential and flow, has not been determined.

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* By "flow conditions" the author refers to solution flow through the plug <u>and</u> electrodes, as well as the potential present due to streaming.

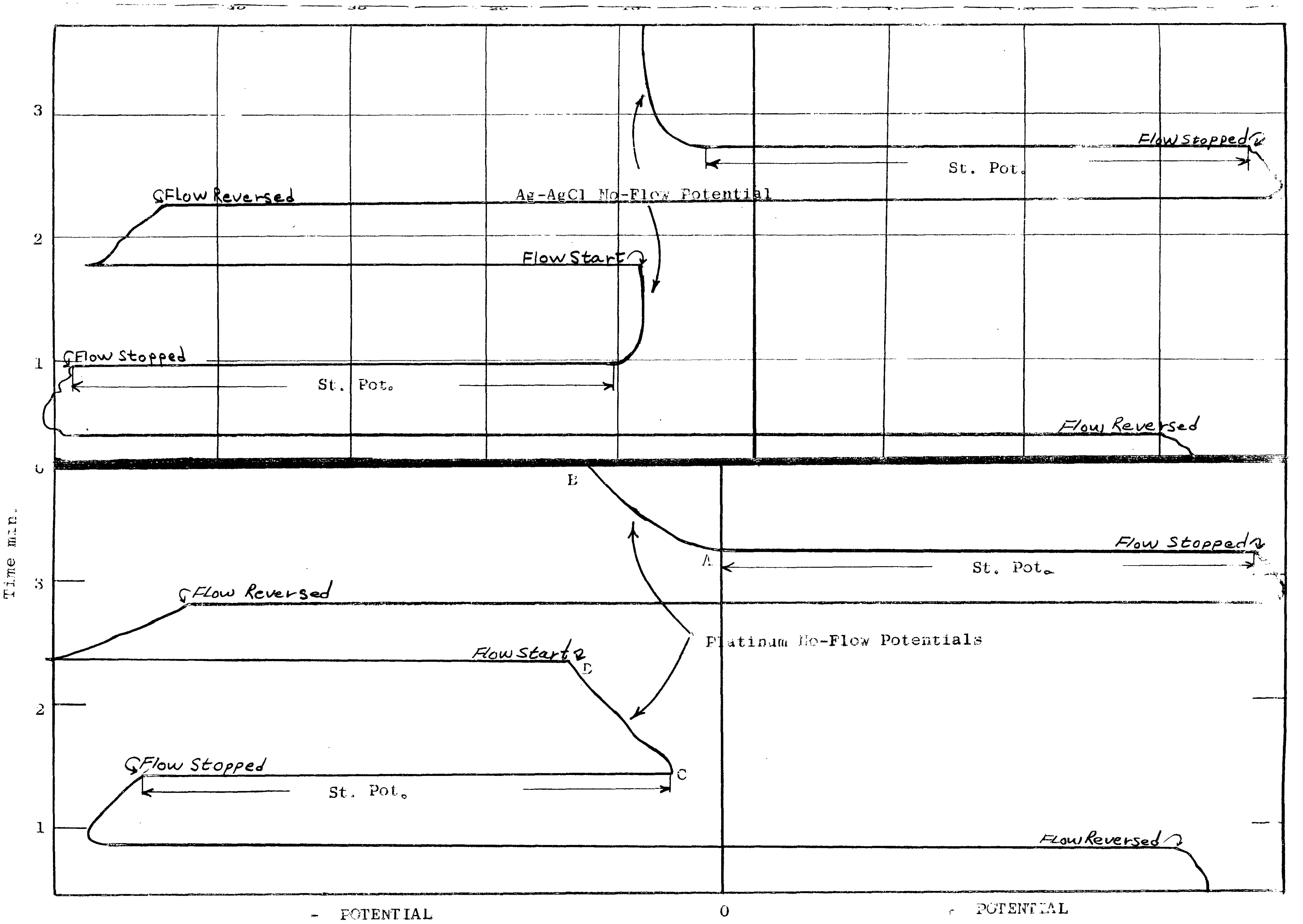

FIGURE 13   POTENTIAL VS. TIME. COPY OF RECORDER DATA FOR Ag-AgCl AND PLATINUM ELECTRODES

The way in which the potential change occurs once the flow has been stopped is interesting. Referring to Figure 13 it can be seen that the potential changed rapidly from A to B, but then slowly decreased with time. Often it has been quite difficult to determine exactly where the potential curve started to change, but not always so. Fortunately, the no-flow potential does not trace a similar pattern when the flow in the opposite direction is stopped. In the latter case, the no-flow potential change was in the opposite direction to the rapid changd C to D and the end point was quite easily determined. It is thought that the slow curve exhibited in Figure 13 at A to B, and C to D, indicates that part of the no-flow potential which is caused by the effect of flow passed the electrodes, and that the near-linear portion of the no-flow potential is due to pure electrode polarization. The important point to be made was that in any case, both types of potential change occur slowly, and the amount of potential change during the time which it takes the recorder to balance, was negligible. The actual error involved was reading the end points, and was approximately ± 0.5 mv. on the 100 mv. scale.

The time at which the flow was stopped was arbitrary. If the solution was flowed until one of the reservoirs was empty, and the difference in the level of liquids applied to the pressure as a correction, the E/P value obtained will be the same E/P obtained if the flow had been stopped when the levels were equal. Stopping the flow when the levels are equal, simplifies calculation as no pressure correction is needed.

Ag-AgCl Electrodes

Streaming potentials on quartz were measured by Method II as a function of pressure and pH with Ag-AgCl electrodes and platinum electrodes concurrently. The data for both electrodes were plotted as streaming potentials (E) against pressure (P) and these data are shown graphically in Figure 14 for pH values of 7.6 and 5.4. The system was ground quartz (- 35 + 48 mesh), 5×10^{-4} M KCl, with HCl and KOH for pH control.

If data are taken according to Method II, and then plotted as E vs. P, a straight line can be obtained which passes through the origin. This evidence presents a good case concerning the validity of the streaming potential data and methods. However, it was decided to check the results.

Modi(7) and Zucker(10) have reported an improvement over the platinum electrodes by using Ag-AgCl electrodes while streaming with solutions containing a finite concentration of Cl^- ions.

If Ag-AgCl electrodes could be incorporated into the streaming potential apparatus, the data from the Ag-AgCl electrodes could be compared with data obtained from platinum electrodes. If the data agreed, there would then be some supporting evidence that the platinum electrodes could be used in conjunction with Method II and would give a true indication of the streaming potential in the presence of polarization potentials. The data obtained with the Ag-AgCl electrodes should be free from error due to polarization as they are reversible so long as they are in chloride solutions.

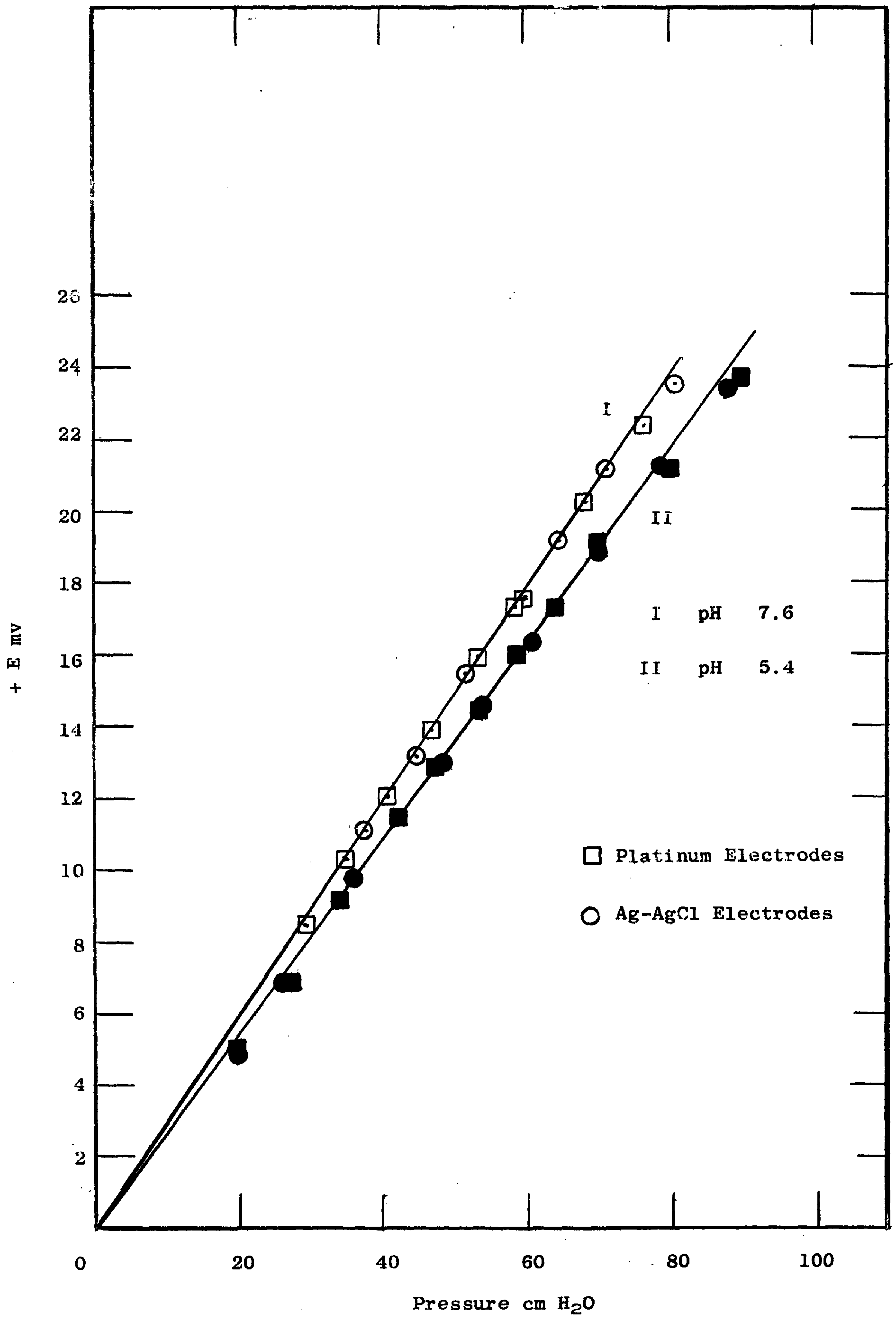

FIGURE 14 COMPARISON OF PLATINUM AND Ag-AgCl ELECTRODES IN STREAMING POTENTIAL MEASUREMENTS

From Figure 14 it can be seen that the data obtained from the Ag-AgCl electrodes are identical to those obtained from the platinum electrodes. The significance of this reproducibility is that platinum electrodes, even with the polarization effect present, gave the same data as did the Ag-AgCl electrodes, which did not show polarization. Figure 13 which shows potential as a function of time, has been taken from an actual recording obtained from the test above. The pressure was held constant. The top portion of Figure 13 is from the Ag-AgCl test and the bottom from the platinum test. From a comparison of these recordings it could be seen that the potential associated with flow was present for both electrodes. This is reasonable since the Ag-AgCl electrodes projected slightly into the flow as can be seen from Figure 5. The obvious difference in the recordings is the absence of a polarization potential in the case of the Ag-AgCl electrodes. There is, however, a constant potential difference between the electrodes, some time after the flow has been stopped. No definite reason could be found for this potential and it was assumed that it was an asymmetry potential. The method for determining the streaming potential from this recorder data was the same for both tests and has been discussed previously. The streaming potential so determined is indicated in Figure 13.

Measurement of ZPC of Hematite with Method II

The zero point of charge of hematite was determined by measuring streaming potentials as a function of pH, and then plotting the experimental quantity E/RP vs. pH, as in Figure 15.

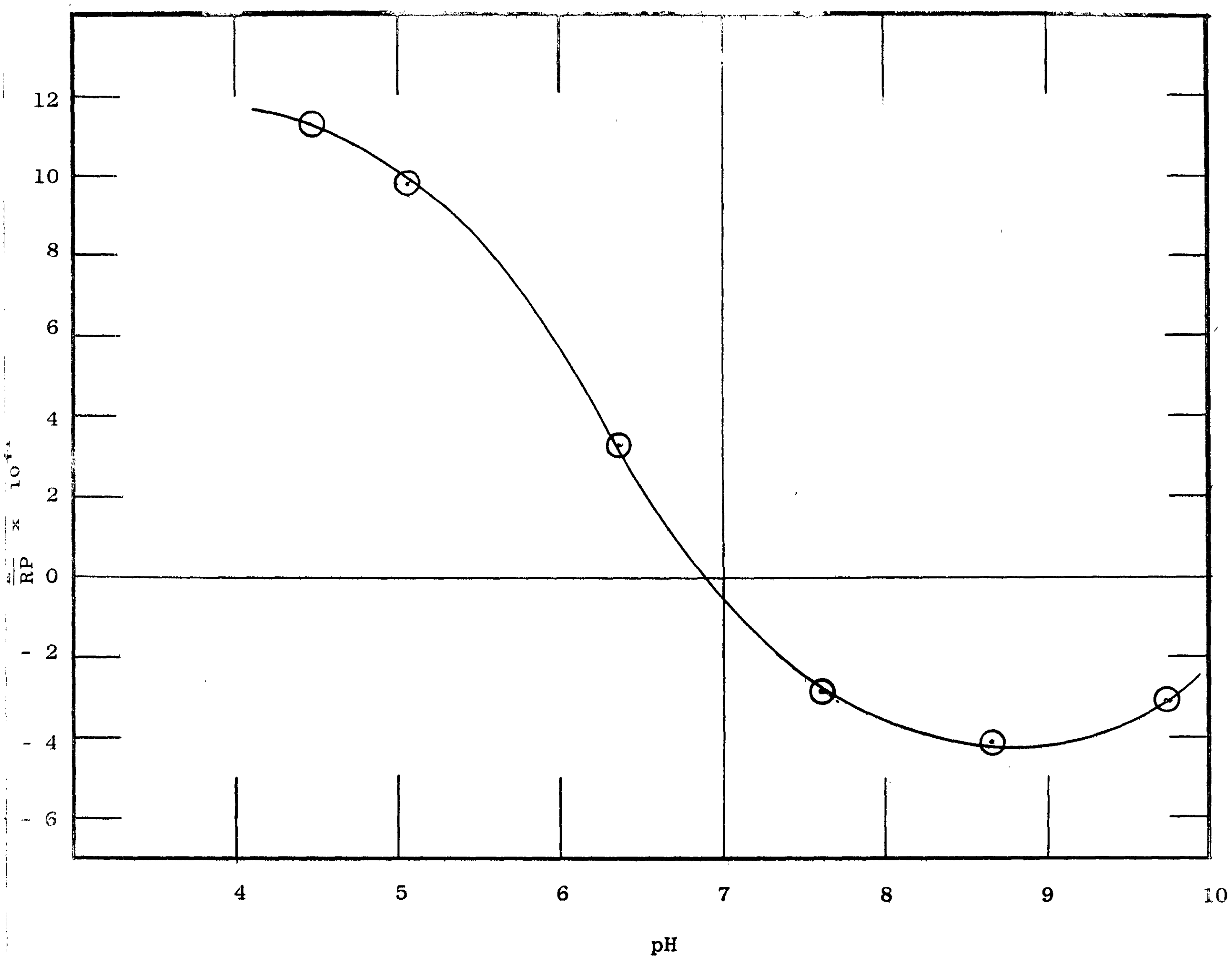

FIGURE 15 $\frac{E}{RP}$ VS pH FOR HEMATITE IN 10^{-4}M KNO_3

When solutions of electrolytes were flowed through a hematite plug, recorder data produced potential vs. time curves very similar to those curves obtained for quartz. Figure 14 graphically presents the data obtained for hematite as E/RP vs. pH, where E is the streaming potential at the pressure P in cm. of Hg., and R is the resistance of the plug at the given pH. The value of E/P was obtained by taking the slope from an E vs. P plot for each concentration change. The quantity E/RP is directly proportional to the zeta potential (see Appendix I), and for the purpose of locating the zero point of charge (zpc), should be more accurate than plotting the zeta potential because the error in determining the cell constant has been eliminated.

The system was ground hematite (- 35 + 48 mesh), 10^{-4} M KNO_3, with HNO_3 and KOH being used for pH control. The E/RP = 0 intercept is approximately at pH 6.8 and indicates the pH where the surface of hematite has zero charge. This value for the pH of the zpc is in good agreement with that determination of Iwasaki(15) and Johansen and Buchanan(16). Their value was 6.7, and was obtained by electrophoresis.

SUMMARY AND CONCLUSIONS

Summary

This investigation was initiated by studying the electrokinetic properties of hematite. The streaming potential apparatus of Li, Modi and Fuerstenau was assembled and made operational, and then quartz and hematite minerals were prepared for the plug. A few trial runs were made with hematite using the "correction method" for determining the actual streaming potentials. This method was necessary because an extraneous potential, which was present during and after streaming, interfered with streaming potential measurements. It became obvious that the correction method did not work when the concentration of the streaming electrolyte was greater than 10^{-3} M because of a diverging nature of the data when it was plotted as potential vs. pressure. The data should have given a straight line, but often produced separate lines of different slope for each direction of flow.

A Brown Electronik Recorder was coupled to the Vibrating Reed Amplifier and a continuous recording of the streaming potential was obtained. By analyzing the recordings, it was possible to determine what the actual streaming potential was and what the polarization potential was. When the actual streaming potential data, for concentrations of 10^{-6} M to 10^{-1} M, were plotted against the pressure at which the data was produced, straight lines were obtained which passed through the origin. This was a definite improvement over the old method of determining streaming potentials, and the research effort was concentrated on improving the new experimental technique.

The circuitry of Li was simplified, a cartesian manostat installed, and the operation of the recorder maximized. A new cell was made and installed in the apparatus. The simplified circuit eliminated the effects of stray currents and permitted the use of the Electrometer for pH or streaming potential measurements. The cartesian manostat made it possible to control the pressure to 0.1 mm. Hg. and to make numerous runs without any pressure changes. This permitted a direct comparison of streaming potential data for flow in opposite directions. High chart speed made changes in potential easy to read on the recordings and fast pen response made it possible to obtain accurate determinations of streaming potentials. The new cell, being shorter in length and larger in diameter than the original, made it possible to measure resistance with the Impedance bridge, eliminating a difficulty which was due to a battery effect of the electrodes when measuring the resistance with a DC compensating type circuit.

Ag-AgCl electrodes were placed in the cell and data was obtained from these electrodes as well as from platinum electrodes, the cell and solution system being the same for each set of data. Identical streaming potentials were obtained from the different electrodes, although the recordings for each electrode differed in some respects.

The new method of measuring streaming potentials was applied to the hematite plug.

Conclusions

The extraneous potential observed by many investigators including the author has been found not to be a function of the plug material, electrolyte, electrical instrumentation, or cell construction, but it was found to be associated with the electrodes. It was made up of two phenomena, one associated with flow and the other with polarization.

It is, therefore, concluded that the electrodes contribute an arbitrary EMF to streaming potentials which continues long after the flow has been stopped, and whereever polarizable electrodes have been used in measuring streaming potentials, Method I cannot give reliable data. However, since it is possible to obtain a complete recording of potential change across the streaming cell while performing such operation as increasing the pressure, stopping and reversing flow, it is the author's belief that such a recording permits the determination of streaming potential values which are free from error introduced by potential measurement techniques. A sensitive recorder with fast pen response will then permit accurate determinations of streaming potentials regardless of electrode polarizability.

SUGGESTIONS FOR FUTURE WORK

This research project had the purpose of developing a valid technique for measuring streaming potentials with platinum electrodes. If the polarization phenomena which was the cause of much difficulty in this and previous studies is to be fully understood and the method of measuring streaming potentials improved, the following suggestions may be of value.

(1) Construct a cell assembly with a very small distance between the electrodes and measure flow potentials. This would definitely establish whether the small streaming potentials observed with an empty cell were developed by the cell or the electrodes.

(2) Construct a cell so that the electrodes are not in the path of the flowing liquid. This should be done for both Ag-AgCl and platinum electrodes and would help to establish the cause and origin of the no-flow potential.

(3) Construct a cell which does not have the plug supported by the platinum electrodes. For quartz plugs, the supports might be vicor or quartz discs, perforated with tiny holes, and sealed to the end of the 24/40 inner joints of the electrode assembly. Platinum electrodes could then be sealed in free from contact with the plug. This would help to determine if the no-flow potentials were caused in some way by the minerals touching the electrodes.

(4) Determine the resistance of a quartz plug at various concentrations of electrolyte and plot the data as in Figure 7 and compare the hematite and quartz resistance data. The comparison should indicate the conductance of hematite relative to quartz. It is the author's opinion that the surface conductance of hematite becomes noticeable very near to the electrolyte concentration at which the quartz surface conductance becomes apparent.

(5) Design an apparatus which would permit continuous flow in, either direction and which would eliminate the ever changing level of liquid in the reservoirs. Some thought has been given this subject and the following diagram in Figure 16 is offered. The difficulty experienced with this type of apparatus was controlling the external flow. The flow must not be greater than the capacity of the overflow pipes and must be great enough to cover the solution demand for flowing through the plug. The flow must also be smooth because pulsating flow through the external flow system caused interferring electrical effects.

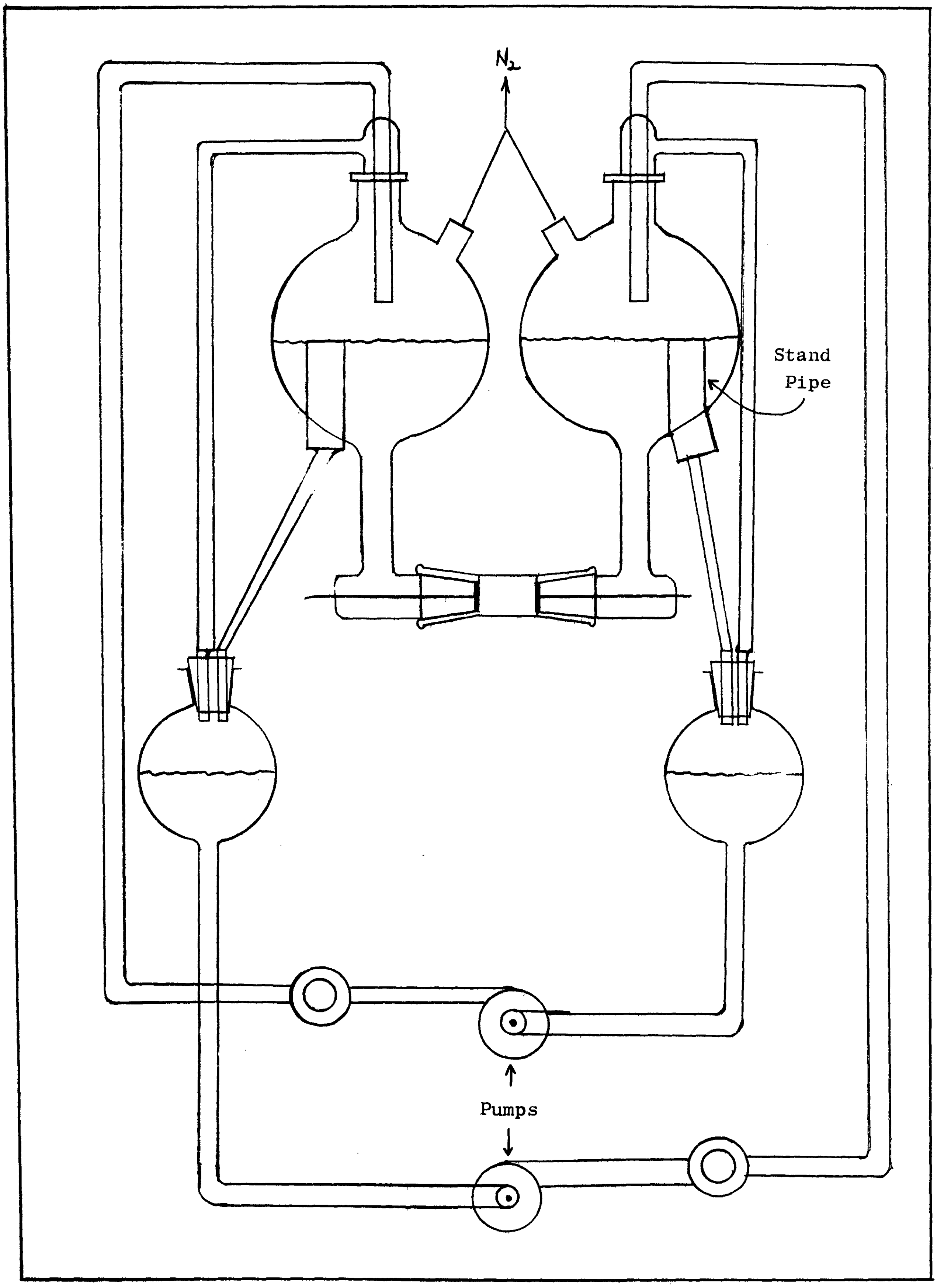

FIGURE 16 A POSSIBLE SCHEME FOR BETTER STREAMING POTENTIAL MEASUREMENTS

BIBLIOGRAPHY

1. O'Connor, Johansen, Buchanan, "Electrokinetic Properties and Surface Reactions of Corundum," Trans. Faraday Soc., 52, 229 (1956).
2. Jyo, O., "The Role of the Electric Potential at the Phase Boundary in Flotation," Science Reports Research Inst., Tohoku University, A 6, 259 (1954).
3. A. S. Buchanan and E. Heymann, "Electrokinetic Potential of Barium Sulphate," Proc. Roy. Soc., (London), A 195, 150 (1948).
4. J. Th. G. Overbeek and P. W. O. Wijga, "On Electro-osmosis and Streaming Potentials in Diaphragms," Rec. tran. chim., 65, 556 (1946).
5. H. R. Kruyt, Colloid Science, Vol. I, Elsevier Publ. Co., New York (1952) Chapters IV, V and VIII.
6. D. W. Fuerstenau, "Streaming Potential Studies on Quartz", Sc.D. Thesis, M.I.T. (1953).
7. H. J. Modi, "Streaming Potential Studies on Corundum," Sc.D. Thesis, M.I.T. (1957).
8. H. C. Li, "Adsorption of Organic and Inorganic Ions on Quartz," Sc.D. Thesis, M.I.T. (1958).
9. G. A. Parks, "A Study of the Surface of Ferric Oxide," Sc.D. Thesis, M.I.T. (1960).
10. G. L. Zucker, "A Critical Evaluation of Streaming Potential Measurements," Sc.D. Thesis, Columbia University (1959).

11. K. H. Kraus, R. W. Holmberg and C. J. Borkowski, ORNL, 383, Automatic Precision Glass-electrode-pH Measurement with a Vibrating Electrometer, 1949.

12. Jany and Taniguchi, "The Silver-Silver Halide Electrodes," Chem. Rev. 53, 397 (1953).

13. M.I.T. Richards Mineral Engineering Laboratory Progress Report NYO-6260, July 1954.

14. A. L. Mular, M. S. Thesis, Montana School of Mines, February 1957, and private communication.

15. I. Iwasaki, Private communication to G. A. Parks, M.I.T., 1959.

16. Johansen and Buchanan, "An Application of the Microelectrophoresis Method to the Study of the Surface Properties of Insoluble Oxides," Australian J. Chem., 10, 398 (1957).

APPENDIX I

Calculation of Zeta-Potentials

Zeta potentials were calculated from the streaming potential equation of Helmholtz and Smoluchowski, which is

$$\zeta = \frac{4\pi\eta}{\Sigma} \lambda \frac{E}{P}$$

where η is the viscosity of streaming solutions, (Σ) the dielectric constant of the solution within the diffuse double layer, E the streaming potential, and P the pressure difference across the plug. λ is the conductivity of the solution in situ and was determined by the relationship $\lambda = \frac{K}{R}$ where K is the cell constant of the plug determined by ordinary methods, and is equal to specific conductance of 0.1 N KCl x the measured plug resistance.

Calculated values of zeta-potentials for hematite could be considered to be accurate, as (Σ) has been taken to be the dielectric constant of the bulk solution, and the contribution of surface and bulk conductance of the hematite is not appreciable in solutions of concentrations greater than 10^{-4} M. If the solutions are less than 10^{-4} M, the contribution of total mineral conductance manifests itself on a plot of zeta-potentials versus log concentration, i.e., at low concentrations the conductance of the mineral particles themselves constitute a potential drop across the cell and the streaming potentials are subsequently less than would have been obtained if the surface and bulk conductance played no part in the streaming picture. This drop of zeta-potential can be seen in Figure 10 where zeta drops at concentrations of 10^{-4} M.

APPENDIX II

Construction of Apparatus and Operation

The apparatus consists essentially of three integral parts: the cell and reservoir assembly, the pressure system, and the electrical measuring instruments. A picture of the apparatus used for measurement of the streaming potential is shown in Figure 17 and the electrical circuit was given previously.

The cell assembly is the same as was used by Modi and Li, except that the cell itself has been enlarged to decrease the resistance between the electrodes. The reservoirs are two 1000 ml. round-bottom flasks with 24/40 ground glass necks. Into the bottom of these flasks have been sealed 9/18 outer ball joints which fit the inner joints of the cell assembly. Special (extra long) pH electrodes were inserted into the top of the flask with little difficulty. The flasks also had sealed onto them near the top, two 10/30 outer ground glass joints. Into one joint nitrogen entered for driving the solution through the plug. In the other was a degassing tube. On the other flask, one joint held the nitrogen inlet and the other a thermometer. See Figure 17 for details.

The pressure system consisted of a gas washing train, ballast bottle, cartesian manostat, manifold and manometers. The electrical system will be discussed.

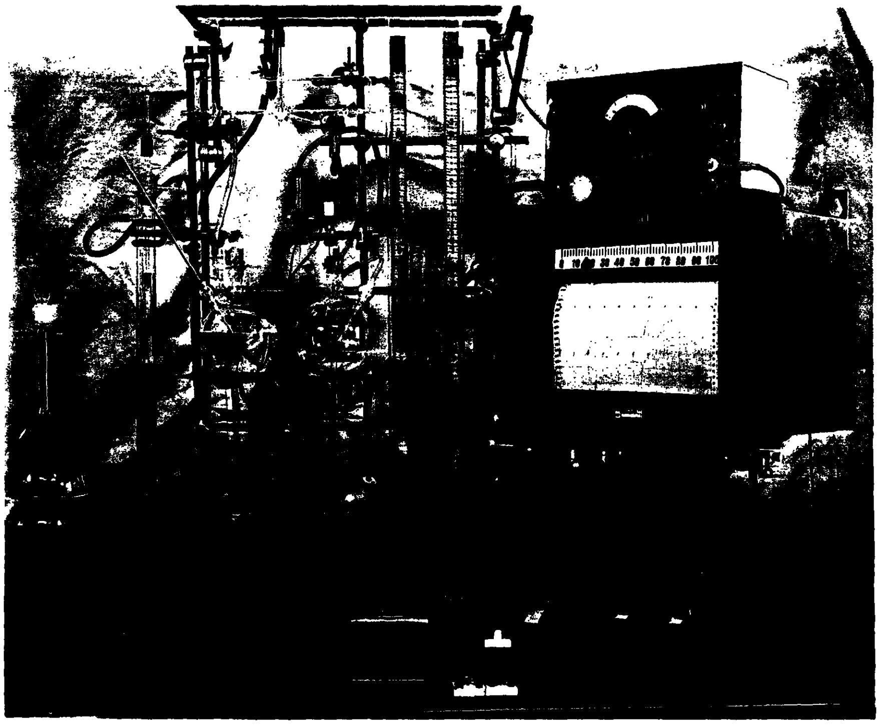

FIGURE 17 STREAMING POTENTIAL APPARATUS

Operation

The cell is disassembled, washed and cleaned, and filled with the mineral particles. The plug is washed in place with the electrolyte which is to be used for streaming until a constant resistance is measured. The manostat is set to the desired pressure and the nitrogen turned on. The Brown recorder is calibrated by feeding into the Vibrating Reed Head a known potential, and making the recorder respond exactly to this potential by changing the resistance between the Amplifier and the recorder. The known potential is removed and the unknown potential put in its place. A potential is developed in the streaming cell by opening one of the control valves, and the flow is stopped by closing the valve on the side of the system which is under pressure. If the cell assembly is not open to atmosphere pressure when the flow is stopped, the wrong potential will result. The recorder may be zeroed at any point on the scale (i.e. in the middle or to the left or right of the middle) by turning the Amplifier's meter control knob. Previous investigators flowed until one of the reservoirs was nearly empty and then measured the difference in the level of liquids and applied the head to the pressure read on the manometer as a correction. This may be necessary for high pressure, which are needed when high concentrations are used and the streaming potentials are small. But for normal work the author stopped the flow when the level of the solutions in the reservoirs were equal.

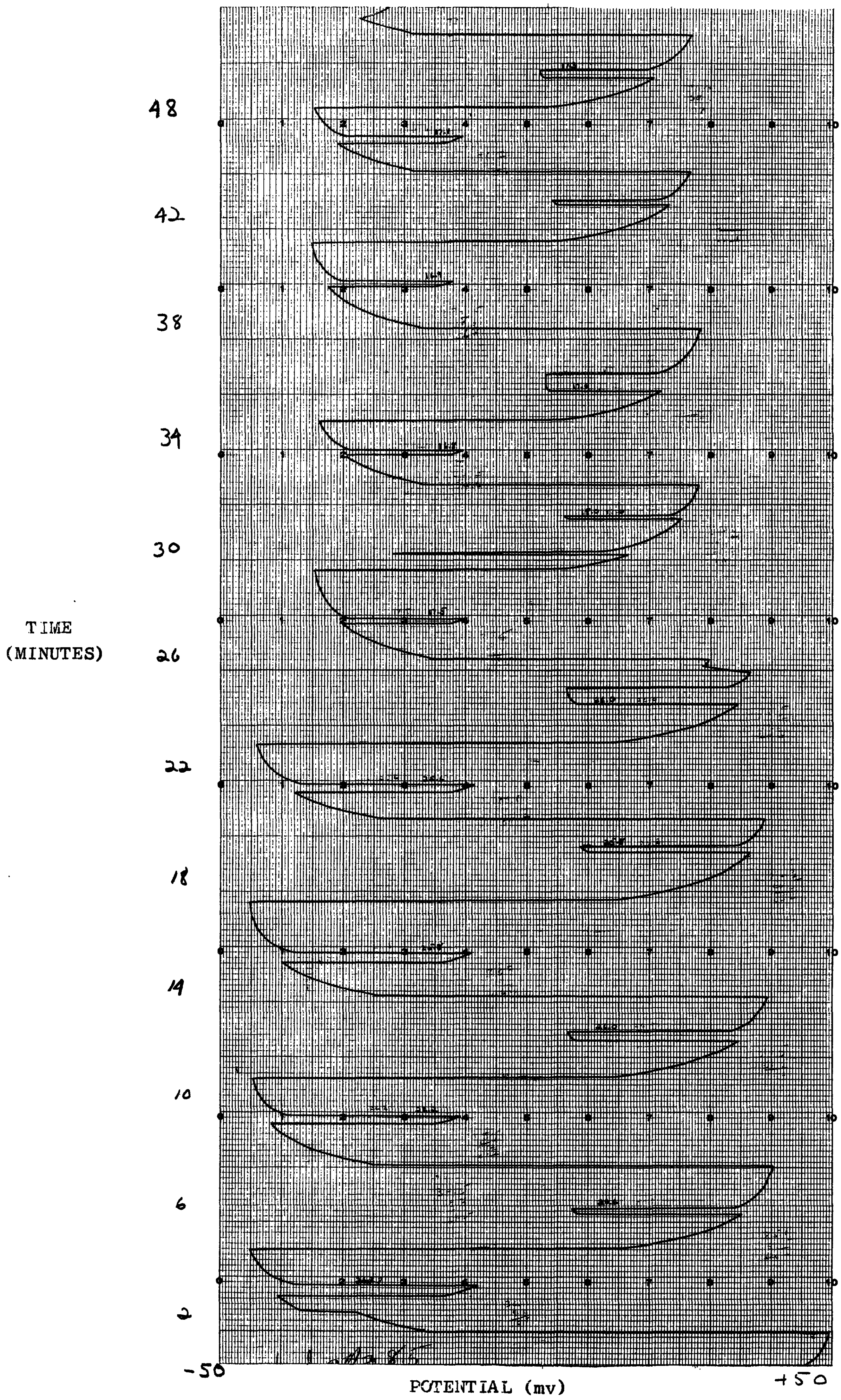

FIG. 18 AN EXAMPLE OF ACTUAL RECORDING DATA

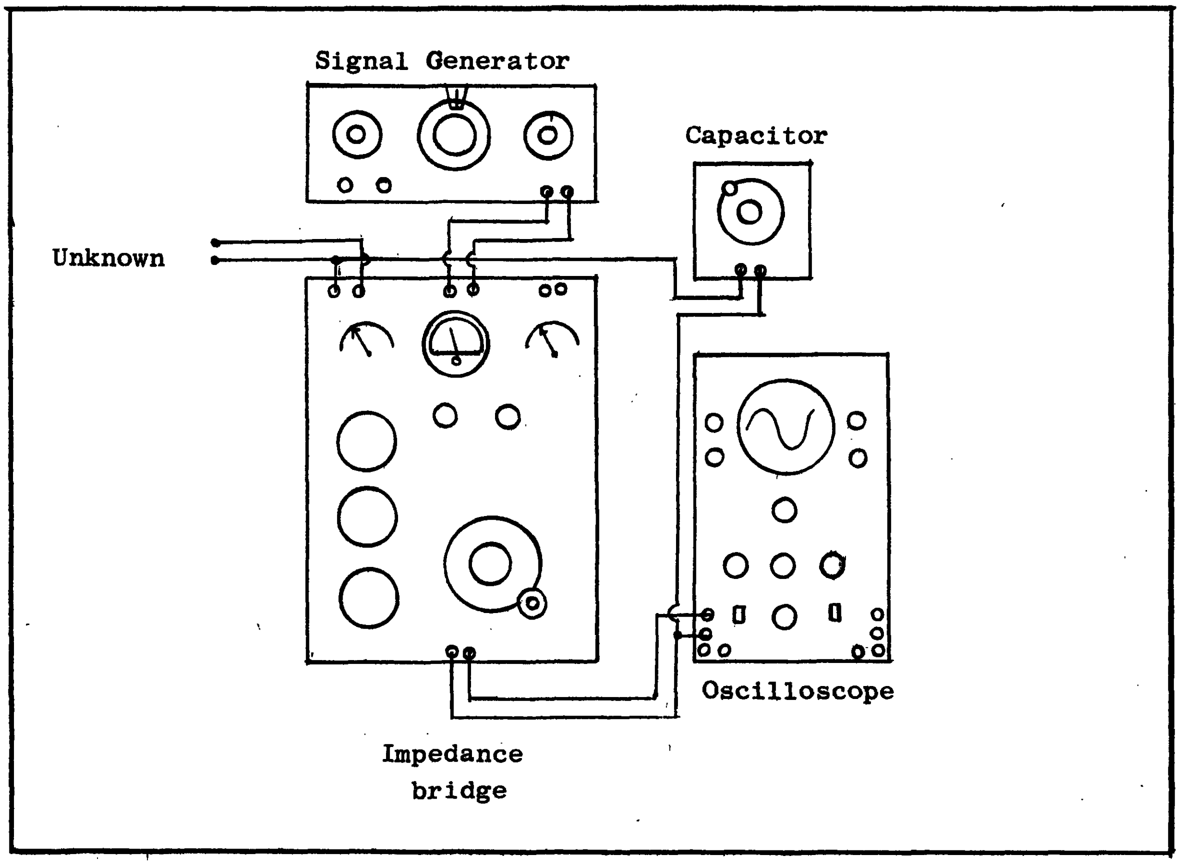

FIGURE 19 - RESISTANCE MEASURING CIRCUIT

This eliminated any pressure correction and insured that the pressure at which the potentials were read, was the same for flow in opposite directions. An example of actual recorder data is shown in Figure 18.

The resistance was measured using the following circuit. The greatest sensitivity was obtained by settling the oscilloscope sweep frequency to at least 3000. Often the bridge could not be balanced and it was necessary to add additional capacitance across the unknown resistance.