01 2991385

CANADA

DEPARTMENT OF
ENERGY, MINES AND RESOURCES
MINES BRANCH
OTTAWA

THE DETERMINATION OF THE ZETA POTENTIAL OF MINERALS

H. P. DIBBS

MINERAL SCIENCES DIVISION

SEPTEMBER 1972

Price 75 cents

Mines Branch Technical Bulletin TB 156

THE DETERMINATION OF THE ZETA POTENTIAL OF MINERALS

by

H. P. Dibbs*

- - -

ABSTRACT

An improved streaming-potential method is described for the determination of the zeta potential of minerals and its application to some oxide and sulphide minerals is discussed.

*Head, Surface Science Group, Mineral Sciences Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.

Direction des mines

Bulletin Technique TB 156

LA DÉTERMINATION DU POTENTIAL ZÊTA DES MINÉRAUX

par

H.P. Dibbs*

RÉSUMÉ

L'auteur décrit une méthode améliorée de potentiel d'écoulement pour la détermination du potentiel zêta des minéraux et de plus il discute l'application de cette méthode pour quelques minéraux sulfurés et oxydés.

*Chef, Groupe des sciences des propriétés de surface, Division des sciences minérales, Direction des mines, ministère de l'Énergie, des Mines et des Ressources, Ottawa, Canada.

CONTENTS

TABLE

FIGURES

=   =   =

INTRODUCTION

In studies of the surface chemistry of the solid/solution interface, widespread attention has been given to electrokinetic phenomena[1-15]. These arise when relative movement occurs between the solid and the solution phase and their interpretation can yield valuable information on the charge distribution and on the structure of the aqueous double layer[8, 15-19]. The electrical parameter obtained from these studies is the zeta potential which may be defined as the potential at the plane of shear between the fixed layer of liquid at the solid surface and the liquid in the bulk solution[1, 9]. The theoretical significance of zeta potential has been questioned[13] due to ambiguity over the precise location and the thickness of the shear plane, although for dilute solutions it is usually identified[12, 15] with the potential of the outer Helmholtz plane (Figure 1a), i.e., at the beginning of the diffuse double layer in the Gouy-Chapman-Stern theory of charged interfaces[20]. For a given solid, the sign and magnitude of the zeta potential depends on the concentration of both the potential-determining ions and the indifferent electrolyte and on the specific adsorption of ions on the solid surface (Figures 1b to 1d). Because many combinations of surface charge and solution composition can give the same value of the zeta potential, a single determination is of limited utility. However, changes in zeta potential resulting from changes in the composition of the solution have been found to be very useful in flotation studies in elucidating the mechanisms of collector and activator adsorption[1, 2, 12, 21, 22] and in indicating the class of collector (cationic or anionic) suitable for the flotation of certain minerals[23]. For oxide minerals, where H^+ and OH^- are the potential-determining ions[24], the mechanism and thermodynamics of the adsorption of long-chain collectors have been evaluated from electrokinetic measurements[2, 14].
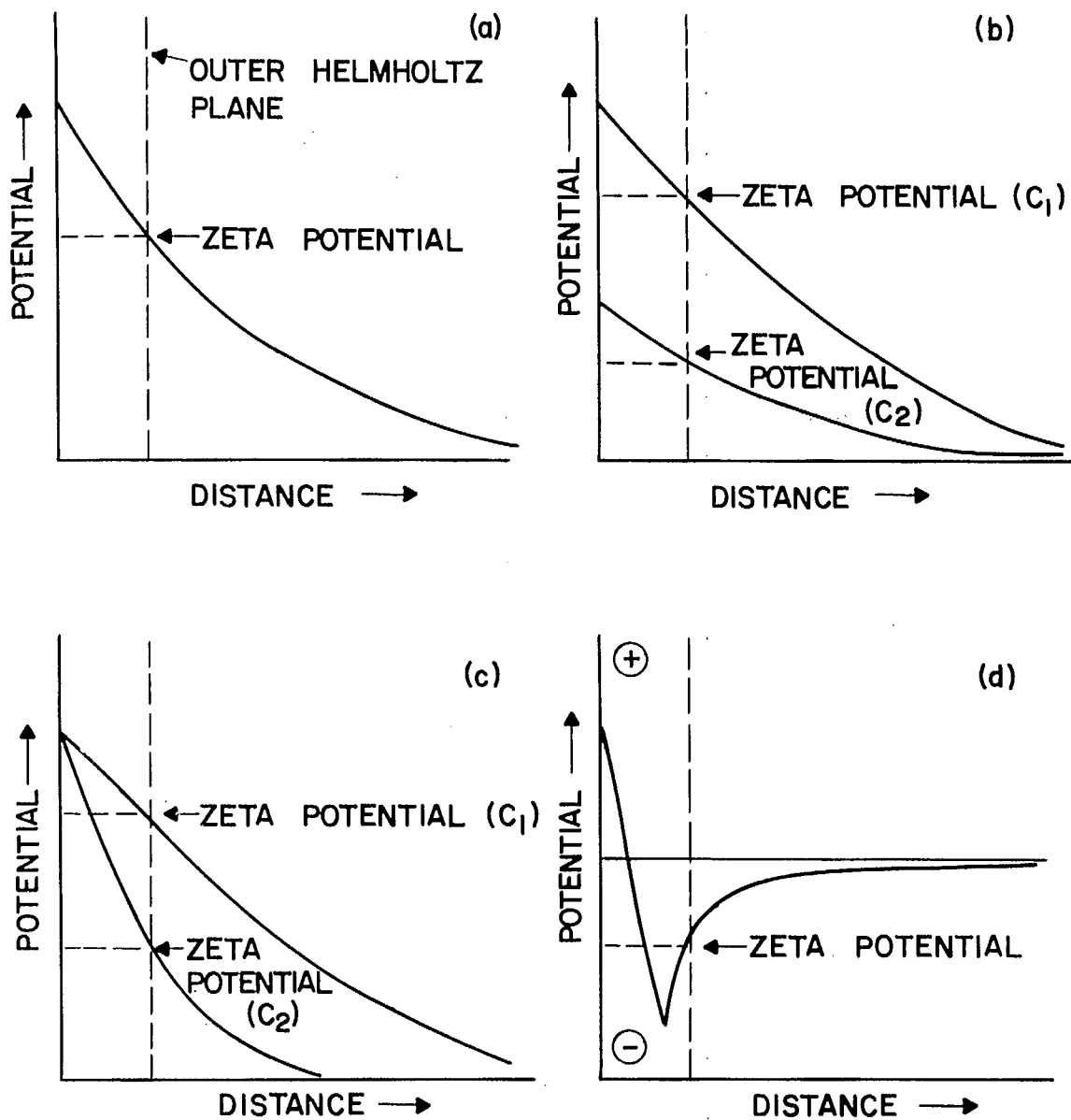
Figure 1. Simplified Potential Distributions in Double Layer with Distance from Solid Surface.
(a) From the theory of diffuse double layer.
(b) With concentration of potential-determining ions ($C_1 > C_2$).
(c) With concentration of indifferent electrolyte ($C_1 < C_2$).
(d) In the presence of specific adsorption of ions.

A number of different methods may be used to determine the zeta potential at the solid/solution interface[4,25], and this report is concerned with the development of an improved technique for its determination for minerals by the streaming-potential method[26-28]. In this method, the solution is forced through a porous plug of the mineral and the voltage (streaming potential) between the ends of the plug is measured. The zeta potential (Z.P.) is then calculated from the Helmholtz-Smoluchowski re-lationship (Equation 1),

$$Z.P. = \frac{4\pi\eta\lambda E_s}{D\Delta P} , \qquad \ldots (Eq. 1)$$

where η = bulk viscosity,

λ = specific conductivity of the solution in the plug,

E_s = streaming potential,

D = dielectric constant,

ΔP = applied pressure difference across the plug.

For aqueous solutions at 25°C, this equation becomes

$$Z.P. \approx 9.69 \times 10^4 \frac{\lambda E_s}{\Delta P} , \qquad \ldots (Eq. 2)$$

where E_s and Z.P. are in millivolts and ΔP is in centimetres of mercury. In the derivation[14] of the Helmholtz-Smoluchowski equation, laminar flow of solution through the plug is assumed and, for the equation to be valid, E_s should be proportional to the applied pressure difference, ΔP.

In the conventional method for the determination of the zeta potential of minerals by the streaming-potential technique[28], the potential developed between the ends of a porous plug of the mineral is measured after a static pressure difference has been established across the plug. To check the validity of Equation 1, a time-consuming, point-by-point plot of E_s against ΔP is required. In an improved experimental approach, suggested by Parreira[29], a pressure transducer was employed to measure changes in the driving pressure which were plotted against simultaneous changes in the streaming potential on an X-Y recorder. A linear plot of E_s versus ΔP was confirmation of the applicability of Equation 1 to his particular system.

In this particular experimental design, however, corrections were necessary for back-pressures developed in the equipment.

In the method to be described here, a sensitive pressure transducer is placed directly across the streaming-potential cell, and its output is plotted against changes in the streaming potential on an X-Y recorder as the driving pressure across the cell is rapidly changed. The slope of the plot ($E_s/\Delta P$) is used in Equation 1.

EXPERIMENTAL METHOD AND RESULTS

The apparatus used for the determination of zeta potential is shown schematically in Figure 2 and consists essentially of three parts: the solution system, the zeta potential cell and the pressure transducer, and the electrical measurement system.

The Solution System

The solution reservoir was a three-necked, five-litre flask with an outer jacket through which water at $25 \pm 0.05°C$ was circulated. The apparatus was maintained free of grease through the use of Teflon sleeves on the standard taper joints and stopcocks with Teflon plugs. All parts of the system that came in contact with the solution were made of Pyrex and were cleaned after each run. High-purity nitrogen was used for solution transfer. The adjustment of the pH of the solution was made by the addition of dilute ($\sim 0.5N$) HCl or NaOH, depending on the pH range being studied, from a burette in the centre neck of the flask. Preliminary tests were made to find the approximate amount of reagent required to bring the solution in the reservoir to any desired pH, with appropriate allowance being made for changes in the volume of the solution as the run proceeded. The potassium chloride solutions for these measurements were prepared from triple-distilled water (conductivity, 1×10^{-6} mhos cm^{-1}) and re-crystallized analytical grade KCl.
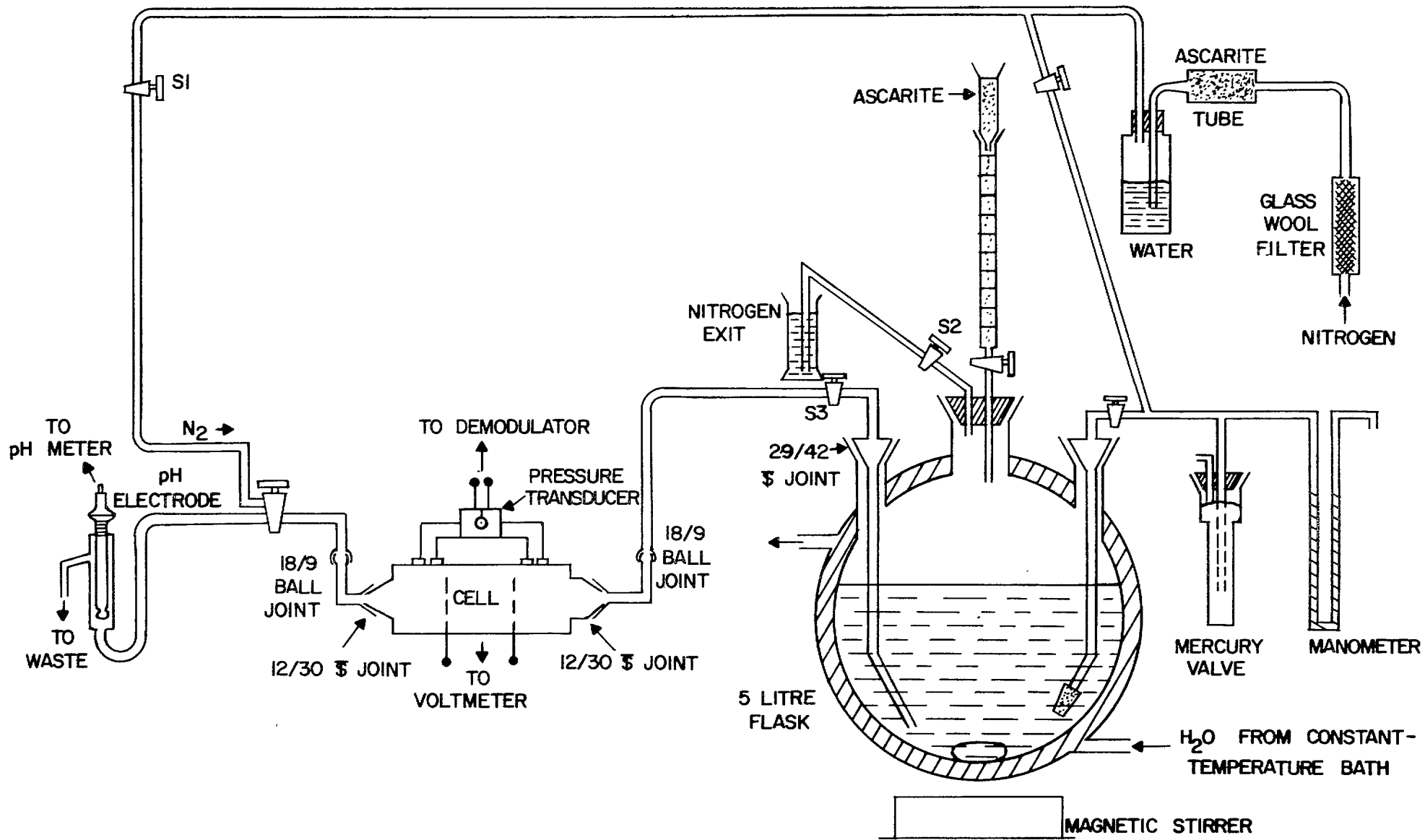
FIGURE 2. STREAMING – POTENTIAL APPARATUS

The Zeta Potential Cell and Pressure Transducer

The zeta potential cell (Figure 3) was made of Teflon, and is based on a design by Dallaire[30]. An outer metal casing, with two clamping rings, held the three sections of the cell together. The pressure drop across the cell was measured with a differential pressure transducer (Whittaker Corporation, Model Pace 7D, $\pm$ 5 psi) connected to ports on each side of the measurement electrodes. The pressure-sensing element in the transducer is a flat diaphragm of stainless steel, and a "pick-off" coil on each side of the diaphragm senses its deflection and forms part of a bridge circuit with a carrier demodulator (Whittaker Corporation, Model CD10). This latter unit provides 5 kHz excitation to the bridge, and its output (which is proportional to the diaphragm deflection) is amplified, demodulated, and filtered for a final DC output. The transducer was calibrated against a differential mercury manometer using a precision cathetometer to measure the heights of the two mercury columns. A pressure calibration graph is shown in Figure 4 and a least squares analysis of the data gave a slope of 1.36 V/cm Hg pressure. This calibration was checked periodically during two years and was found to remain essentially unchanged.

For most of the measurements to be reported, the electrodes were prepared[30] from discs of high-purity platinum (diameter, 2.5 cm; thickness, 0.8 mm) in which a series of 0.175-mm holes were drilled. A platinum wire was welded to the circumference of the disc for connection to the electrical measurement system. Preliminary tests with these electrodes showed that they had unstable rest potentials and that, when they were used for blank streaming-potential runs with an empty cell, significant and nonreproducible flow-induced potentials developed which persisted for some time after the solution flow had stopped. To overcome these polarization effects which can seriously decrease the accuracy of zeta-potential determinations[31], silver/silver chloride electrodes were prepared by an electrolytic method[32] using the platinum electrodes as a substrate. Blank runs with these (Pt) Ag/AgCl electrodes gave very low (< 0.2-mV) flow-

PORTS FOR PRESSURE TRANSDUCER

12/30 STANDARD
TAPER

5·7 cm

MINERAL POWDER

1·1 cm

"O" RING
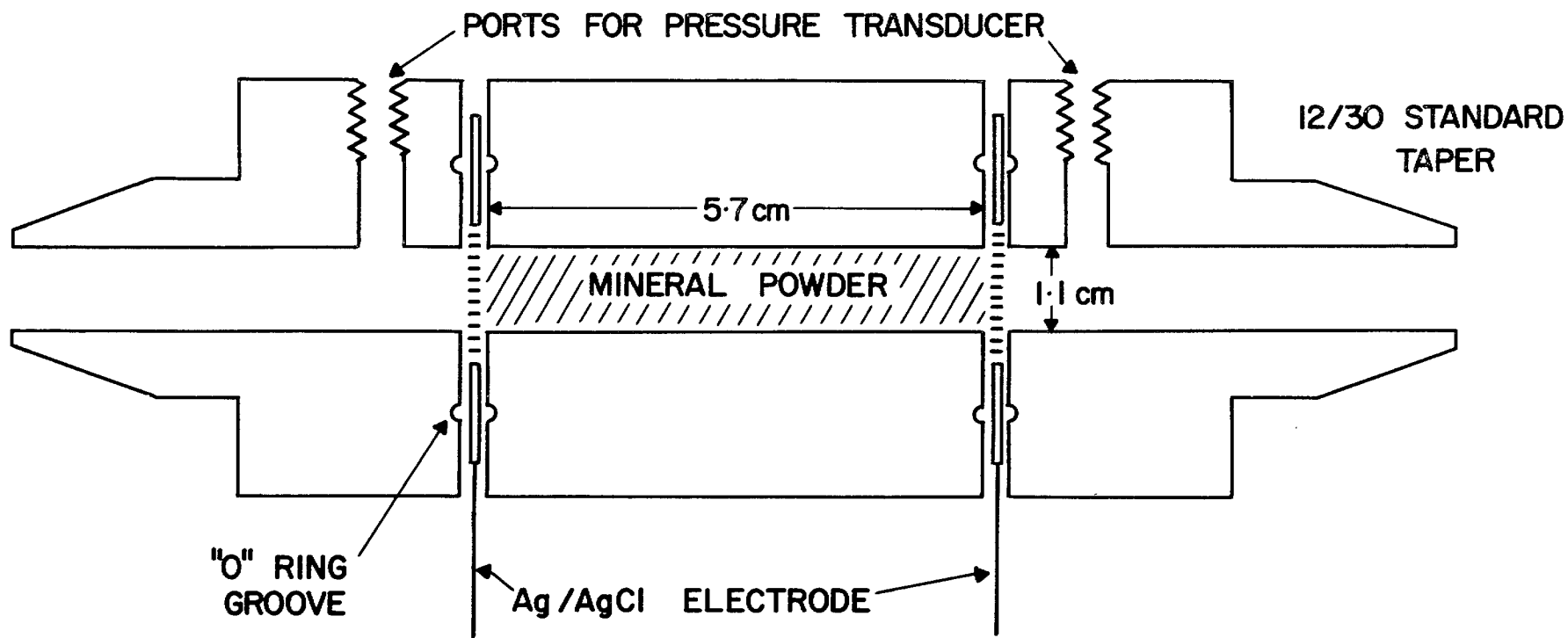GROOVE

Ag /AgCl ELECTRODE

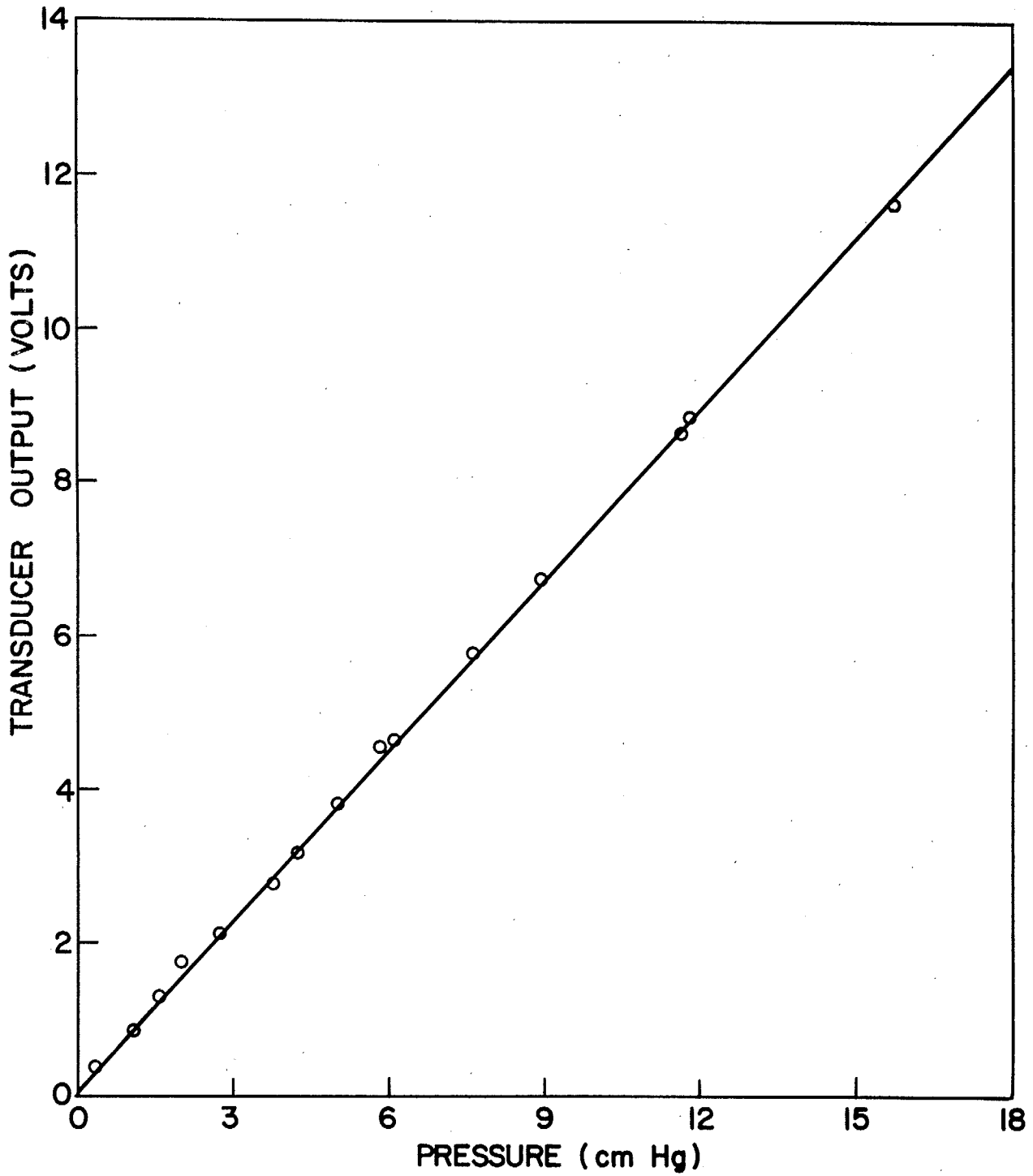FIGURE 3. SCHEMATIC OF STREAMING - POTENTIAL CELL

FIGURE 4. PRESSURE TRANSDUCER CALIBRATION CURVE

induced potentials which decayed almost immediately when the solution flow had stopped. The chief disadvantage with (Pt) Ag/AgCl electrodes is that they are time-consuming to prepare; the silver plating step in particular requires six hours. Additional electrodes were therefore prepared from high-purity silver discs that had only to be chloridized to give Ag/AgCl electrodes. The electrical characteristics of these electrodes were not quite as good as those of the (Pt) Ag/AgCl electrodes but they were suitable for all but the most concentrated solutions ($>10^{-3}$ N) in which the streaming potentials are very low.

To load the cell, it was mounted vertically with the lower electrode installed, and small aliquots of a slurry of the 65 to 100-mesh mineral were added. Following each addition, a slight vacuum (from a water pump) was applied to the lower end of the cell. This procedure served to remove excess moisture and to give uniform packing of the mineral and was continued until the mineral was level with the upper electrode position. This electrode was then installed and its clamping ring was fastened; the loaded cell was now ready for installation in the measurement system.

Electrical Measurement System

Streaming Potential

It may be seen from Equation 2 that, to calculate zeta potential from streaming-potential measurements, it is necessary to know the change of streaming potential with the change in driving pressure and the specific conductivity of the solution in the mineral plug. The streaming potential was measured with a high-impedence voltmeter (Keithly Instrument Co., Model 610 C), whose output was fed to the Y axis of an X-Y recorder (Honeywell Ltd., Model 550), and the pressure-transducer's output was fed to the X axis of the recorder. Thus, as soon as solution is forced through the zeta potential cell, the recorder plots the relationship between E_s and ΔP, and the slope of this line is used in Equation 2. The specific conductivity of the solution in the plug was obtained by conventional means[33], in which

the resistance (R) of the plug was measured after each run at a given pH, and then, after the series of runs was completed, the cell constant (C) of the plug was calculated from its resistance in a 0.1N KCl solution. The specific conductivity (λ) is then given by $\lambda = C/R$. For different runs the plug resistance varied widely, depending on the solution concentration and on the pH, and was measured with a Beckman conductivity bridge (Model RC 18A). The maximum resistance that may be measured with this bridge is 0.11 MΩ, and to measure larger cell resistances, a 0.1-MΩ precision resistance was placed in parallel with the cell.

Streaming Current

As the conductivity of the streaming solution increases, the streaming potential which is the product of the streaming current (I_s) and the plug resistance decreases and, for high conductivity solutions ($\sim 10^{-2}$N), the streaming potential is only a few millivolts; this renders accurate voltage measurements difficult. However, if E_s and λ in Equation 2 are replaced by $I_s R$ and C/R, Equation 3 is obtained,

$$Z.P. = 9.69 \times 10^4 \frac{CI_s}{\Delta P} \qquad \text{... (Eq. 3)}$$

and the slope of $I_s/\Delta P$ may be used to calculate the zeta potential. In practice, the streaming current which is of the order of 10^{-8} amp may be readily found from the voltage developed across a known resistance (R_p) in parallel with the cell. If R_p is much smaller than the cell resistance, then virtually all the charge displaced by the flow of solution through the cell will be returned to the first electrode by the external path. Some zeta-potential measurements were made by the streaming-current method, the voltage across R_p being measured with a microvoltmeter (Keithly Instrument Co., Model 150B) whose output was fed to the Y axis of the X-Y recorder.

Measurement Procedure

With the loaded cell in place, and the solution reservoir filled, a slow stream of nitrogen was passed through the cell and the solution for a number of hours. The connecting lines from the cell to the pressure transducer were also flushed with nitrogen by opening bleed screws on each side of the transducer. Stopcocks S_1 and S_2 were then closed and solution passed through the cell to waste until its pH was constant. The solution reservoir was then pressurized (~15 cm Hg) with nitrogen (Stopcocks S_2 and S_3 closed). With the X-Y recorder in the record mode, Stopcock S_3 was opened briefly, and a plot was obtained of the increase in E_s as ΔP increased across the cell. This stopcock was then closed and the recorder returned to its initial zero pressure/zero streaming-potential position. By displacing the X axis of the recorder, a family of plots (Figures 5 and 6) of E_s against ΔP was obtained very quickly. The slopes of these plots usually agreed to within a few per cent and their average value was used in Equation 2. Although most runs were made with the driving pressure increasing across the cell, similar slopes could be obtained by recording the decrease in E_s as ΔP decreased after Stopcock S_3 was closed (Figure 7). After the run was completed, the pH was noted and the cell resistance measured under conditions of no solution flow through the cell. The procedure was then repeated for the pH range being studied. At the end of the run, the cell was filled with 0.1 N KCl and its cell constant was determined.

Zeta-potential determinations were made, with samples of quartz, hematite, and rutile, prepared as described elsewhere[36], over a pH range from about 2 to 11 in potassium chloride solutions of various concentrations. The results are shown in Figures 8 to 10 and compare well with other measurements for these oxides[2,5,12,36-38].

As part of a study on the flotation of quartz [6], the variation of its zeta potential in dodecylamine hydrochloride (DAC) solutions of various pH's was determined (Figure 11) and was found to be in good agreement with similar measurements reported by other authors[12,40]. A comparison
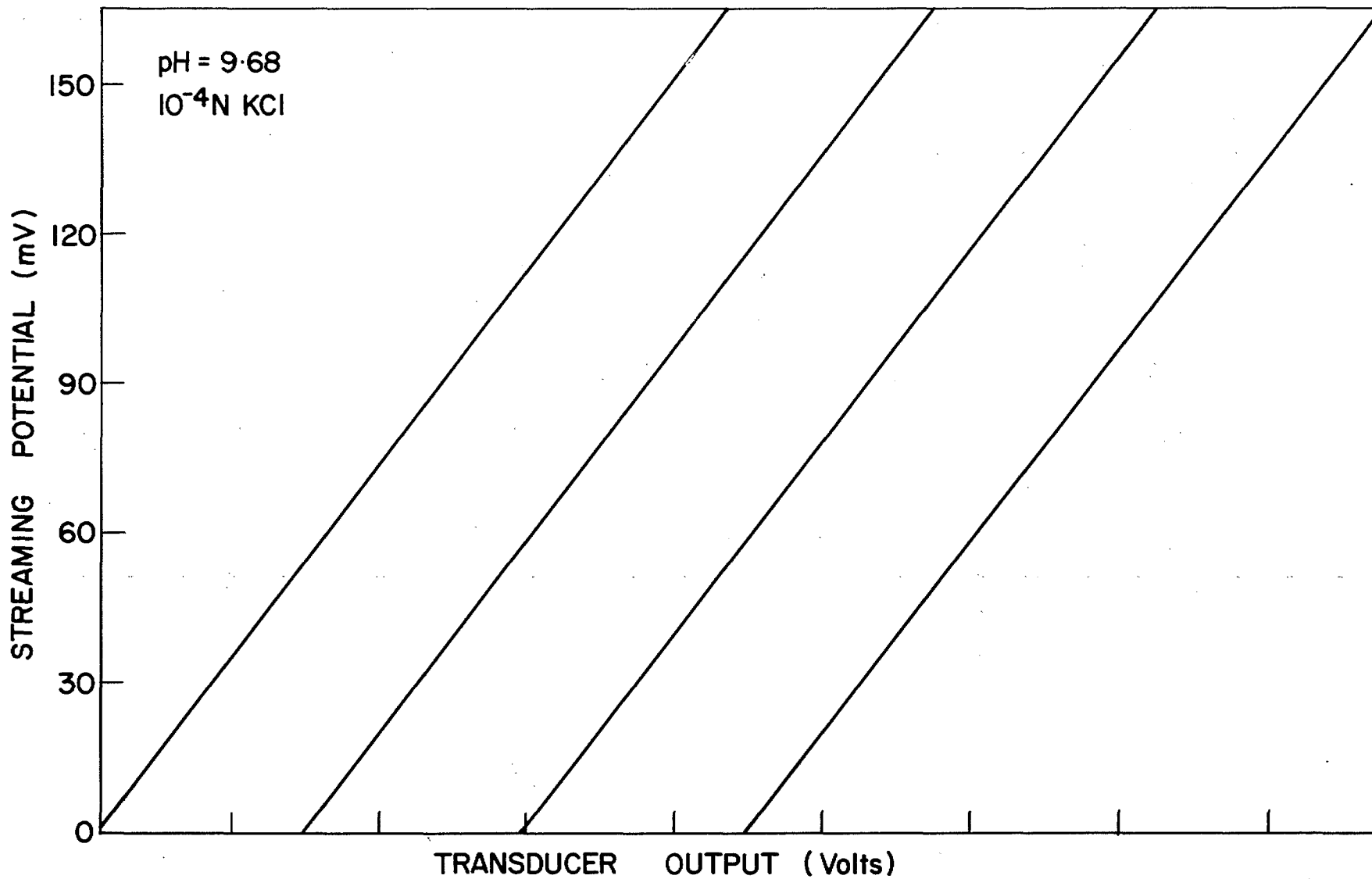
FIGURE 5. STREAMING POTENTIAL VERSUS TRANSDUCER OUTPUT FOR HEMATITE IN 10^{-4}N KCl SOLUTION
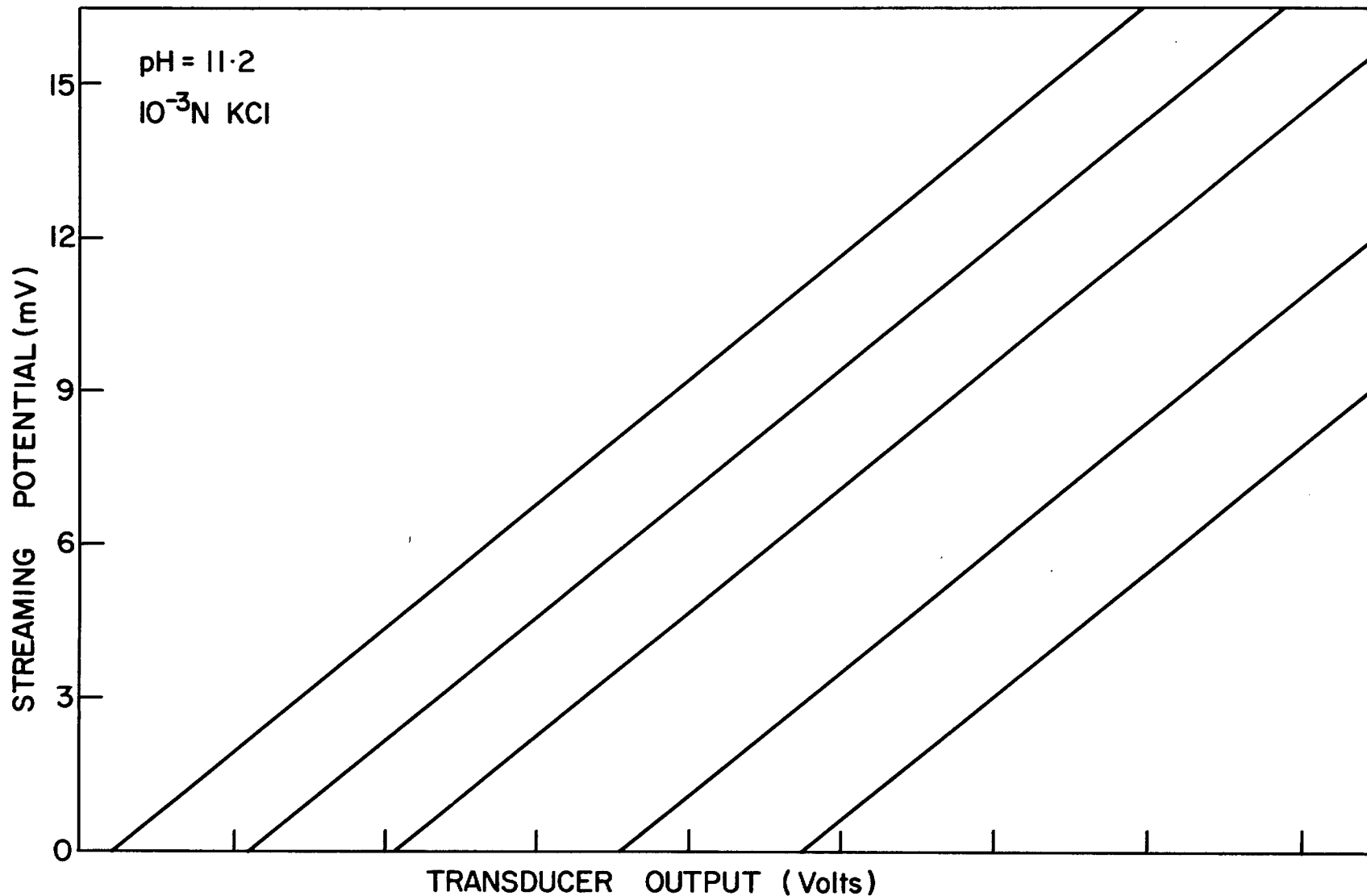
FIGURE 6.   STREAMING   POTENTIAL   VERSUS   TRANSDUCER   OUTPUT
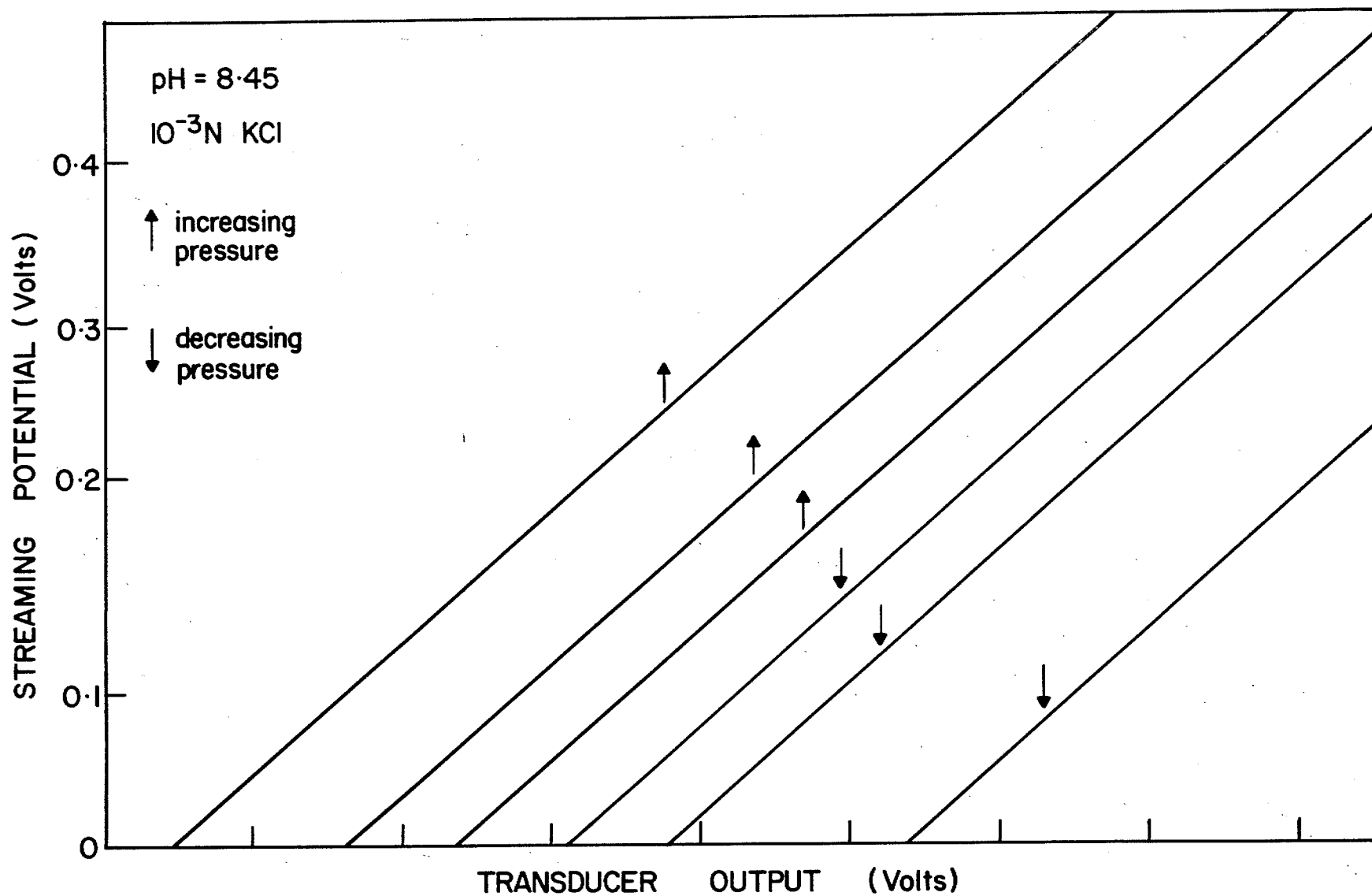FOR   QUARTZ   IN 10^{-3}N   KCl   SOLUTION   AT   pH 11·2

FIGURE 7. STREAMING POTENTIAL VERSUS TRANSDUCER OUTPUT
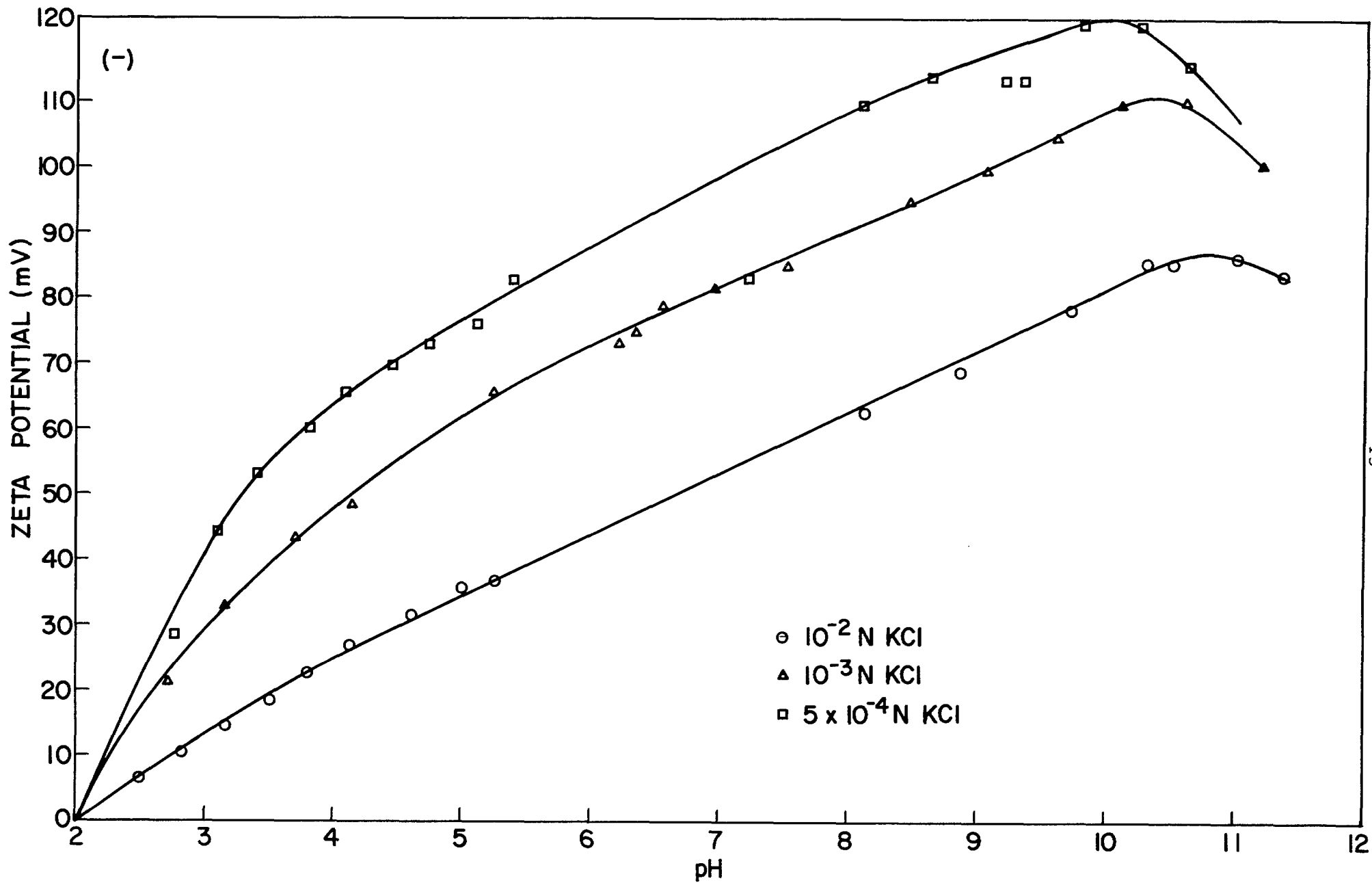FOR QUARTZ IN 10^{-3}N KCl SOLUTION AT pH 8·45

FIGURE 8. ZETA POTENTIAL OF QUARTZ, AS A FUNCTION OF pH, IN KCl SOLUTIONS OF VARIOUS CONCENTRATIONS
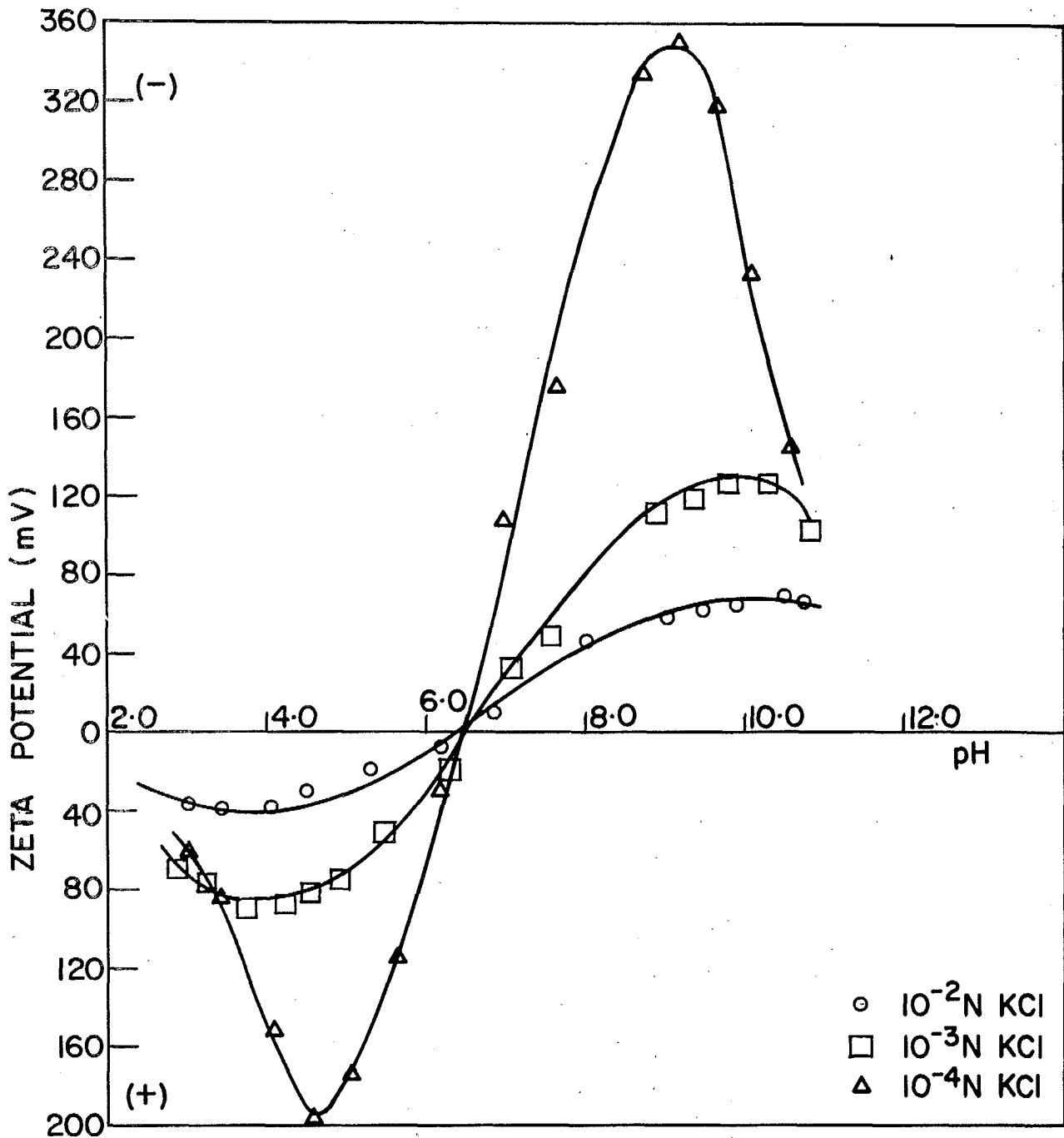
FIGURE 9. THE ZETA POTENTIAL OF HEMATITE, AS A
FUNCTION OF pH, IN KCl SOLUTIONS
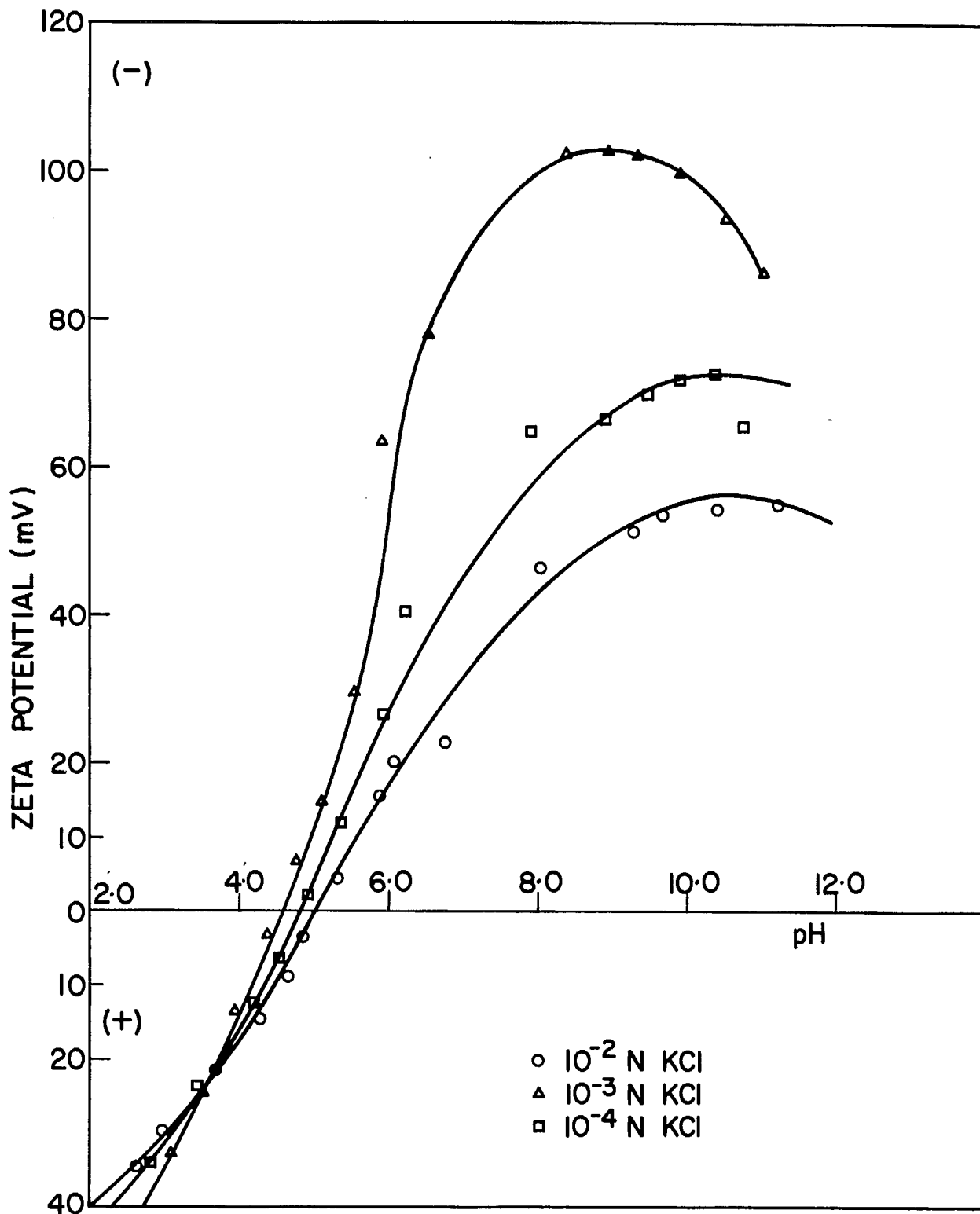OF VARIOUS CONCENTRATIONS

FIGURE IO. THE ZETA POTENTIAL OF RUTILE, AS A FUNCTION OF pH, IN KCl SOLUTIONS OF VARIOUS CONCENTRATIONS
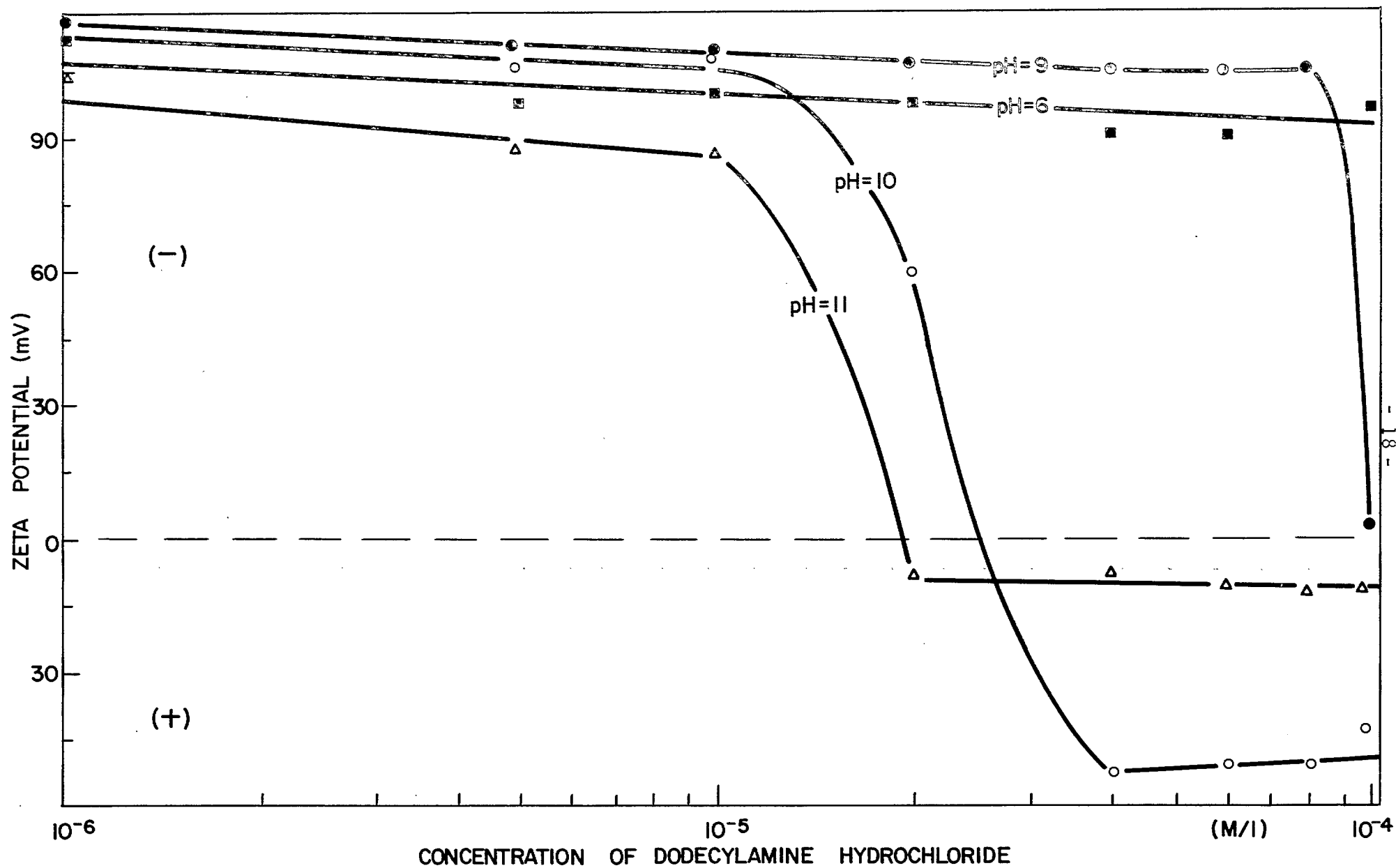
FIGURE II. VARIATION OF ZETA POTENTIAL OF QUARTZ WITH CONCENTRATION OF DODECYLAMINE HYDROCHLORIDE AT VARIOUS pH's

of the streaming-potential and streaming-current methods for the determination of the zeta potential of quartz in 2×10^{-5} M DAC is given in Table 1.

A limited investigation was also made of the application of the streaming-current and streaming-potential methods to the determination of the zeta potential of selected samples of naturally occurring sphalerite, chalcopyrite, and pyrite. Consistent results were obtained only with sphalerite (Figure 12). With the other two sulphide minerals, very irreproducible results were obtained; these results may have their origins in complex formation resulting from sample dissolution.

TABLE 1

The Zeta Potential of Quartz in 2×10^{-5} Molar Dodecylamine
Hydrochloride Solution Determined by the Streaming-Potential and
the Streaming-Current Method

pH	Zeta Potential (mV)	
	Streaming-Potential Method	Streaming-Current Method
7.1	-101.7	-101.5
8.15	-103.3	-103.2
8.6	-106.1	-103.5
9.1	-107.2	-104.1
9.7	- 91.4	- 89.6
10.25	- 33.3	- 29.7
10.6	+ 27.5	+ 29.3
10.9	+ 11.3	+ 11.8
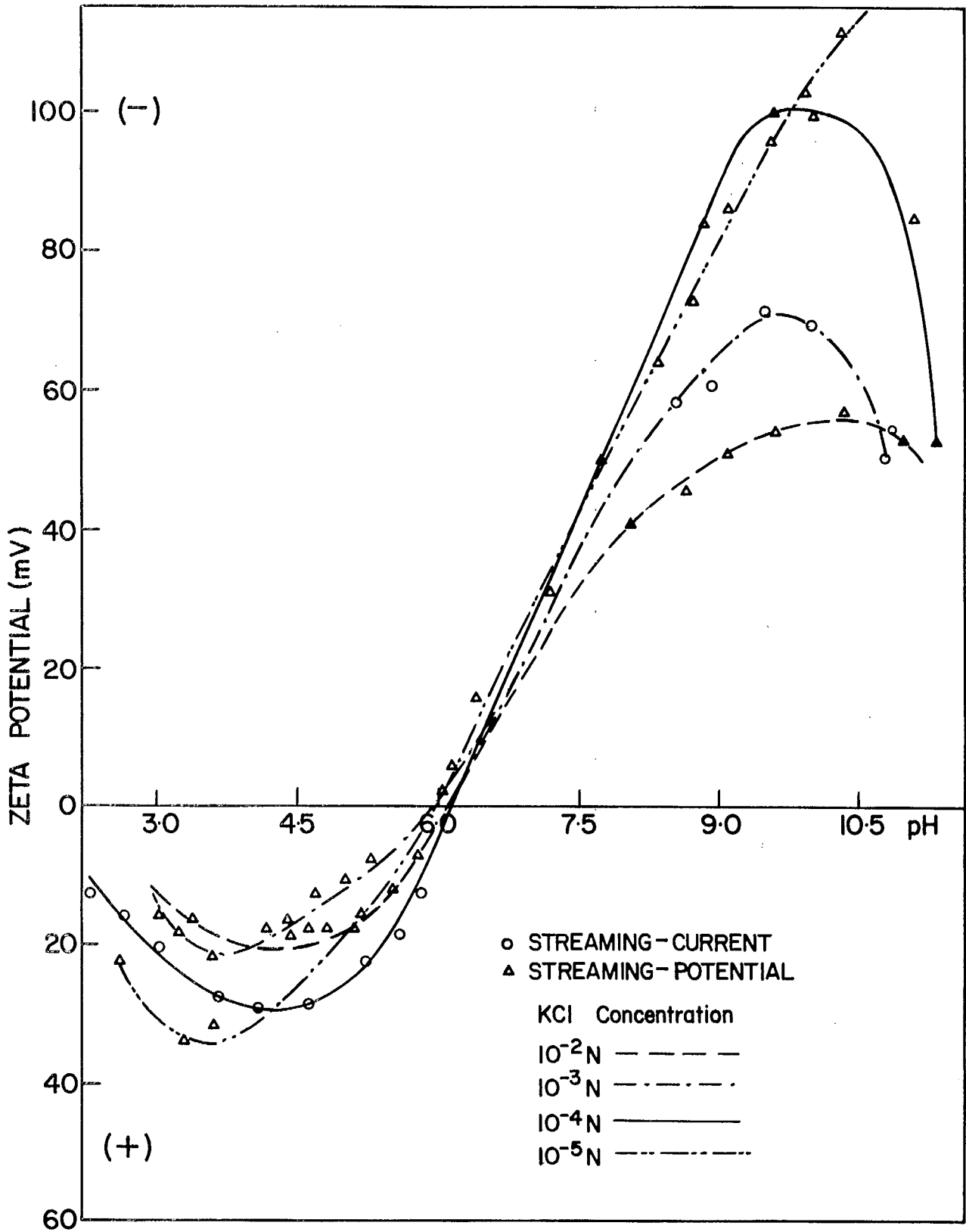
FIGURE 12. THE ZETA POTENTIAL OF SPHALERITE AS A FUNCTION OF pH, IN KCl SOLUTIONS OF VARIOUS CONCENTRATIONS, DETERMINED BY STREAMING-CURRENT AND STREAMING-POTENTIAL METHODS

SUMMARY

The determination of the zeta potential of oxide minerals by a continuous-recording method in which simultaneous measurements are made of the streaming potential (or streaming current) and the driving pressure has been found to be accurate, reproducible, and rapid. The method was found to be unsuitable for zeta-potential determinations with pyrite and chalcopyrite.

ACKNOWLEDGEMENTS

REFERENCES

1. Mackenzie, J.M.W., Minerals Sci. Eng., 3(3), 25 (1971).

2. Fuerstenau, D.W., Pure Appl. Chem., 24, 135 (1970).

3. Hunter, J.R. and Wright, H.J.L., J. Colloid Interface Sci., 37, 564 (1971).

4. Davies, J.T. and Rideal, E.K., "Interfacial Phenomena" (Academic Press, New York, 1961).

5. Cases, J.L., Sciences de la Terre, No. 13 (1968).

6. Dibbs, H.P., Sirois, L. and Bredin, R., Mines Branch Research Report R248, Dept. Energy, Mines and Resources, Ottawa (1972).

7. Haydon, D.A., "Recent Progress in Surface Science", Vol. 1, Danielli, J.F., Pankhurst, K.G.A. and Riddiford, A.C., eds. (Academic Press, New York, 1964), p. 94.

8. Wiese, G.R., James, R.O. and Healy, T.W., Discussions Faraday Soc., 52, 302 (1971).

9. Sennett, P. and Olivier, J.P., "Chemistry and Physics of Interfaces", (American Chemical Society, Washington, 1965), p. 75.

10. Ottewill, R.H. and Watanabe, A., Kolloid Z., 170, 38 (1960).

11. Purcell C. and Sun, S.C., Trans. AIME, 226, 6 (1967).

12. Li, H.C. and DeBruyn, P.L., Surface Sci., 5, 203 (1966).

13. Lyklema, J. and Overbeek, J.Th.G., J. Colloid Sci., 16, 501 (1961).

14. Ball, B. and Fuerstenau, D.W., Discussions Faraday Soc., 52, 361 (1971).

15. Kruyt, H.R., ed., "Colloid Science", Vol 1., (Elsevier, New York, 1971).

16. Healy, T.W. and Fuerstenau, D.W., J. Colloid Sci., 20, 376 (1965).

17. Honig, E.P. and Hengst, J.H.Th., J. Colloid Interface Sci., 29, 510 (1969).

18. Honig, E.P., Trans. Faraday Soc., 65, 1 (1969).

19. Ahmed S., "Current Concepts: Oxide Films", Diggle, J.W., ed. (Dekker, New York, In press).

20. Mohilner, D.M., "Electroanalytical Chemistry", Vol. 1, Bard, A.J., ed. (Dekker, New York, 1966), p. 241.

21. Fuerstenau, D. W. and Modi, J. , J. Electrochem. Soc. , $\underline{106}$, 336 (1959).

22. Somasundaran, P. and Fuerstenau, D. W. , J. Phys. Chem. , $\underline{70}$, 90 (1966).

23. Iwasaki, I. , Cooke, S. R. B. and Choi, H.S. , Trans. AIME, $\underline{217}$, 237 (1960).

24. Ahmed, S. , Can. J. Chem. , $\underline{44}$, 1663 (1966).

25. Schmut, R. , Ind. Eng. Chem. , $\underline{56}$(10), 28 (1964).

26. O'Connor, D. J. , Johansen, P. G. and Buchanan, A. S. , Trans. Faraday Soc. , $\underline{52}$, 299 (1956).

27. Eriksen, W. and Caines, R. , J. Phys. Chem. Solids, $\underline{14}$, 87 (1960).

28. Fuerstenau, D. W. , Trans. AIME, $\underline{205}$, 834 (1956).

29. Parreira, H. C. , J. Colloid Sci. , $\underline{20}$, 1 (1965).

30. Dallaire, R. , Personal communication.

31. Zucker, G. L. , Eng. Sc. D. thesis, Columbia University (1959).

32. Janz, G. J. and Taniguchi, H. , Chem. Rev. , $\underline{53}$, 397 (1953).

33. Buchanan, A. S. and Heymann, E. , J. Colloid Sci. , $\underline{4}$, 137 (1949).

34. Hurd, R. M. and Hackermann, J. , J. Electrochem. Soc. , $\underline{102}$, 594 (1955).

35. Pravdic, V. , Croatica Chimica Acta, $\underline{35}$, 233 (1963).

36. Ahmed, S. and Maksimov, D. , Mines Branch Research Report R 196, Dept. Energy, Mines and Resources, Ottawa (1968).

37. O'Connor, D. J. , Street, N. and Buchanan, A. S. , Austr. J. Chem. , $\underline{7}$, 245 (1954).

38. Johansen, P. G. and Buchanan, A. S. , Austr. J. Chem. , $\underline{10}$, 392 (1957).

39. Gaudin, A. M. and Fuerstenau, D. W. , Trans. AIME, $\underline{202}$, 958 (1955).

= = =