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*I hereby recommend that the thesis prepared under my supervision by* Carroll J. Wobroty

*entitled* Electrokinetic Phenomena in Capillaries

*be accepted as fulfilling this part of the requirements for the degree of* Doctor of Philosophy.

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# ELECTROKINETIC PHENOMENA IN CAPILLARIES

A dissertation submitted to the

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requirements for the degree of

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by

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To The Faculty of The Graduate School,
University of Cincinnati,
Cincinnati, Ohio.

Gentlemen:

I wish to submit the following dissertation, entitled ''Electrokinetic Phenomena in Capillries'', in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

The purpose of this study is to check the validity of the assumption of an electro-osmotic back pressure as the cause for lowered streaming potentials in small capillaries and as the source of a large portion of the filtration resistance for compressible slurries.

Both the theoretical investigation and the experimental data lead to the conclusion that the effect of the electro-osmotic back pressure is negligible, and other caused are shown to be responsible for the changes in streaming potentials.

Respectfully submitted

Carroll J. Dobratz

Acknowledgement.

In submitting this dissertation, the author wishes to express his appreciation to Professor W. L. Licht, Jr., who suggested the topic and directed the research, and to Professor E. F. Farnau for his helpful guidance and criticisms.

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Introduction:

B. F. Ruth, in his papers on the Theory of Filtration, states that an electro-osmotic back pressure is an appreciable factor in the filtration resistance for compressible slurries.

"A considerable portion of the increase in resistance to fluid flow through itself that is offered by a compressible filter medium under increasing pressure stress appears to be due to electro-osmotic flow of fluid in the reverse direction, and not solely to the contraction of the capillary voids. This hypothesis is well founded in the electrokinetic theory and is supported by a number of observations made in these laboratories, as well as by others to be found in the literature and in industrial practice." (17)

In support of this statement Ruth also reports (18) that the rate of flow through filter beds of crushed minerals can be predicted for all save the smallest sizes where this electro-osmotic back pressure would be effective. Also, the decrease with time of the rate of flow through a compressible slurry is said to be caused by the build-up of an electrical potential.

Other workers have also recognized the possibility of such an electro-osmotic effect. McCormack, in his book "Applications of Chemical Engineering" (11), gives directions for a filtration experiment to show the effect of changing concentration on filtration rate. An increase

in salt concentration with the corresponding increase in the electrical conductivity of the solution should decrease the electro-osmotic back pressure, and thus give an increase in filtration rates.

The basis for these assumptions of electro-osmotic back pressure with flow of fluids through capillaries is found in some of the more recent works on electrokinetics. It has been found that the streaming potential produced in very small capillaries is lower than that produced under the same conditions in larger capillaries, and several different explanations have been offered. Bull (3) credits this decrease to the electro-osmatic flow caused by the streaming potential built up across the ends of the capillary. Reichardt (15) also gives the electro-osmotic flow as the cause for the decreased streaming potential, deriving, however, a different equation to express the magnitude of the effect. Monaghan, Urban and White (22) have also carried out streaming potential measurements; but they report the decrease in potential in small capillaries as due primarily to the effect of increased conductivity due to surface conductance on the walls of the capillary. In smaller capillaries, having a relatively much larger surface, the conductivity is increased sufficiently to have a noticeable effect.

In none of the experimental work carried out by the above investigators, however, was there any attempt to measure the rate of flow. According to electrokinetic theory a streaming potential is produced by charges

being carried along by the stream of liquid flowing through a capillary. Therefore, measurement of the change in streaming potential should also indicate the change in rate of flow, but no confirmatory tests have been made..

The disagreement as to the cause for lowered streaming potential and the lack of data on the change in rate of flow to support the statements regarding filtration indicate the need for further research on this subject. A determination of the effect of capillary size on the rate of flow, streaming potential, and surface conductivity in capillaries should help to fill the apparent gap in the electokinetic theory. It would aid in presenting a clearer picture of the electrical effect, if any, to be found in filtration, and perhaps suggest methods of counteracting such an effect if it reaches the magnitude suggested by Bull and Reichardt.

Electrokinetic Theory:

The phenomenon of electro-osmosis, the movement of a liquid through a capillary under the influence of an electrical potential, was first discovered by Reuss in 1808, and the reverse of this process, the production of an electrical potential (streaming potential) across the ends of a capillary through which a liquid is flowing, was observed by Quincke in 1859. Quincke carried out a number of experiments and came to the conclusion "that the electromotive force produced by the streaming of pure water under a given pressure through a clay plate is independent of the size and thickness of the diaphragm; the electromotive force is, however, proportional to the pressure." Quincke, in his researches, was the first to postulate the existence of an electrical double layer at the phase boundary between liquid and solid, that is, a charged capillary wall surface and an oppositely charged liquid layer, which can be used to explain electro-osmosis and streaming potential. If it is assumed that the positive layer of the double layer is in the liquid in a glass capillary, a gradient of potential along the axis of the capillary will displace the positively charged water layer along the negatively charged, but fixed, wall, dragging the rest of the liquid in the ttube along because of internal friction. Similarly, if the liquid is moved by mechanical means, the streaming liquid displaces

the positive charges of the water molecules along the wall, and gives rise to an electrical potential along the tube (1).

In 1879 Helmholtz presented a theoretical treatment of the properties of the electrical double layer at two phase boundaries in tangential motion to one another. The general form of his final equation relating mobility to potential, although subsequently modified, is still in use. He made the following assumptions in his derivation:

(1) The liquid is oppositely charged to the rigid wall of the capillary, forming an electrical double layer along the wall.

(2) The thickness of the double layer is extremely small, but not vanishingly so. It is, furthermore, small when compared with the radius of the tube.

(3) The layer of liquid molecules in contact with the wall is not movable. It is fixed to the wall regardless of the mechanical force imposed on the liquid in the tube. The rest of the molecules in the liquid, near the walls and in the double layer, are movable and subject to the ordinary laws of friction of normal liquids.

(4) Only laminar flow of the liquid can occur.

(5) The wall is an insulator and the contained liquid possesses the property of electrical conductance.

(6) Any external difference of potential is simply superimposed upon the difference of potential in the liquid itself.

Working from these assumptions, Helmholtz derived expressions for streaming potential and electro-osmosis which gave the relationship connecting the electrokinetic potential to the potential across the double layer, the viscosity and electrical conductivity of the liquid, the pressure drop through the capillary and the electrical potential across the ends of the capillary. These derivations follow in the form given by MacDougal (12).

Electro-Osmosis:

Let $\sigma$ be the density of charge on the capillary wall and $-\sigma$ the corresponding charge on the liquid layer. Let d be the distance between the two layers, the thickness of the double layer, and let $\mathfrak{D}$ be the di-electric constant of the medium. Then the electrical potential of the wall with respect to the liquid layer will be given by the equation

$$(1) \qquad \zeta = \frac{4\pi\sigma d}{\mathfrak{D}} \quad , \quad \zeta = \text{electrokinetic potential}$$

Consider first the electro-osmotic flow in a capillary of radius r under the action of an external potential E. The force on a unit area of the Helmholtz double layer will be given by $E\sigma/l$ , $l$ = length of the capillary, and it will move with a velocity u . The liquid in the interior of the capillary will be carried along with the double layer and soon the whole cross-section will be moving with this velocity. The only frictional resistance is in the double layer. If we assume the velocity gradient between the two layers to be u/d , assuming no slip at the wall, and if $\eta$ is the coefficient of viscosity of the loquid, the frictional force on a unit area will be given by $\eta u/d$. Thus, in the steady state, we have

$$(2) \qquad \sigma E/l = \eta \frac{u}{d}$$

If we eliminate $\sigma$ and d by means of equation (1) and rearrange, we obtain the electro-osmotic velocity as

(3) $$u = \zeta D E / 4\pi l \eta$$

Assuming d to be very small in comparison to the radius, r, of the capillary, the volume of liquid flow, V, will be given by $V = \pi r^2 u$, or

(4) $$V = \zeta D E r^2 / 4 l \eta$$

If the electro-osmotic experiment is carried out so that the liquids on opposite sides of the capillary are allowed to change in level as electro-osmotic flow takes place, a hydrostatoc head will be built up, causing glow in the reverse direction. If this head be P, the volume of reverse flow will be given by Poiseuille's equation

(5) $$V = \frac{\pi P r^4}{8 \eta l}$$

If conditions of equilibrium are attained, so that there is equal flow in both directions, we can equate (4) and (5) and obtain an expression for the electro-osmotic pressure as

(6) $$P = \frac{2 \zeta D E}{\pi r^2}$$

Streaming Potential:

The velocity of the liquid flowing under a pressure P at a point at a distance y from the wall of a capillary is given by

$$(7) \qquad u = \frac{P}{4\eta l}(2ry - y^2)$$

P = applied pressure
$\eta$ = coefficient of viscosity
l = length of capillary
r = radius of capillary
y = distance of liquid from wall

Considering d , the thickness of the double layer, as very small compared to r , the velocity of the charged liquid layer would be given be

$$(8) \qquad u = \frac{P d r}{2\eta l}$$

The electrical current, I , produced by the movement of the electrical charges in the double layer, $\sigma$ = density of charge, will be given by

$$(9) \qquad I = 2\pi r u = \frac{\pi r^2 P d \sigma}{\eta l}$$

The accumulation of these charges will build up a potential, E , across the ends of the capillary; and this potential will cause a current to flow through the liquid, this current being given by the following equation

$$(10) \qquad I = E \frac{\pi r^2 K}{l}$$

When equilibrium is reached these two currents will be equal, and we can combine (9) and (10) to obtain

$$(11) \qquad E = \frac{P d\sigma}{\eta K}$$

Eliminating $d\sigma$ by use of (1) , we finally have the equation for the streaming potential produced by flow through a capillary

$$(12) \qquad E = \frac{P \Phi S}{4 \pi \eta K}$$

Helmholtz's original assumption of a planar double layer has been modified by Guoy (1) with the assumption of a "diffuse double layer", in which the charges are distributed throughout a region parallel to the walls; but this produces no change in the basec equations for electro-osmosis and streaming potentials.

These two equations have formed the basis for considerable research in the determination of the electrokinetic potential for many substances. The measurement of streaming potential offered a simple, direct method of determinaing the electrokinetic potential, but discrepancies have appeared in the measurements made with very small capillaries. The electrokinetic potential determined from measurements on these small capillaries has been found to be generally lower than that from larger capillaries. This effect can apparently be explained on the basis of an electro-osmotic back pressure produced by the streaming potential, which would decrease the effective pressure, causing flow through the capillary. This is the same effect which has been mentioned

in connection with filtration.

Bull (3) was one of the first to develop an expression which would enable the calculation of the electro-osmotic back pressure. The derivation follows:

Let $P_2$ = actual pressure causing flow through the capillary.
$P$ = applied pressure.
$P_1$ = electro-osmotic back pressure.

then the streaming potential will be given by

$$E = \frac{P_2 \phi \zeta}{4 \pi \eta K} \qquad or \qquad P_2 = \frac{4 \pi \eta K E}{\zeta \phi}$$

and the electro-osmotic pressure by

$$P_1 = \frac{2 \zeta \phi E}{\pi r^2}$$

The total applied pressure is given by

$$P = P_2 + P_1$$

and on substituting for $P_2$ and $P_1$

$$(13) \qquad P = \frac{4 \pi \eta K E}{\zeta \phi} + \frac{2 \zeta \phi E}{\pi r^2}$$

If this expression is divided through by $P_1 = \frac{2 \zeta \phi E}{\pi r^2}$ we obtain

$$(14) \qquad \frac{P}{P_1} = \frac{2 \pi^2 r^2 \eta K}{\zeta^2 \phi^2} + 1$$

This equation can then be used to calculate the electro-osmotic back pressure if the size of the capillary and the electrokinetic potential are known. Bull presented calculated values which showed that in solutions of 2 x 10 N NaCl, the ratio of $P_1 / P_2$ became of appreciable size for capillaries of radius less than . . . Bull's [illegible]

of radius less than 0.5 $\mu$. Ruth's statements concerning the electro-osmotic effect in filtration are based on this equation. It can be shown (see Appendix A) that the size of the capillaries in a compressible slurry such as ferric hydroxide is of the order of magnitude which should show this effect, hence an electro-osmotic back pressure is to be expected if Bull's equation is valid.

Equation (14) can be rearranged to put it in a form which will give a closer check on the actual change in rates of flow to be expected.

Since $P_2 = P(1 - P_1/P)$ is the actual pressure causing flow, Poiseuille's equation for viscous flow becomes

$$\bar{u} = \frac{P r^2}{8 \eta l}\left(1 - \frac{P_1}{P}\right) \tag{15}$$

Introducing equation (14), we obtain

$$\bar{u} = \frac{P r^2}{8 \eta l}\left[1 - \frac{\zeta^2 \mathfrak{D}^2}{2\pi^2 r^2 \eta K + \zeta^2 \mathfrak{D}^2}\right]$$

or

$$\bar{u} = \frac{P r^2}{8 \eta l}(1 - \psi) \quad , \quad \psi = \frac{1}{\frac{2\pi^2 r^2 \eta K}{\zeta^2 \mathfrak{D}^2} + 1} \tag{16}$$

Reichardt (15) has also attacked the problem of variation in the streaming potential produced in small capillaries. He presents as his basic flow equation for the fluid in the double layer

$$u = \frac{P}{2l}\int_0^y \frac{(r - y)}{\eta}\, dy + \frac{E}{4\pi l}\int_0^y \frac{\phi}{\eta}\left(\frac{d\phi}{dy}\right) dy \tag{17}$$

$l$ = length of capillary
$\mathfrak{D}$ = di-electric constant
$\eta$ = viscosity
$E$ = potential across ends of capillary
$r$ = radius of capillary
$y$ = distance from wall
$P$ = applied pressure
$\phi$ = potential at any point in double layer

If this expression is integrated, holding $\mathfrak{D}$ and $\eta$ constant, we obtain

$$u_y = \frac{P}{4\eta l}\left[(r-y)^2\right]_0^y + \frac{E\mathfrak{D}}{4\pi l\eta}\left[\phi\right]_0^y$$

$$(18) \qquad u_y = \frac{P}{4\eta l}(2ry - y^2) + \frac{E\mathfrak{D}}{4\pi l\eta}(\phi_y - \phi_0)$$

The average velocity will be given by

$$(19) \qquad \bar{u} = \frac{1}{\pi r^2}\int_0^r u_y\, 2\pi(r-y)\, dy$$

If this integration is carried out on equation (18), letting d = thickness of the double layer, we obtain

$$(20) \qquad \bar{u} = \frac{Pr^2}{8\eta l} + \frac{E\mathfrak{D}}{2\pi l\eta r^2}\left[\int_0^d(\phi_y - \phi_0)(r-y)\,dy + \int_d^r(\phi_y - \phi_0)(r-y)\,dy\right]$$

In the range from d to r, $\phi_y$ is constant and $\phi_d - \phi_0 = \zeta$. Also, for the purpose of integration, we can assume $\phi_y - \phi_0 = y\frac{\zeta}{d}$ in the range (0 → d). Then we obtain the following

$$(21) \qquad \bar{u} = \frac{Pr^2}{8\eta l} + \frac{E\mathfrak{D}}{2\pi l\eta r^2}\left[\frac{\zeta r^2}{2}\left(1 - \frac{d}{r} + \frac{d^2}{3r^2}\right)\right]$$

If we consider E as caused by streaming potentials, it will be acting in a direction in reverse to that of the pressure, and could be expressed, from the Helmholtz equation, approximately as $E = -\frac{\zeta P\mathfrak{D}}{4\pi\eta K}$. On substituting this value for E, we obtain

$$(22) \qquad \bar{u} = \frac{Pr^2}{8\eta l} - \frac{Pr^2}{8\eta l}\,\frac{\zeta^2\mathfrak{D}^2}{2\pi^2 r^2\eta K}\left(1 - \frac{d}{r} + \frac{d^2}{3r^2}\right)$$

Equation (22) can also be rearranged and written as

$$(23) \qquad \bar{u} = \frac{Pr^2}{8\eta l}(1-\psi), \qquad \psi = \frac{\zeta^2\mathfrak{D}^2}{2\pi^2 r^2\eta K}\left(1 - \frac{d}{r} + \frac{d^2}{3r^2}\right)$$

Reichardt (4) also presents a different equation developed with the assumption that the relationship between $\phi$ and $\zeta$ is given by

$$\phi = \zeta \left( e^{-\frac{4y}{d}} - 1 \right)$$

This equation being

$$(24) \quad \bar{u} = \frac{P r^2}{8 \eta l} (1 - \psi) \qquad \psi = \frac{2 A^2 d \lambda_0}{B r \lambda}$$

$A = 1 - d/r + \frac{1}{3} d^2/r^2$
$B = 1 - \frac{1}{2} d/r$
$\lambda_0$ = bulk specific conductance
$\lambda$ = conductance in capillary

Some experimental work has been done by these investigators in an attempt to determine the magnitude of the electro-osmotic effect on the streaming potential in capillaries of different sizes; but in most cases measurements were taken only of pressure and potential, and little attention was given to the rate of flow.

Urban, White, Monaghan (22) also determined the streaming potentials in a series of glass capillaries and found a decrease in the potentials obtained with small capillaries. However, they believe that this is due to an increase in the apparent conductivity of the liquid in the capillary due to surface conductance, which can be of appreciable magnitude for dilute solutions in small capillaries. They report that after corrections for surface conductance are made, the change in the values of the streaming potential is within the limits of experimental error for their measurements.

A variation in the viscosity of liquids in thin films or capillaries has also been suggested as an explanation for decreased streaming potentials. However, the work of Bostow and Bowden (2) indicates that there is no deviation from Poiseuille's law in the flow of water through slits down to one micron in width, and decreases in streaming potential are found in capillaries of considerably larger size.

If the expressions, as developed by Bull and Reichardt, are considered carefully, it will be noted that an important error has been made in the basic assumptions for their derivations, this error having been carried along from the original statements of Helmholtz. This is the assumption that an electrical force acts on the liquid in the double layer as though the liquid itself were charged. A more correct hypothesis would be that the charge on the capillary wall is produced by the preferential adsorption of ions from the liquid, and that the liquid double layer is really a region of increased concentration of ions of the opposite kind attracted to the vicinity of the charged wall. The phenomena of electro-osmosis and streaming potential can be as readily explained on this basis as by the original Helmholtz assumptions. The ions would be carried along by the liquid to produce a streaming potential in exactly the same manner as the charged liquid, as postulated by Helmholtz. And under the influence of an external electrical potential these ions in the double layer would move and carry the liquid with them to produce electro-osmosis. This transport of water by ions

is a recognized factor in the determination of transference numbers, although there is no agreement as to the exact magnitude of the amount transported by different ions.

On this basis the velocity of an ion in the double layer should be given by the expression

$$(27) \quad u_I = u_y - C\,E/l$$

where $u_y$ is the velocity of the liquid, $E/l$ is the potential drop along the tube and C is the ionic mobility. Using equation (7) to give the velocity of the liquid, we then obtain

$$(28) \quad u_I = \frac{P}{4\eta l}(2ry - y^2) - C\,E/l$$

If we consider the potential drop along the tube as due to streaming potential, we can substitute the value of E/P obtainable from streaming potential measurements in the above equation and write

$$(29) \quad u_I = \frac{P}{4\eta l}\left[(2ry - y^2) - 4\frac{E}{P}C\eta\right]$$

Equation (29) will give the effective velocity of the ions in the double layer which actually carry the charges to produce the streaming potential. It would also enable the calculation of the actual flow of liquid through the capillary if the amount of solution carried along with the ions were known. But, as has been mentioned before, there is no agreement as to the magnitude of this transport of solution by ions; and its effect could only be determined

qualitatively, even if the actual number of ions carrying current in the double layer were know; and the determination of this latter value appears inpossible. Although the streaming current can readily be measured, it is produced by ions moving with a velocity dependent on their distance from the capillary wall, and neither this distance nor the total number of ions is readily measurable.

Another factor which will make the theoretical calculation of the electro-osmotic back flow more difficult is that the only ionic velocities available are those determined in dilute solutions. In the present case the ions are under the influence of a high potential gradient (If $\zeta$ = 30 mv and the thickness of the double layer is $10^{-6}$ cm , we have a potential gradient of 30,000 volts/cm.) which will doubtlessly affect their velocity. However, this high potential gradient would have the effect of decreasing the velocity under the influence of an external potential, and the calculated values would indicate the maximum change in streaming potential or rate of flow to be expected.

If we consider a capillary $10^{-3}$ cm in diameter in which a streaming potential of 60 mv./cm. Hg is produced at 25° C by 1 x $10^{-4}$ N NaCl solution with specific conductivity equal to 1 x $10^{-5}$ ohms$^{-1}$ cm$^{-1}$ , we can easily show that the effect of the ionic mobility can not be neglected. The average mobility of ions other than the hydrogen ion is 6 x $10^{-7}$ cm/sec when a potential gradient of one millivolt per centimeter is applied. Then equation (29) gives the

velocity of an ion at a distance y from the capillary wall as

$$u_I = \frac{P}{4\eta l}\left[(y \times 10^{-7} - y^2) - \frac{4 \times 60 \times 6 \times 10^{-7} \times .009}{13.6 \times 980}\right]$$

$$= \frac{P}{4\eta l}\left[(y \times 10^{-7} - y^2) - 0.97 \times 10^{-14}\right]$$

From this it can be seen that the ions will have a positive velocity only when the distance from the capillary wall is $10^{-7}$ cm or greater, which distance is approximately the thickness of the double layer according the Reichardt (14). Actually the double layer must extend further than this in order to have a positive velocity of ions to produce the streaming potential; and the measured streaming potential will be lower because of this reversed flow in that portion of the double layer closer to the wall.

An equation for the streaming potential produced by the flow of a liquid through a capillary can be derived, using equation (28) to give the velocity of the ions carrying the streaming current. The current carried by an infinitesimal cross-section of the capillary will be

$$dI = 2\pi(r - y)\, u_I \sigma\, dy$$

and the total current

$$(30) \qquad I = \int_0^d 2\pi(r-y)\, u_I \sigma\, dy$$

On introducing $u_I$ from (28) and using Poisson's equation to express the relationship between $\phi$ and $\sigma$, we obtain

$$(31) \qquad I = \int_0^d 2\pi(r-y)\left[\frac{P}{4\eta l}(2ry - y^2) - cE/l\right]\frac{D}{4\pi}\frac{d^2\phi}{dy^2}\, dy$$

If we consider d<<r and neglect $c\,E/\ell$, integration of (31) gives the original Helmholtz equation for streaming current. Inclusion of the term $c\,E/\ell$, still assuming d<<r , will give the following equation for the streaming current:

$$(32) \qquad I = \frac{r^2 P \mathcal{D} \zeta}{4 \eta \ell} - \frac{E c \mathcal{D} \zeta}{2 \ell}$$

The magnitude of the current carried through the bulk of the capillary and by surface conductance on the walls will be given by

$$(33) \qquad I = \frac{E}{\ell}\left[\pi r^2 K_B + 2\pi r K_S\right]$$

$$= \frac{\pi r^2 E}{\ell}\left(K_B + \frac{2K_S}{r}\right)$$

$K_B$ = bulk conductivity
$K_S$ = surface conductivity

When equilibrium has been attained these two currents will be equal, and combining them will give the following equation for streaming potential in capillaries.

$$(34) \qquad \frac{E}{P} = \frac{\mathcal{D} \zeta}{4\pi\eta\left(K_B + \frac{2K_S}{r} + \frac{c\mathcal{D}\zeta}{2\pi r^2}\right)}$$

In all save the smallest capillaries the term $\frac{c\mathcal{D}\zeta}{2\pi r^2}$ can be neglected. Equation (34) is then equivalent to the original Helmholtz equation except that a corrective term for surface conductivity has been included.

If the usual arrangement of a filter bed prepared from small particles is used to provide capillaries, it is quite difficult to determine the actual surface to be used in calculating surface conductivity. For such a case, much better results are supposedly obtained if the resistance

across the capillary bed is measured and used to calculate the conductivity. This should give the effective conductivity in the capillary which can then be used instead of $\left(K_B + 2\frac{K_S}{r}\right)$ in equation (34) to give the following expression

$$(35) \qquad \frac{E}{P} = \frac{\mathscr{D} \zeta}{4\pi\eta\left(K_E + \frac{C\mathscr{D}\zeta}{2\pi r^2}\right)}$$

For purposes of comparison, the changes in the streaming potential caused by this ionic mobility as in equation (35) (making no correction for surface conductance) were calculated, and are presented in table I along with those calculated according to equation (14). The data of Bull and Gortner (4), as used by Bull in his original article were used in these calculations, and the average ionic mobility was taken to be $6 \times 10^{-7}$ $\frac{cm/sec.}{mv./cm.}$.

Table I

Calculated Streaming Potentials in Small Capillaries

$2 \times 10^{-4}$ M NaCl , $K_E = 2.9 \times 10^{-5}$ mhos

| Capillary Radius (microns) | Streaming Potential, E/P, as calculated by equation: (14) | (35) | (34) | Electro-osmotic factor, $\epsilon$ Eq'n(35) | Eq'n(34) | $\left(K_B + \frac{2K_S}{r}\right)$ / $K_E$ |
|---|---|---|---|---|---|---|
| 5 | 30.0 | 30.0 | 23.5 | $9.7\times10^{-5}$ | $7.8\times10^{-5}$ | $3.7\times10^{-5}$ |
| 2 | 29.9 | 30.0 | 17.7 | $6.1\times10^{-4}$ | $3.6\times10^{-4}$ | $4.9\times10^{-5}$ |
| 1 | 29.6 | 29.95 | 12.6 | $2.4\times10^{-3}$ | $1.0\times10^{-3}$ | $6.9\times10^{-5}$ |
| 0.5 | 28.6 | 29.85 | 8.0 | $9.7\times10^{-3}$ | $2.6\times10^{-3}$ | $10.9\times10^{-5}$ |
| 0.2 | 23.0 | 28.3 | 3.7 | 0.061 | $7.7\times10^{-3}$ | $22.9\times10^{-5}$ |
| 0.1 | 13.5 | 24.1 | 2.0 | 0.243 | 0.017 | $42.8\times10^{-5}$ |

Actually, any change in streaming potential with change in capillary size as indicated in table I would be masked by the change in the effective conductance of the capillary caused by surface conductivity.

Surface conductivity has been reported by diffenent investigators(8, 9, 10, 20, 21, 22, 23, 24) as ranging from $4 \times 10^{-8}$ to $2 \times 10^{-9}$ ohms$^{-1}$ per sq. cm. for solutions of NaCld of approximately $2 \times 10^{-4}$ N . Even if the lowest of these reported values is used, a much greater change in streaming potential will be produced than that calculated from electro-osmotic effects. This is shown clearly in the values calculated from equation (34), which also appear in table I.

This increase in effective conductance across the capillary will also decrease the electro-osmotic effect. Equation (35) could be written as

$$(36) \qquad \frac{E}{P} = \frac{\mathcal{D}S'}{4\pi\eta K_E(1+\epsilon)} \quad , \quad \epsilon = \frac{c\mathcal{D}S'}{2\pi r^2 K_E}$$

with the factor $\epsilon$ representing the electro-osmotic effect. Table I also shows the change in $K_E$ , $(K_E = K_B + \frac{2K_2}{r})$, produced in capillaries of different sizes, with the corresponding change in $\epsilon$ ; and it can be readily seen that most of the change in E/P is due to surface conductance.

Procedure:

The choice of the type of capillary tube used for the experimental work in this investigation was influenced by the results obtained by previous workers. When using a number of capillaries in parallel, as in a filter bed, the effects of partial clogging of one capillary are not very pronounced, and apparently more consistent results are obtainable by this method than by using only a single capillary. Therefore, it was decided to use a bed of graded sand to provide the capillaries. Since the sand used was of such a size that it would all pass 100 mesh, it was found necessary to use samples of crushed quartz for the tests made on larger sized particles.

The sand was prepared by grinding several pounds in a ball mill until 85% passed through a 200 mesh screen. Then the coarser fraction, above 270 mesh, was graded by using a set of standard screens in a Ro-Tap shaker. An attempt was made to classify the finer fraction of sand by use of an air classifier, but it was not too successful. Five fractions were thus obtained; two of these were further classified in a makeshift elutriator to give more uniformly sized fractions. The average diameter of the particles in each of the finer samples was determined by measuring, with a micrometer ocular, the diameter of 60-70 particles on a microscope slide. These diameters were all measured in one direction only, parallel to one of the crosshairs of the micrometer, and should be truly average diameters. The

larger particles, which would not fit in the field of view of a standard microscope, were placed on a macrometallograph and their images measured on the ground glass screen. Magnification was checked by measuring the image of a section of a meter stick placed on the stage. It was found that average diameters determined by this method did not agree with the results of screen analysis. For example, a sample passing a 200 mesh standard screen and held on a 270 mesh standard screen should have particle diameters between 74 and 52 microns or an average size of 63 microns. The average diameter found by microscopic measurements, however, was 102 microns. This was probably due to the definitely elongated shape of the particles, The screen separation would be based on the smallest dimension of a particle and would be inexact for any but equi-axed grains. Because of this variation the average diameter obtained from microscopic measurements was used in preference to an average screen size.

The sand, after being classified, was covered with aqua regia and allowed to stand for 24 hours; then it was washed 15-20 times with distilled water having a specific conductivity equal to $3 \times 10^{-6}$ mhos. As a check on the washing of the sand, distilled water, after standing over the sand for one hour, showed no change in conductivity. The sand was then rinsed 4-5 times with the solution to be used in the test, covered with this solution, placed in a stoppered flask, and allowed to stand at least 24 hours before being used. In some cased this time was one or two weeks, but no apparent

variation in results was observed. The sand was packed into a cell, made by fusing together a pair of T graound glass joints as shown in the accompanying diagram.

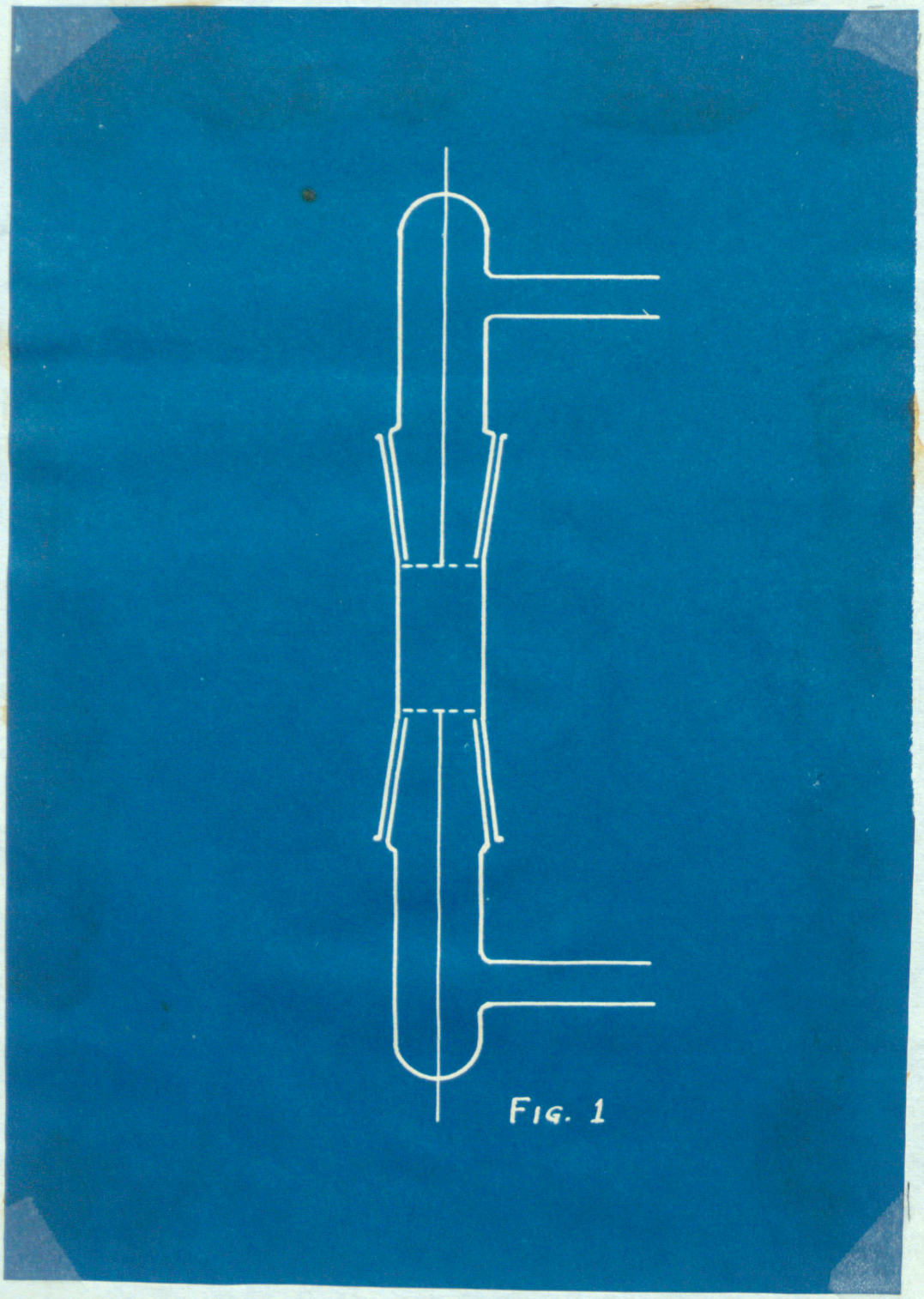


FIG. 1

Disks of perforated platinum, of a size to just fit over the end of the male joint, served both as electrodes and as support for the sand bed. Platinum wires were welded to these disks, and led out through glass seals to make connections with a potentiometer. In filling the cell, a disk of cloth was placed over the lower electrode and served as a filter cloth to hold back the sand. For the finer particle sizes, less than 100 microns, which would have passed through the cloth, a layer of approximately 5 mm of 100-200 mesh sand was placed on the cloth to act as an auxiliary filter bed.

The manner in which the cell was connected to a water supply and to the electrical circuit is shown in Fig. 2 . A 20-liter glass carboy was used as a reservoir for the solutions used in the tests, and a second carboy was used as a pressure tank to aid in maintaining a constant pressure in the system. Compressed air was bubbled through a water bottle, the rate of flow being judged from the number of bubbles, at such a rate as to maintain a constant pressure in the system. Since the rate of flow through the cell varied for each type of packing and for each different pressure, the rate of air input to maintain constant pressure had to be learned by experience. There were some slight leaks in the system, but these could be readily taken account of by adjusting the rate of air input; and since seals would have had to be broken to change solutions, it was not thought worth while to make the system completely air tight.

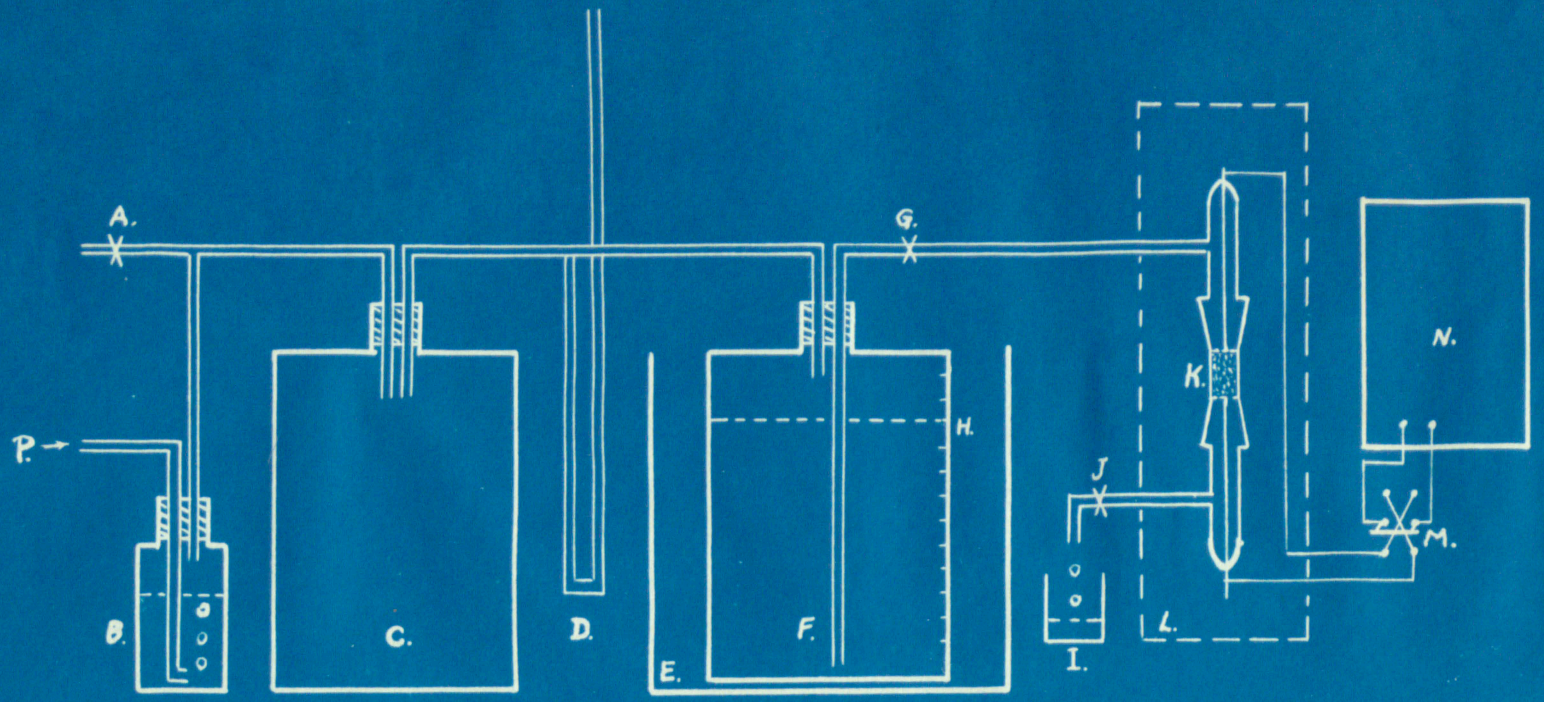



Figure 2.

A. Stopcock
B. Air Bubbler
C. Pressure leveler
D. Mercury Manometer
E. Water bath
F. Solution reservoir
G. Stopcock
H. Scale
I. Solution receiver
J. Stopcock
K. Streaming cell
L. Electrostatic screen
M. Reversing switch
N. Potentiometer
P. Compressed air

An open end mercury manometer was used to measure the pressure on the system; this reading was corrected for the gravity lead of the solution by using a scale, fastened in place on the carboy used as reservoir, to measure the head of solution. This solution head was converted to centimeters of mercury by assuming that the density of the solution was the same as that of pure water.

The temperature was controlled by placing the reservoir carboy into a thermostatically controlled water bath maintained at a temperature a few degrees above the average room temperature. The temperature of the room varied, but was very seldom more than 5 C off from the temperature of the bath. It is a reasonable assumption that no appreciable change in temperature would occur in the solution as it flowed through the cell. This method was used because of the need for complete electrical shielding of the cell which would have been noticeably affected by the electrical current in the thermostatic controller and the heating elements.

The rate of flow was measured by collecting and weighing the effluent over a time interval measured with a stop watch. For the coarser packings, where a comparatively rapid flow was maintained, a sample of 40-50 cc. of water was collected over an even time interval and weighed to 0.1 gram on a trip balance. In the case of the finer sand packings, this method was not applicable because of the low rates of flow. Therefore, a small sample was collected in a weighing bottle, which was stoppered immediately after

filling, and weighed on an analytical balance. Since flow was dropwise at these low rates, the time was measured from the point of fall of a drop, assuming that the size of the drops was uniform.

The streaming potential was measured by use of a vacuum tube potentiometer. Because of the high internal resistance of the cell, about one megohm, not enough current would flow to affect the galvanometer of a standard potentiometer. Also, any flow of current through the potentiometer would affect readings of the cell due to polaruzation. Therefore the vacuum tube potentiometer, originally developed by John Eastes (6) for use with glass electrodes, was used. With this instrument, readings could readily be made with an accuracy of one millivolt. An Eplab standard cell was used to set the potentiometer, and was frequently checked by comparison with two other standard cells.

Since bare platinum electrodes were used, some difficulties were experienced with polarization of the electrodes. But it was found that if stopcock C were closed, stopping flow through the cell, and at the same time the reversing switch D were thrown, the polarization potential could be measured. It was found that this polarizing potential would show some variation but would usually remain constant for several minutes if the pressure did not vary. When using the coarser sand for packing, so that the effect of closing the stopcock was almost instantaneous, this polarization potential could be checked very closely. If the potentiometer was set at the

proper value before the stopcock was closed, and the tap key of the potentiometer pressed immediately after closing, there would be no deflection of the galvanometer. Similarly, the full value of the streaming potential appeared immediately on opening the stopcock.

In the first tests the resistance in the cell was measured by determining the difference in potential produced by connecting a high resistance shunt (megohm carbon radio resistors, whose resistances were checked against a 100,000 ohm plug box as wall as against a standard wirewound megohm resistor) in parallel with the cell. From the difference in measured potential the resistance of the cell itself could be measured, since the streaming potential should be directly proportional to the resistance across the ends of the capillary.

However, this method introduced difficulty due to the increased polarization caused by current flowing through the electrodes. Also, this polarization was more difficult to measure because current would flow through the shunt, tending to didcharge the electrodes. On closing the stopcock, the potential would reverse to reach a maximum, which value was assumed to be the true polarization, and then would start to fall off as the electrodes discharged through the shunt. However, if the proper value of the polarization were found and the potentiometer set before closing the stopcocks, results could be checked with seeming accuracy. If the shunt were disconnected at the same time that the

stopcocks were closed, the polarization would be so great that the difference between the polarization and potential readings would be almost the same as in the case when no shunt were used.

To check the resistance reading a D.C. Wheatstone bridge was set up, using the cell and the shunt as one arm and two 10,000 ohm resistance boxes for the other. A D.C. current of 40 volts and a small portable galvanometer were used to check the bridge balance, with the circuit so arranged that the current could be reversed through the cell to counteract polarization. The point of balance was taken as that point at which, on closing the switch, the galvanometer needle would pause on zero for a moment and then gradually fall away as the elctrodes became slightly polarized. This behavior remained the same when the current was reversed repeatedly.

There was some discrepancy in resistances measured by the above methods, and as a further check, measurements were also made with audio frequency alternating current. The resistance cell was balanced against a standard wirewound megohm resistor by means of a 100,000 ohm decade potentiometer. A vacuum tube oscillator, giving almost a pure sine wave, was used as a source of alternating current. The use of a variable air condenser to balance capacitance and inductance in the circuit made it possible to obtain a sharp minimum in the head phones.

In all cases the resistance was measured after the

solution had been forced through the cell under high pressure. It was found that resistance measurements made immediately after the cell was filled and before the bed had been thoroughly packed by the streaming liquid were usually noticeably lower, especially for the smaller sized particles, and showed much greater variability.

The first tests were made with different solutions through the same sand bed without changing the packing. A set of readings was taken, using distilled water; then a small amount of NaCl was added and two or three liters of the resulting solution forced through the cell so that the concentration became constant throughout. This was allowed to stand so as to attain equilibrium at the surface, and a second set of readings was taken. This process was continued until the limiting concentration of $1 \times 10^{-4}$ N was reached, below which most of the conductivity would have been due to impurities in the water. However, such a series of runs usually required 3 to 4 days, and it was found that the sand bed apparently became clogged and the rate of flow decreased. Using the rate of flow as a standard, results apparently were more uniform if readings were taken sooner after the cell was packed. The passage of solution through a cell apparently was the contributing factor, since one cell was packed and allowed to stand for over a month and still showed this effect. Hence it was decided that the best results would be obtained from freshly packed sand beds.

In making a test run, the cell was partially assembled,

placing the two lower pieces together as shown in the diagram, filled with test solution and the filter cloth placed over the perforated lower electrode. The sand, suspended in water, was then poured in and allowed to settle by gravity. The cell was tapped gently to aid in packing. It was filled to the same level each time, to within 1 or 2 mm. of the position taken by the upper electrode when the cell was closed. It was necessary to have the cell filled with water to cover the filter cloth at all times, since, if bubbles of air were trapped beneath the electrode they were very difficult to remove after the cell was packed. The upper electrode was also filled with water before assembling, so that there would be no air trapped in the system. Air trapped in the upper part of the cell would probably have caused little interference save that due to its compressibility it would have been impossible to have flow stop immediately after closing the stopcocks. If bubbles of air collected on the lower electrode, readings were very erratic.

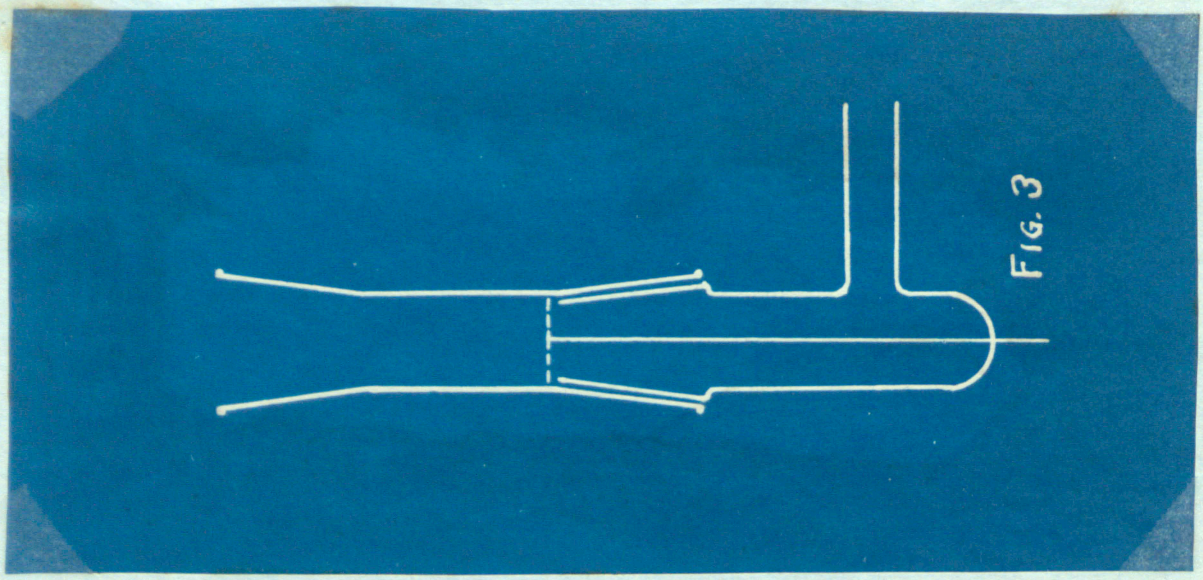


FIG. 3

After filling, the cell was connected to the circuit previously described, using rubber tubing to make connections. Small bubbles were almost invariably trapped in making connections, but in the upper part of the circuit they collected at the top of the cell, causing little interference, and in the lower part they were carried out with the flow of liquid. At the start, the valve to the compressed air supply was opened until the pressure reached the maximum to be used in the run, and was then adjusted so that the air bubbled into the sustem just rapidly enough to maintain the pressure. It was found that flow could be closely enough controlled from the outlet valve of the laboratory compressed air supply.

Approximately two liters of solution were forced through at this high pressure before taking data for all cases except the finest packings. For these packings the rate of flow was so low that this would have required too long a time, hence it was assumed that in any case equilibrium packing had been attained in two hours. Since the sand had been covered with the test solution and this solution was also used in filling the cell, the concentration in the cell could be considered identical with that in bulk, even though only a small quantity of solution had passed through the cell.

After this treatment it was assumed that the conditions in the cell would not change during the test run, which assumption seems verified by the results.

In order to prevent back pressure from causing reverse flow and loosening the sand in the cell when pressure was

being reduced, stopcocks A and C were opened and B was left closed. Then, when the pressure had been reduced to the desired value, A was closed, B opened and the solution started to flow again.

The experimental data obtained in the various tests are tabulated in Appendix B and have been used for calculations which will be considered later in this report.

Rate of Flow:

The rate of flow of a fluid through a bed of sized particles should be predictable if the size and shape of the particles, the dimensions of the packed bed, the packing characteristics of the particles and the viscosity of the fluid are known. The exact determination of particle size and shape for the usual heterogeneous mix is very difficult, as is the determination of the packing characteristics. However, if a homogeneous material is crushed and subsequently separated into fractions, the shape factor should be approximately constant for all particle sizes, and the packing characteristics should be almost the same. For such fractions the determination of an average diameter, while it will not enable the calculation of the exact volume of the particles, the exact surface area or the exact capillary size, should make possible the calculation of the ratio of surface areas or the ratio of capillary sizes for filter beds prepared from different sized particles.

The assumption of the same shape factor and packing characteristics for all sizes of particles leads directly to the assumption of a constant void volume, independent of particle size. This can readily be shown for spheres or regular prisms, and should hold for other shapes, allowing for different void volumes with different shape factors. On the basis of these assumptions, an expression relating the rate of flow of fluid through a packed filter bed to the size of the particles can be derived.

From Poiseuille's equation for viscous flow, the quantity of fluid flowing through a system of N capillaries is given by

(37) $$Q = N \frac{\pi r^4 P}{8 \eta l}$$

Q = quantity of liquid
N = number of capillaries
r = radius of capillaries
P = pressure
$\eta$ = viscosity
l = length of capillaries

If we introduce the above assumptions, we can write $N\pi r^2 = C_1$, and $r = C_2 D$ . Then we obtain

(38) $$Q/P = \frac{C_1 (C_2 D)^2}{8 \eta l} = C D^2$$

Thus the rate of flow through a filter bed should be directly proportional to the square of the particle size. Ruth (5) has carried out experimental work with beds of crushed minerals and reports good agreement except for very small sizes where an electro-osmotic back pressure would be effective.

The primary purpose of the present investigation was to determine the magnitude of this electro-osmotic back pressure. This should be most simply achieved by comparing the value of $Q/D^2$ for filter beds made from different sized particles. Accordingly, values of $Q/D^2$ were calculated from the experimental data presented in Appendix B, and are tabulated in Table II .

An equivalent capillary radius was also calculated and presented in Table II to enable a more direct comparison with earlier statements based on capillary size. This calculation is based on a combination of Poiseuille's law for flow in

capillaries and the measurement of the rate of flow and the electrical conductivity for the sand bed.

The quantity of liquid flowing through a system of capillaries is given by equation (37); and the conductivity of the liquid (if surface conductivity can be neglected) carried in a system of capillaries, is given by the equation

$$(39) \qquad K_c = N \frac{\pi r^2}{l} K_B$$

$K_c$ = conductivity across system of capillaries
$K_B$ = specific conductivity of solution

Thus, we can substitute the expression

$$(40) \qquad \frac{N \pi r^2}{l} = \frac{K_c}{K_B}$$

into equation (37) and obtain the following

$$(41) \qquad Q = \frac{r^2 P}{8 \eta} \frac{K_c}{K_B}$$

Equation (41) is independent of any assumptions as to the number of length of capillaries present. The ratio $K_c/K_B$ should be constant for all sizes of packing (assuming constant void volume) if surface conductivity can be neglected. If surface conductivity can not be neglected, the correct value of $K_c$ which should be used can be determined by plotting values of $K_c$ for different sizes against $1/D$, the reciprocal of the particle size, and extrapolating to $1/D = 0$. Thus, all the quantities in the equation except the capillary radius can in turn be calculated.

An average ratio of $\frac{K_c}{K_B} = 0.035$ , and the individual rate of flow values were used in calculating the equivalent capillary radii presented in Table II .

TABLE II

Rate of flow through sand filter beds.

a. $5 \times 10^{-4}$ M NaCl, Temp. 30° C .

| Particle size D(microns) | Equivalent capillary radius (microns) | Rate of flow $Q(\frac{cms}{cmHg\ min})$ | $\frac{Q}{D^2} \times 10^4$ |
|---|---|---|---|
| 6.0 | 0.83 | 0.0050 | 0.83 |
| 8.2 | 00.98 | 0.0042 | 0.66 |
| 10.7 | 1.65 | 0.012 | 1.00 |
| 50 | 7.45 | 0.244 | 0.97 |
| 71 | 9.88 | 0.428 | 0.87 |
| 108 | 14.3 | 0.900 | 0.78 |
| | | | average 0.85±0.10 |

b. $2 \times 10^{-4}$ M NaCl, Temp. 25° C .

| | | | |
|---|---|---|---|
| 6.0 | 0.81 | 0.0026 | 0.72 |
| 10.7 | 1.54 | 0.0094 | 0.82 |
| 12.0 | 1.595 | 0.0100 | 0.695 |
| 31.5 | 4.75 | 0.0895 | 0.90 |
| 50.0 | 6.52 | 0.168 | 0.67 |
| 57.0 | 8.27 | 0.270 | 0.83 |
| 71.0 | 10.37 | 0.425 | 0.82 |
| 72.5 | 10.41 | 0.430 | 0.84 |
| 1108 | 14.80 | 0.865 | 0.74 |
| 134 | 16.40 | 1.07 | 0.5955 |
| 160 | 21.00 | 1.75 | 0.68 |
| | | | average 0.77±0.08 |

c. $1 \times 10^{-4}$ M NaCl, Temp. 25° C .

| | | | |
|---|---|---|---|
| 6.0 | 0.675 | 0.00180 | 0.50 |
| 14.5 | 2.03 | 0.0163 | 0.77 |
| 31.5 | 4.57 | 0.083 | 0.84 |
| 57.0 | 8.50 | 0.287 | 0.89 |
| 72.5 | 9.45 | 0.355 | 0.675 |
| 108 | 14.7 | 0.860 | 0.74 |
| 160 | 19.2 | 1.46 | 0.57 |
| | | | average 0.71±0.11 |

TABLE II (continued)

d. Distilled water, Temp. 25° C .

| Particle size D(microns) | Equivalent capillary radius (microns) | Rate of flow $Q(\frac{gms.}{cmHg\ min.})$ | $\frac{Q}{D^2} \times 10^4$ |
|---|---|---|---|
| 6. | | | |
| 6/ 6.0 | 0.83 | 0.00273 | 0.76 |
| 14.5 | 1.94 | 0.0150 | 0.715 |
| 31.5 | 4.23 | 0.0706 | 0.71 |
| 57.0 | 7.52 | 0.224 | 0.69 |
| 72.5 | 10.3 | 0416 | 0.79 |
| 134 | 16.7 | 1.11 | 0.62 |
| | | average | 0.71±0.05 |

e. Distilled water, Temp. 25° C .

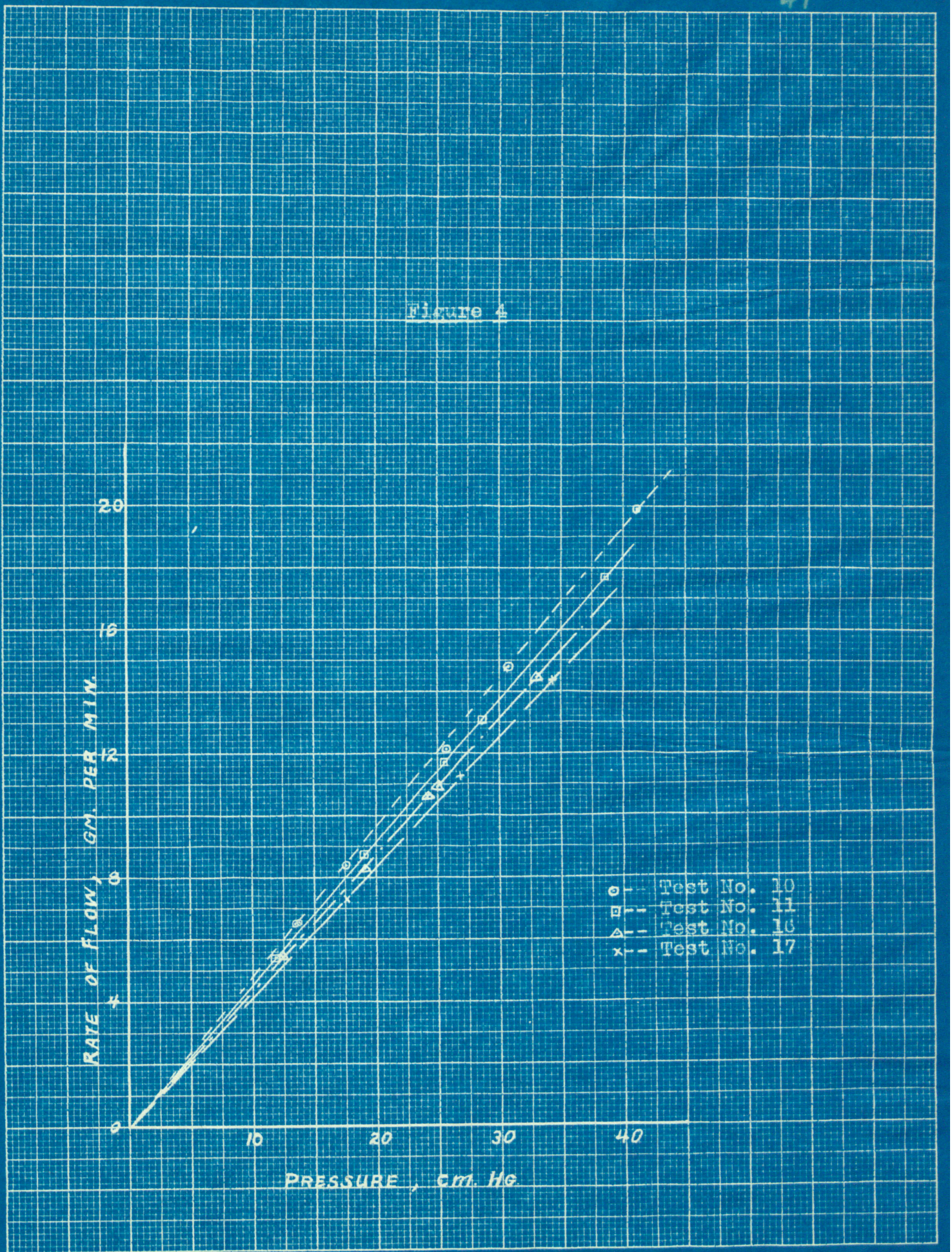
| Screen analysis, $D_s$ (microns) | Micro.Meas. $D_m$(microns) | Equiv. capillary radius (microns) | Rate of flow, $Q$ $\frac{gms.}{cmHg\ min.}$ | $\frac{Q}{D_s^2} \times 10^4$ | $\frac{Q}{D_m^2} \times 10^4$ |
|---|---|---|---|---|---|
| 63 | 102 | 13.9 | 0.77 | 1.94 | 0.74 |
| 96 | 141 | 18.4 | 1.34 | 1.45 | 0.67 |
| 135 | 195 | 27.4 | 2.95 | 1.62 | 0.77 |
| 177 | 321 | 35.3 | 4.94 | 1.57 | 0.48 |
| 251 | 510 | 53.9 | 11.5 | 1.83 | 0.44 |
| 356 | 670 | 61.7 | 15.1 | 1.19 | 0.34 |
| 503 | 910 | 82.5 | 26.9 | 1.08 | 0.32 |
| 611 | 1440 | 106 | 44.9 | 1.20 | 0.21 |
| 1000 | 1860 | 133 | 69.5 | 0.695 | 0.20 |

The values of $Q/D^2$ in table II show considerable variation, but the only definite indication of a change with varying particle size is in section e . The data in this section of the table are from material different from that used in the remainder of the tests, and of a different size range, and will therefore be discussed separately. To place all the other values on the same basis, those from table IIa can be corrected for the change in viscosity from 30° C. to 25° C ; then the average value of $Q/D^2$ changes from 0.85 to 0.76 . There is a slight decrease in $Q/D^2$ in passing to the more dilute solutions, but not enough to justify any state-

ment to the effect that the rate of flow increases with increasing concentration. Because of changes in packing characteristics on repacking and the effect of clogging of the filter beds during use, so much variation was found in tests on beds of the same sized particles, using the same solution, that not much significance can be attached to the changes reported above. This can be seen in Figure 4 which shows the variation in rate of flow obtained on repeated repacking of the cell with the same sized fraction, using solutions having the same conductivity, at the same temperature. It can be seen that the rate of flow, when plotted vs. P , for any one run held very closely to a straight line, but that there was as much as 10% variation in the rates of flow for different packings. This is very likely due to differences in the way the particles settled and packed in the cell. The thickness of the packed layer varied not more than 2 mm. in a total depth of 70 mm., hence could not be responsible for the variation in rate of flow. Also noted with these packed sand diaphragms was a gradual falling off in the rate of flow with time.

It was thought that this change in rate of flow could be caused either by clogging of the capillaries or by settling or reforming of the packed sand diaphragm. In order to be free of the possibility of changes in the packing characteristics during flow, a series of tests were carried out on a sintered glass filter crucible. After standing in chromic acid cleaning solution for one hour, the crucible was washed

Figure 4



several times with distilled water and placed in the streaming circuit as previously described, except that no provision was made for measuring streaming potentials or resistance in the cell. Distilled water was then forced through under a pressure of approximately 20 cm. of mercury, and after 300 cc. of distilled water had passed through the filter a series of measurements were made of the rate of flow and the conductivity of the effluent.

If one considers the expressions developed by Bull and Reichardt for the electro-osmotic back pressure,

$$u = \frac{P r^2}{8 \eta l}(1-\psi), \qquad \psi = \frac{1}{\frac{2\pi^2 r^2 \eta K}{\zeta^2 \beta^2} + 1}, \quad \text{Eqn (16)}$$

$$\psi = \frac{\zeta^2 \beta^2}{2\pi^2 r^2 \eta K}\left(1 - \frac{d}{r} + \frac{d^2}{3r^2}\right), \quad \text{Eqn (23)}$$

it is evident that a change in conductivity of the solution should also affect $\psi$ . This is shown by the figures in table table III , which show the effect of change in conductivity and size of capillary on this calculated electro-osmotic back pressure. The data of Bull and Gortner (4), which were used by Bull (3) in his original article were used.

E/P = 30 mv./cm.Hg

$K_s = 2.89 \times 10^{-5}$ ohm$^{-1}$cm.$^{-1}$

$\eta$ = 0.01 poises

Using the Helmholtz equation to equate E and $\zeta$

$$\frac{2\pi^2 r^2 \eta K}{\zeta^2 \beta^2} = \frac{r^2}{8 (E/P)^2 \eta K}$$

and on substituting the above values and converting to elec-

trostatic units, we obtain

$$\frac{12\pi r^2 \eta K}{\zeta^{12} D^2} = 8.25 \times 10^9 r^2$$

Using this equation we can calculate the value of $\psi$ for various capillary sizes as shown in table IIIa . If the assumption is made that $\zeta$ does not change appreciably with concentration we can also calculate the value of $\psi$ at other concentrations.

TABLE III

Electro-osmotic back pressure $\psi$ for different sized capillaries, at different conductivities.

$K = 3 \times 10^{-5}$ ohms$^{-1}$ cm.$^{-1}$

| r, microns | $\psi$; Eq'n(16) | $\psi$; Eq'n(23) |
|---|---|---|
| 5 | 0.0005 | 0.0005 |
| 2 | 0.003 | 0.003 |
| 1 | 0.012 | 0.012 |
| 0.5 | 0.046 | 0.049 |
| 0.2 | 0.233 | 0.303 |
| 0.1 | 0.548 | 1.2 (impossible) |

$K = 3 \times 10^{-6}$ ohms$^{-1}$ cm.$^{-1}$

| | | |
|---|---|---|
| 5 | 0.005 | 0.005 |
| 2 | 0.0295 | 0.030 |
| 1 | 0.118 | 0.121 |
| 0.5 | 0.326 | 0.485 |
| 0.2 | 0.75 | ----- |

Thus a noticeable change in the rate of flow with change in concentration should be found for capillaries having radii of the order of 1 micron, and measurement of change in flow rates accompanying changes in condentration should provide a check on the electrical back pressure.

As can be seen from the data for the glass filter crucible, as presented in table IV, the conductivity decreased at the start as the filter was being washed free of electrolytes by the distilled water, and there was a corresponding decrease in the rate of flow. But the rate of flow continued to decrease when NaCl was added to the streaming solution to increase the conductivity. No definite conclusions could be reached as to whether or not the increased conductivity partially counterbalanced the decrease in flow due to clogging of the filter.

TABLE IV.

Rate of flow through sintered glass filter, $T = 24^{\circ}$ C .

| P(cm.Hg) | Q(gm./min.) | Q/P | K,($ohm^{-1}$ $cm.^{-1}$) |
|---|---|---|---|
| 18.66 | 54.2 | 2.9 | $8.0 \times 10^{-5}$ |
| 15.87 | 38.3 | 2.41 | $5.14 \times 10^{-5}$ |
| 19.42 | 44.5 | 2.29 | $4.35 \times 10^{-5}$ |
| 18.24 | 35.2 | 1.93 | $1.47 \times 10^{-4}$ |
| 17.65 | 33.5 | 1.89 | $1.14 \times 10^{-3}$ |

To prevent this clogging effect in the filter, two sintered glass filter crucibles were placed in the circuit in series and a manometer connected between them, so that only the pressure drop causing flow through the second filter would be measured. With this arrangement, the results tabulated in table V were obtained. It can be seen that there is again no noticeable change in the rate of flow with conductivity.

TABLE V.

Rate of flow of pre-filtered solution through sintered glass filter, T = 21° C .

| | P(in.Hg) | Q(gms./min.) | Q/P | $K$(ohm$^{-1}$ cm.$^{-1}$) |
|---|---|---|---|---|
| | 8.12 | 95.3 | 11.7 | $4.03 \times 10^{-6}$ |
| | 7.78 | 91.3 | 11.7 | $2.57 \times 10^{-5}$ |
| | 7.68 | 87.7 | 11.4 | $2.1 \times 10^{-5}$ |
| | 7.85 | 90.0 | 11.4 | $1.04 \times 10^{-4}$ |
| 8. | 8.05 | 93.3 | 11.6 | $9.4 \times 10^{-2}$ |

To check whether or not the size is such that an electro-osmotic back pressure is to be expected, the equivalent radius of the capillaries in the sintered glass filter bed can be calculated. Assuming that the voids occupy approximately 20% of the cross-sectional area, as indicated by conductivity measurements on the sand beds, we can proceed as follows.

Dimensions of packing, 0.3 cm, thick
2.5 cm. diameter

Cross-sectional area $= 0.20 \times \pi \times \frac{(2.5)^2}{4} = 0.982$ cm.$^2 \simeq 1$ cm.$^2$

Rate of flow $= 11.5 \frac{\text{cc./min.}}{\text{in.Hg}}$

Poiseuille's equation, $Q/P = \frac{N \pi r^4}{8 \eta l}$

$Q$ = gms./sec.
$\eta$ = 0.01 poise
$P$ = dynes/cm.$^2$

Cross-sectional area $= N \pi r^2 = 1.0$ cm.$^2$

$$r^2 = \frac{11.5 \times 8 \times 0.01 \times 0.3}{13.6 \times 2.54 \times 980 \times 60} = 13.6 \times 10^{-8}$$

$$r = 3.7 \times 10^{-4} \text{ cm.}$$

A change in the rate of flow of approximately 1% should be expected with capillaries of this size on a change in conductivity from $4 \times 10^{-6}$ to $2 \times 10^{-5}$ $ohm^{-1} cm.^{-1}$, but no such change could be detected.

To obtain a further check on this change in rate of flow with concentration, a series of tests were conducted on a sand bed prepared from the finest sand sample, packed in the regular streaming potential cell. Distilled water and N/100 NaCl were alternately streamed through the cell and the rates of flow measured. The cell was not disturbed during the tests save for changing of connections, and therefore there should be no changes due to differece in packing. Conductivity measurements were made in the bed itself, since the rate of flow was too slow, 10 cc. per hour, for ready colledtion of a sample for a conductivity test. When the resistance across the bed did not change after a days flow, it was assumed that the concentration of the solution in the bed was the same as that in the bulk of the liquid.

The results obtained in this test are tabulated in table VI , and show a gradual clogging of the filter bed as the run progressed, but no apparent change with change in concentration. Previous calculations have indicated an equivalent capillary radius of approximately 1 micron, and according to Bull's equation there should be a decrease in the flow rate of approximately 10% in passing from a N/100 NaCl solution to distilled water with a conductivity of $4.5 \times 10^{-6}$ $ohm^{-1} cm^{-1}$.

TABLE VI.

Effect of change in concentration on flow through sand beds.

| Date | Temp. (°C) | $R_c$ (megohm) | Q (gms./min.) | P (cm.Hg) | Q/P |
|---|---|---|---|---|---|
| Jan. 19 | 25.5 | 1.8 | 0.1255 | 44.0 | 0.00285 |
| 19 | 24.5 | 0.03 | 0.118 | 43.0 | 0.00274 |
| 19 | 24.0 | 0.03 | 0.113 | 42.8 | 0.00263 |
| 19 | 24.0 | 0.0257 | 0.1136 | 42.8 | 0.00264 |
| 19 | 24.0 | 0.0233 | 0.1112 | 42.4 | 0.00262 |
| 20 | 23.5 | 0.0213 | 0.1075 | 41.9 | 0.00257 |
| 21 | 24.5 | 0.0212 | 0.109 | 41.8 | 0.00260 |
| 22 | 25.5 | 1.75 | 0.106 | 42.9 | 0.00247 |
| 23 | 25.5 | 2.025 | 0.1057 | 42.9 | 0.00246 |
| 24 | 27.0 | 2.00 | 0.110 | 43.0 | 0.00256 |
| 24 | 27.0 | 0.123 | 0.0955 | 42.4 | 0.00223 |
| 25 | 26.8 | 0.0213 | 0.0954 | 43.3 | 0.00220 |
| 26 | 23.2 | 1.65 | 0.0862 | 44.9 | 0.00192 |
| 26 | 23.2 | 0.0345 | 0.0839 | 42.7 | 0.00197 |

Because the change in rate induced by changed concentration could have been masked by the gradual clogging of the sand bed, this test was repeated using two cells in series, measuring the pressure drop over the second cell only. The results appear in table VII, and do show the predicted change in rate of flow with change in conductivity of the solution. However, the magnitude of the change is less than that calculated by Equation (16) or (23) and is in agreement with the ideas previously expressed in this paper. That is, the electrical back pressure is less than that calculated on the basis of the liquid itself being charged.

TABLE VII.

Effect of change in concentration on flow of pre-filtered solution through sand beds.

| Date | Temp. (°C) | $K_B \times 10^6$ (mhos) | $R_c$ (ohms) | P (cm.Hg) | Q (gms/min) | Q/P |
|---|---|---|---|---|---|---|
| Mar 8 | 25.0 | 4.7 | 450,000 | 19.05 | 0.179 | 0.0094 |
| 9 | 25.0 | 4.7 | 490,000 | 18.88 | 0.1755 | 0.0093 |
| 10 | 25.0 | 4.7 | 490,000 | 18.6 | 0.170 | 0.00905 |
| 10 | 25.0 | 70.0 | 99,000 | 28.9 | 0.279 | 0.00965 |
| 10 | 25.0 | 70.0 | 87,000 | 12.27 | 0.117 | 0.00955 |
| 10 | 25.0 | 70.0 | 83,500 | 21.8 | 0.207 | 0.00950 |
| 11 | 25.0 | 4.7 | 470,000 | 15.57 | 0.1385 | 0.0089 |
| 11 | 25.0 | 4.7 | 470,000 | 15.37 | 0.137 | 0.0089 |
| 12 | 25.0 | 70.0 | 85,000 | 14.95 | 0.139 | 0.0093 |

As for the implication that this effect is of importance in filtration, consider the case of a solution having a conductivity of $3 \times 10^{-4}$ ohms$^{-1}$ cm.$^{-1}$. (tap water as supplied in the laboratory had a conductivity of $2.5 \times 10^{-4}$ ohms$^{-1}$cm.$^{-1}$) With such a solution a 3% decrease in rate of flow is calculated by equations (16) or (23), (neglecting surface conductivity), for capillaries with a radius of 0.2 microns, which is about the minimum size for ordinary filtrations. And it has been shown that the actual change is less than this calculated value. Hence, one should be justified in saying that the electro-osmotic effect is negligible in filtration. The data in table IIIe, which were mentioned previously, present some interesting facts. First, there is the extreme difference between the average diameter on the basis of screen analysis and as measured by a microscope. This must be due to the particles being, on the whole, relatively long or

ellipsoidal in shape rather than equi-axed or spherical. The screen analysis gives an average of the mimimum dimensions whereas the microscopic measurement gives a more truly average diameter which will not agree with the screen analysis except in the case of equi-axed particles. Similar disagreements in size analysis have been recently reported by Rittenhouse (18).

On the basis of the rate of flow, the average screen diameter seems to give a better measure of the capillary size. However, if the question of turbulent flow is considered, this apparent agreement is shown to be in error.

Experimental work on the flow of fluids through sand beds indicates that deviation from the linear relationship between pressure and velocity is caused by the start of turbulent flow. This first appears when the Reynolds number, computed with the average particle size from screen analysis as the diameter, is 5 or larger (14). On this basis, the limiting velocity for viscous flow of a bed of particles having an average size of 100 microns would be 0.5 cm. per sec. From the equivalent capillary radius determined for this sized fraction from rate of flow and conductivity, a pressure drop of 6.5 cm. of mercury would produce turbulent flow in the cell used in this investigation. There would then no longer be a linear relationship between velocity through the bed and the pressure drop across it. However, because of the very gradual transition from viscous to turbulent flow in packed beds, probably no great deviation would be found in the pressure range to 10 cm.Hg as used in the

present case. Therefore the assumption of viscous flow should still be applicable.

When we consider the beds packed with larger particles, however, it is apparent that the assumption of viscous flow is no longer valid, and that the relationship between pressure drop and rate of flow will not be the same. For example, the limiting pressure drop for the 177 micron fraction would be 1.1 cm. of mercury, which indicates that all the measurements were in the turbulent range. Thus the values of $Q/D^2$ based on the average diameter from microscopic measurements are probably the more correct. They decrease for particles larger than 177 microns, which is to be expected if turbulent flow is encountered, since the friction drop becomes proportionately greater.

Also, this may explain the slightly lower values obtained with the largest particles in the other tests, since they are just in the size range where turbulent flow will first appear.

Streaming Potential and Surface Conductance:

As has been shown previously, the streaming potential obtained in a system of capillaries depends directly on the electrical conductivity between the ends of the capillary. Hence, anything which changes this conductivity will change the streaming potential. Also, it was mentioned that the chief effect of change in capillary size on streaming potential measurements would be that caused by a change in in resistance due to increased surface conductivity.

For irregular particles one can not obtain the surface area as a specific function of the particle size, and hence cannot obtain an exact expression for the change in conductivity. However, if we can assume a constant shape factor, the surface area should be directly proportional to the reciprocal of the diameter of the particle. This can be readily shown for spheres and regular prisms and should hold for all solids possessing the same shape factor. Then the effective specific conductivity in a filter bed would be given by

$$K_E = K_B + K_s \, G/D$$

when G is a constant which takes into consideration the shape of the particle. (In this investigation, the constant G was taken to be $\pi\sqrt{2}$, which is the theoretical value calculated for close packed spheres. It also agrees quite closely with results based on the rate of solution of crushed quartz in hydrofluoric acid (7) ). Thus the streaming potential would

be given by

$$E/P = \frac{D\,S}{4\pi\eta K_E} = \frac{D\,S}{4\pi\eta\left(K_B + K_S\,G/D\right)}$$

or

$$(42)\quad \frac{P}{E} = \frac{4\pi\eta K_B}{D\,S} + \frac{4\pi\eta K_S}{D\,S}\,\frac{G}{D}$$

Wherein both $\frac{4\pi\eta K_B}{D\,S}$ and $\frac{4\pi\eta K_S\,G}{D\,S}$ are constant for any given test. This equation indicates that the plotting of 1/D vs. P/E should give a straight line. Extrapolation of this line to 1/D = 0 should then give the value of E/P independent of surface conductance and enable the calculation of the true value of the elctrokinetic potential. It will be shown later that measurement of the resistance across the capillary will not always give the correct value for use as $K_E$ in the streaming potential equation. Also, the surface conductivity can be determined directly from the equation of the line obtained when plotting P/E vs. 1/D . This equationcan be represented as

$$(43)\quad P/E = A\ 1/D + B \qquad A = \frac{4\pi\eta K_S\,G}{D\,S}$$

$$B = \frac{4\pi\eta K_B}{D\,S}$$

and the surface conductivity is given by

$$(44)\quad K_S = \frac{A}{B}\,\frac{K_B}{G}$$

Average values of P/E and 1/D from the data in Appendix B are tabulated in table IX and plotted in Figure 5 . The constants A and B , to determine the lines as drawn, were evaluated analytically by the method of least squares, and most

of the points fall very close to these lines. Values of surface conductivity were calculated from these constants and are indicated on the graph. The electrokinetic potential for the different solutions were also calculated from the values of P/E at 1/D = 0 , and are listed in table IX; they agree very well with the values reported by Bull and Gortner (4) for similar materials and show the same changes with concentration as reported by other investigators (1).

TABLE IX.

Experimental values of 1/D and P/E.

a. $5 \times 10^{-4}$ N NaCl, T = 30° C.
$K_B = 7.5 \times 10^{-5}$ mhos., $\zeta$ = 66 mv.

| D(microns) | 1/D($cm.^{-1}$) | P/E | $1/R_c$ |
|---|---|---|---|
| 6 | 1667 | 0.170 | 3.22 |
| 8.2 | 1220 | 0.161 | 2.50 |
| 10.7 | 935 | 0.137 | 2.38 |
| 50 | 200 | 0.106 | 2.13 |
| 71 | 141 | 0.105 | -- |
| 108 | 92.5 | 0.098 | 2.04 |
| ∞ | 0 | 0.0964 | -- |

b. $2 \times 10^{-4}$ N NaCl, T = 25° C.
$K_B = 2.6 \times 10^{-5}$ mhos., $\zeta$ = 76.5 mv.

| | | | |
|---|---|---|---|
| 10.7 | 935 | 0.0578 | 1.07 |
| 12 | 833 | 0.0538 | 1.064 |
| 31.5 | 317 | 0.0435 | 1.05 |
| 50 | 200 | 0.0352 | 1.02 |
| 57 | 175 | 0.0351 | 1.06 |
| 71 | 141 | 0.0364 | 1.00 |
| 72.5 | 138 | 0.0351 | 1.04 |
| 108 | 92.5 | 0.0333 | 1.05 |
| 134 | 74.5 | 0.0336 | 0.955 |
| 160 | 62.5 | 0.0375 | --- |
| ∞ | 0 | 0.03215 | --- |

TABLE IX (continued).

c. $1 \times 10^{-4}$ N NaCl, $T = 25^{0}$ C.
$K_B = 1.21 \times 10^{-5}$ mhos., $\zeta = 86.5$ mv.

| D(microns) | $1/D(cm.^{-1})$ | P/E | $1/R_c$(B.C.) | $1/R_c$(A.C.) |
|---|---|---|---|---|
| 6 | 1667 | 0.0585 | 0.848 | 3.11 |
| 14.5 | 690 | 0.0263 | 0.642 | 2.58 |
| 31.5 | 317 | 0.0216 | 0.591 | 2.48 |
| 57 | 175 | 0.0183 | 0.543 | 2.16 |
| 72.5 | 138 | 0.01795 | 0.495 | 2.06 |
| 108 | 92.5 | 0.0151 | 0.465 | -- |
| 134 | 74.5 | ---- | --- | 1.91 |
| 160 | 62.5 | 0.0168 | 0.400 | -- |
| | 0 | 0.01325 | 0.391 | 1.74 |

d. Distilled water, $T = 25^{\circ}$ C.
$K_B = 1.97 \times 10^{-6}$ mhos., $\zeta = 50$ mv.

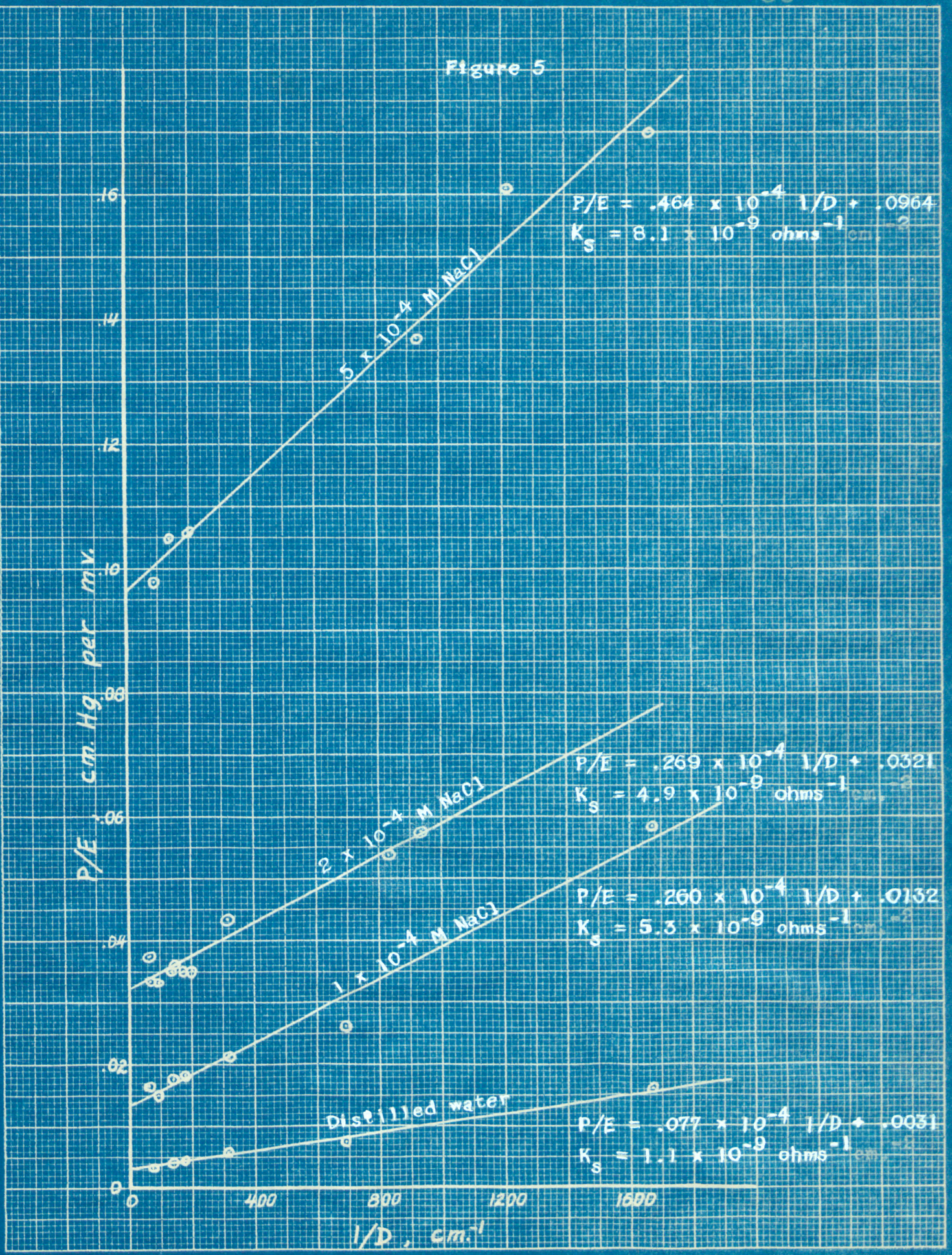
| | | | |
|---|---|---|---|
| 6 | 1667 | 0.0161 | 0.185 |
| 14.5 | 690 | 0.00758 | 0.157 |
| 31.5 | 317 | 0.00592 | 0.156 |
| 57 | 175 | 0.00475 | 0.130 |
| 72.5 | 138 | 0.00415 | 0.118 |
| 134 | 74.5 | 0.00345 | 0.102 |
| | 0 | 0.00306 | 0.088 |

e. Distilled water, $T = 25^{\circ}$ C.
$K_B = 1.97 \times 10^{-6}$ mhos.

| $D_s$ | $D_m$ | P/E | $1/R_c$ | $1/D_s$ | $1/D_m$ |
|---|---|---|---|---|---|
| 63 | 102 | 0.00388 | 0.124 | 159 | 98.0 |
| 96 | 141 | 0.00357 | 0.119 | 104 | 71.0 |
| 135 | 195 | 0.00298 | 0.109 | 74.1 | 51.3 |
| 177 | 321 | 0.00289 | 0.102 | 56.5 | 31.2 |
| 251 | 516 | 0.00301 | 0.099 | 39.8 | 19.6 |
| 356 | 670 | 0.00283 | 0.091 | 2811 | 14.9 |
| 503 | 910 | 0.00293 | 0.086 | 19.9 | 11.0 |
| 611 | 1440 | 0.00273 | 0.0825 | 16.4 | 7.06 |
| 1000 | 1860 | 0.00316 | 0.0800 | 10.0 | 5.38 |

The measured values of resistance across the cell should also enable the determination of surface conductivity, and should serve as a check on the values calculated from streaming potentials. The conductivity across the cell can

Figure 5



be expressed by

$$(42\ a) \qquad 1/R_c = C K_E = C\left(K_B + K_s \frac{G}{D}\right)$$

and a plot of $1/R_c$ vs. $1/D$ should enable the determination of surface conductivity in the same way as from streaming potentials. The above equation can be written

$$(43\ a) \qquad 1/R_c = A' \frac{1}{D} + B' \qquad A' = C K_s G \qquad B' = C K_B$$

and determination of the constants A' and B' will give the surface conductivity as $K_s = \frac{A'}{B'} \frac{K_B}{G}$. Values of $1/R_c$ from the data in Appendix B are also tabulated in table IX and are plotted against 1/D in Figure 6.

The data from the first two tests were not included in the plots since they were thought to be considerably in error. These first resistance measurements were based on the change in streaming potential produced by placing a shunt across the ends of the filter bed. Apparently they are in error because of the extreme difficulty of measuring the increased electrode polarization caused by the current flowing through the shunt. This is indicated by the fact that no change in resitance was detected with change in particle size when using the $2 \times 10^{-4}$ N NaCl solution, although there was a marked change in streaming potential.

The other direct current resistance measurements were made with a Wheatstone bridge, the resistance of the cell being high enough and the current accordingly so low that polarization was almost negligible. Frequent reversals of

current direction also aided in counteracting the effect of polarization.

These measurements give results in agreement with those from streaming potentials if only the larger sized particles are considered, but there is a definite difference for the smaller sizes. Since there was the possibility of polarization errors in these direct current resistance measurements, they were further checked by use of a thousand cycle alternating current bridge. Since no streaming potentials were to be measured, a smaller cell which could be placed in a thermostatically controlled water bath was used for these measurements. The values of 1/R from the alternating current measurements with a 1 x $10^{-4}$ N NaCl solution are also tabulated in table IX and plotted on Figure 6. It can be seen that they agree quite closely with the direct current measurements. Values of surface conductivity were also calculated from the plots in Figure 6, the measurements for the two smaller sizes being omitted from consideration. This omission will be justified later on in the report.

A number of measurements were also made on a series of particles in the larger size range to determine whether or not the linear relationship between 1/D and $1/R_c$ or P/E could be considered as valid for all the larger sizes. The streaming potential and direct current resistance measurements are tabulated in table IXe. The streaming potentials for the largest particles are evidently low because of the effect of turbulent flow as previously discussed.

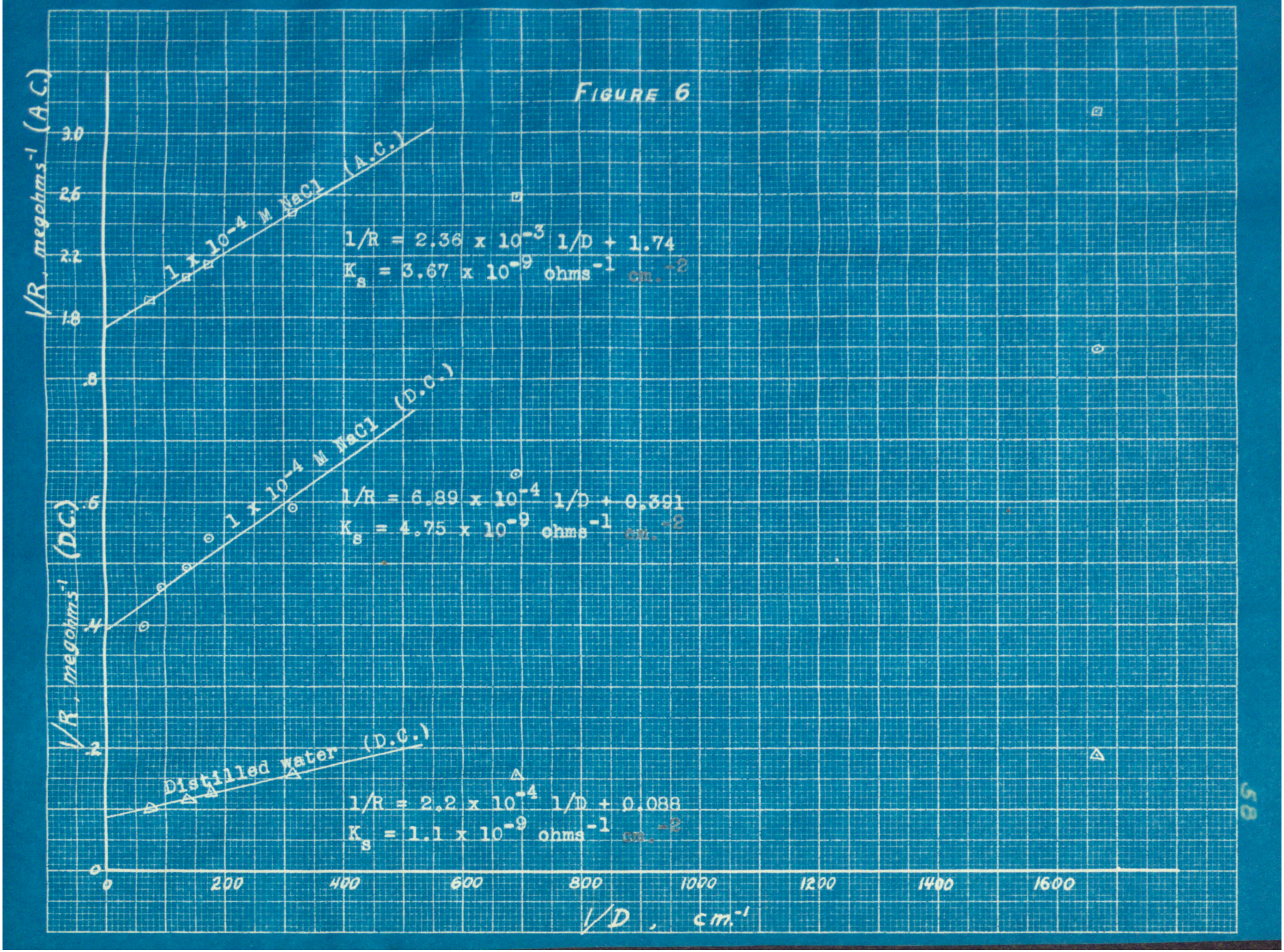


FIGURE 6
1/R, megohms⁻¹ (A.C.)
1 x 10⁻⁴ M NaCl (A.C.)
1/R = 2.36 x 10⁻³ 1/D + 1.74
K_s = 3.67 x 10⁻⁹ ohms⁻¹ cm.⁻²
1/R, megohms⁻¹ (D.C.)
1 x 10⁻⁴ M NaCl (D.C.)
1/R = 6.89 x 10⁻⁴ 1/D + 0.391
K_s = 4.75 x 10⁻⁹ ohms⁻¹ cm.⁻²
Distilled Water (D.C.)
1/R = 2.2 x 10⁻⁴ 1/D + 0.088
K_s = 1.1 x 10⁻⁹ ohms⁻¹ cm.⁻²
3.0
2.6
2.2
1.8
.8
.6
.4
.2
0
0
200
400
600
800
1000
1200
1400
1600
1/D, cm.⁻¹

Because of this error no attempt was made to determine surface conductivity or electrokinetic potential from these streaming potential measurements.

However, values of 1/D and $1/R_c$ are plotted in Figure 7, and the surface conductivity is calculated. Because of the different size range, these plots had to be made to a larger scale and could not be combined with the previous ones.

Both the values of D from screen analysis and from microscopic measurement were used, but there is no indication of a closer correspondence to a straight line plot for either set of measurements.

A series of alternating current reistance measurements were also carried out with this set of larger particles. The results are tabulated in table X and values of 1/D and $1/R_c$ are plotted in Figure 7 to determine surface conductivity. These measurements all indicate fair agreement with the previous results, and again do not indicate either method of size analysis as being more correct.

Also, it can be seen from the measured resistances with solutions of high conductivity, for which surface conductance is negligible, that the errors due to variations in filling of the cell and in seating the ground joints are probably not greater than 1%.

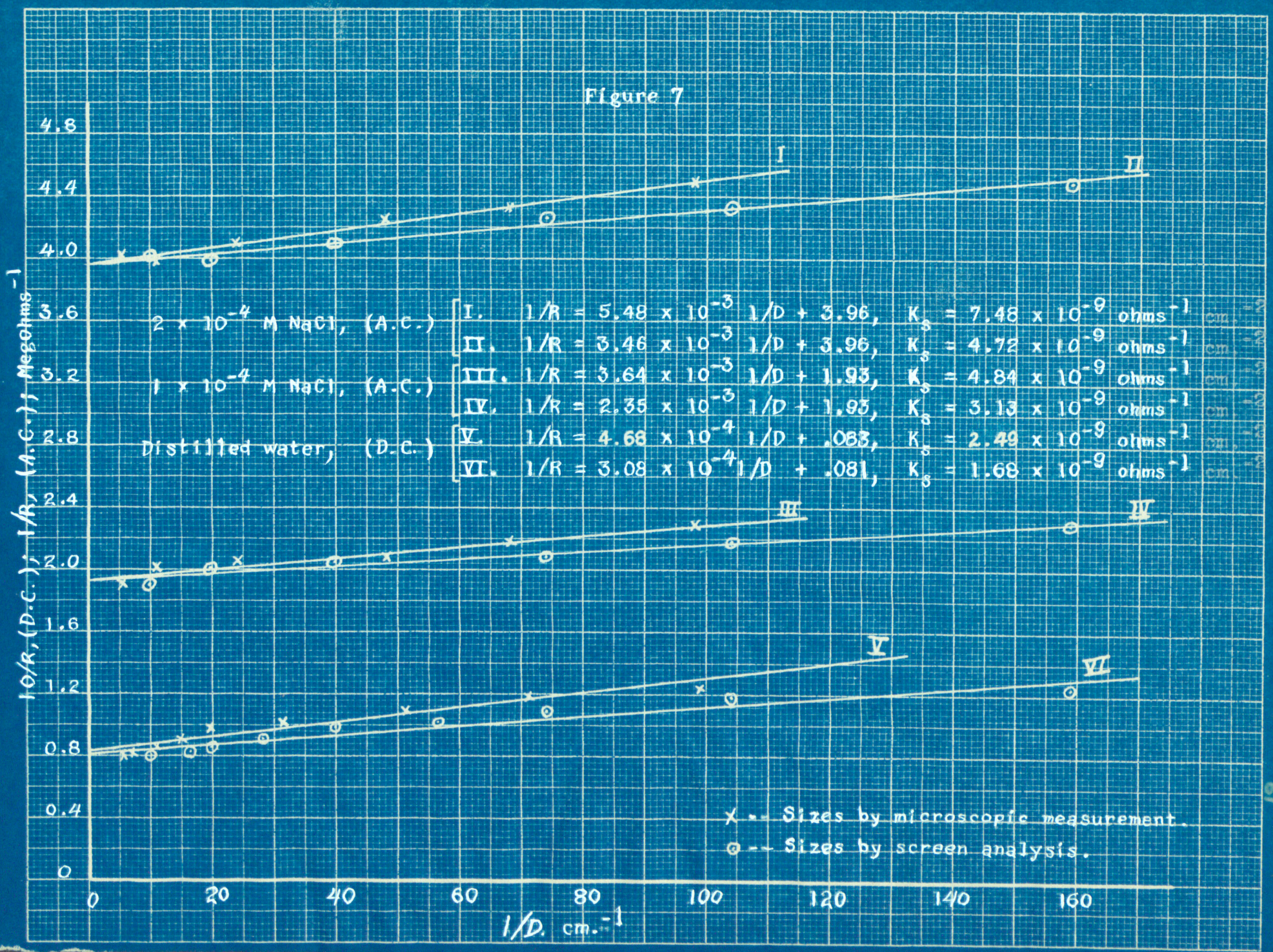
TABLE X.

A.C. Resistance measurements on filter beds of crushed quartz.

| $K_B$ | $D_s$ | $D_m$ | Cell Resistance | $10^6/R_c$ | $1/D_s$ | $1/D_m$ |
|---|---|---|---|---|---|---|
| $1.23 \times 10^{-3}$ | 63 | 102 | 4610 | | | |
| " | 135 | 208 | 4640 | | | |
| " | 503 | 910 | 4630 | | | |
| $2.50 \times 10^{-4}$ | 165 | 102 | 22,800 | | | |
| " | 135 | 208 | 23,200 | | | |
| " | 503 | 910 | 25,000 | | | |
| $2.42 \times 10^{-5}$ | 63 | 102 | 222,000 | 4.50 | 159 | 98.0 |
| " | 96 | 147 | 231,000 | 4.33 | 104 | 68.0 |
| " | 135 | 208 | 235,000 | 4.26 | 74.1 | 48.1 |
| " | 251 | 418 | 244,000 | 4.10 | 39.8 | 23.9 |
| " | 503 | 910 | 251,000 | 3.99 | 19.9 | 11.0 |
| " | 1000 | 1860 | 249,000 | 4.02 | 10 | 5.38 |
| $1.14 \times 10^{-5}$ | 63 | 102 | 435,000 | 2.30 | 159 | 98.0 |
| " | 96 | 147 | 458,000 | 2.18 | 104 | 68.0 |
| " | 135 | 208 | 481,000 | 2.08 | 74.1 | 48.1 |
| " | 251 | 418 | 488,000 | 2.05 | 39.8 | 23.9 |
| " | 503 | 910 | 497,000 | 2.01 | 19.9 | 11.0 |
| " | 1000 | 1860 | 525,000 | 1.91 | 10 | 5.38 |

A plausible explanation for the lack of correlation between resistance and streaming potential measurements for beds of small sized particles is that there is a decrease in the area effective for surface conductivity below the theoretical value; this decrease being due to an increase in the apparent contact area between the particles because of the effect of the double layer. This is shown in Figure 8, and an analytical expression showing the magnitude of this effect can be derived on the basis of a filter bed packed with spheres. This analysis, while not directly applicable, should give at least a qualitative explanation for the variations noted in beds of particles having various other shapes.

Figure 7



For a sphere having a diameter D and carrying a double layer of thickness d, the effective surface area should be $\pi(D + 2d)^2$ , and when $d << D$ , the surface area is $\pi D^2$. Also, the number of spheres in a unit volume, assuming close packing, is $\sqrt{2}/D^3$ ; therefore the effective surface area per unit volume of packing should be $\frac{\pi\sqrt{2}}{D}$ .

However, because of interference of the double layers, the effective surface area of a given sphere is less than the supposed value of $\pi D^2$ . This is shown in Figure 8. The actual effective surface is shown by ABC and the supposed surface by A'B'C'. This is equivalent to having the contact area enlarged from a point, as at A', to a circle of radius AA', The ineffective surface area at the point of contact will be that of a spherical segment of height d from a sphere of radius (D/2 + d). Since for close packed spheres there are 12 points of contact for each sphere, and the area of a spherical segment is given as $A = 2\pi rh$ , the effective surface area will be given by

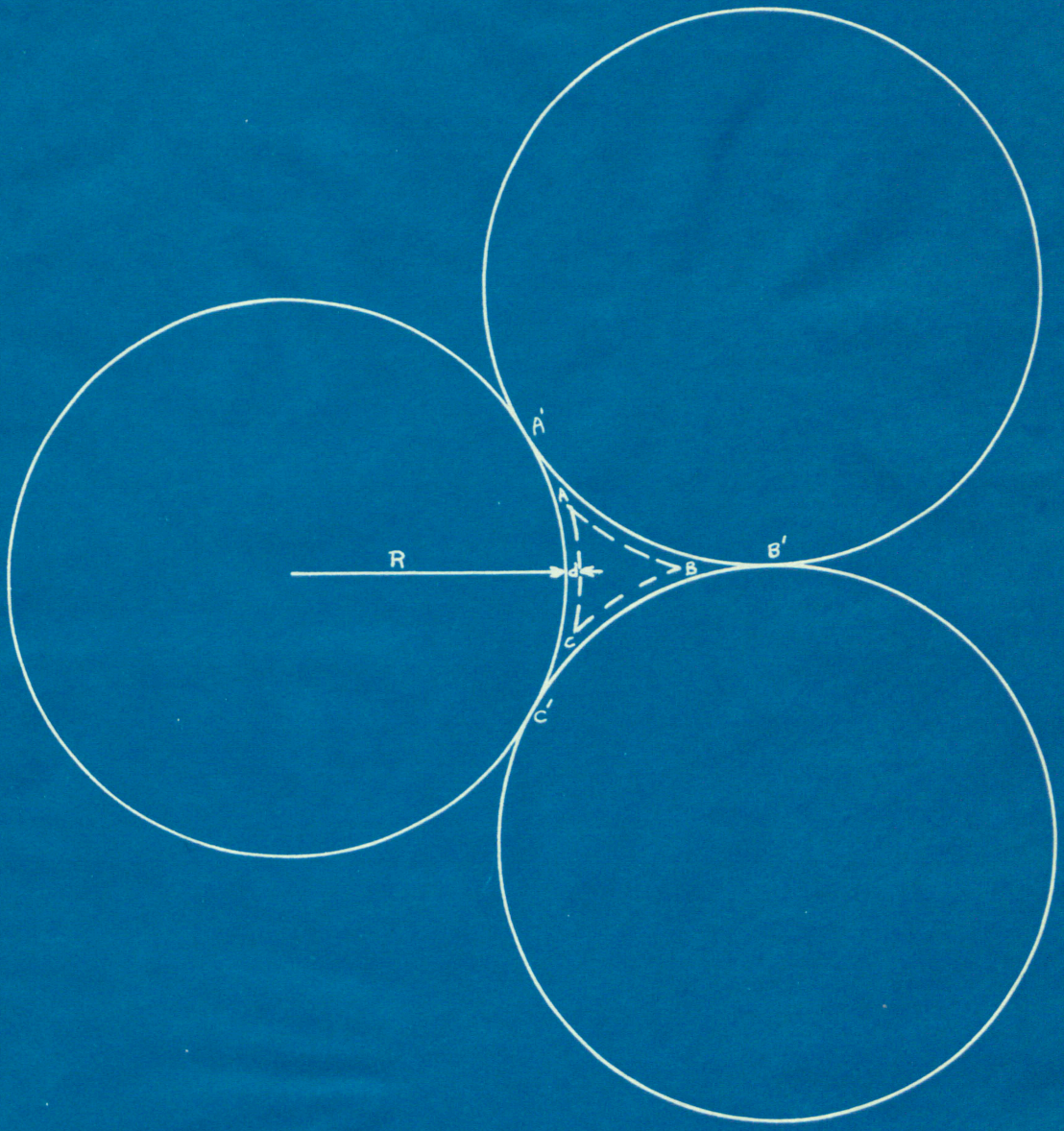
$$(45) \quad S = \pi (D+2d)^2 - 24\pi (D/2 + d) d$$

This can be simplified to give $S = \pi(D^2 - 8dD - 20d^2)$ ; then the effective surface area per unit volune is

$$(46) \quad S' = \frac{\pi\sqrt{2}}{D}\left(1 - \frac{8d}{D} - 20\frac{d^2}{D^2}\right)$$

For the purpose of comparison with the experimental data, values of $\frac{1}{D} - \frac{8d}{D^2} - \frac{20d^2}{D^3}$ , assuming d = 1, were calculated and are plotted vs. 1/D in Figure 9. This shows

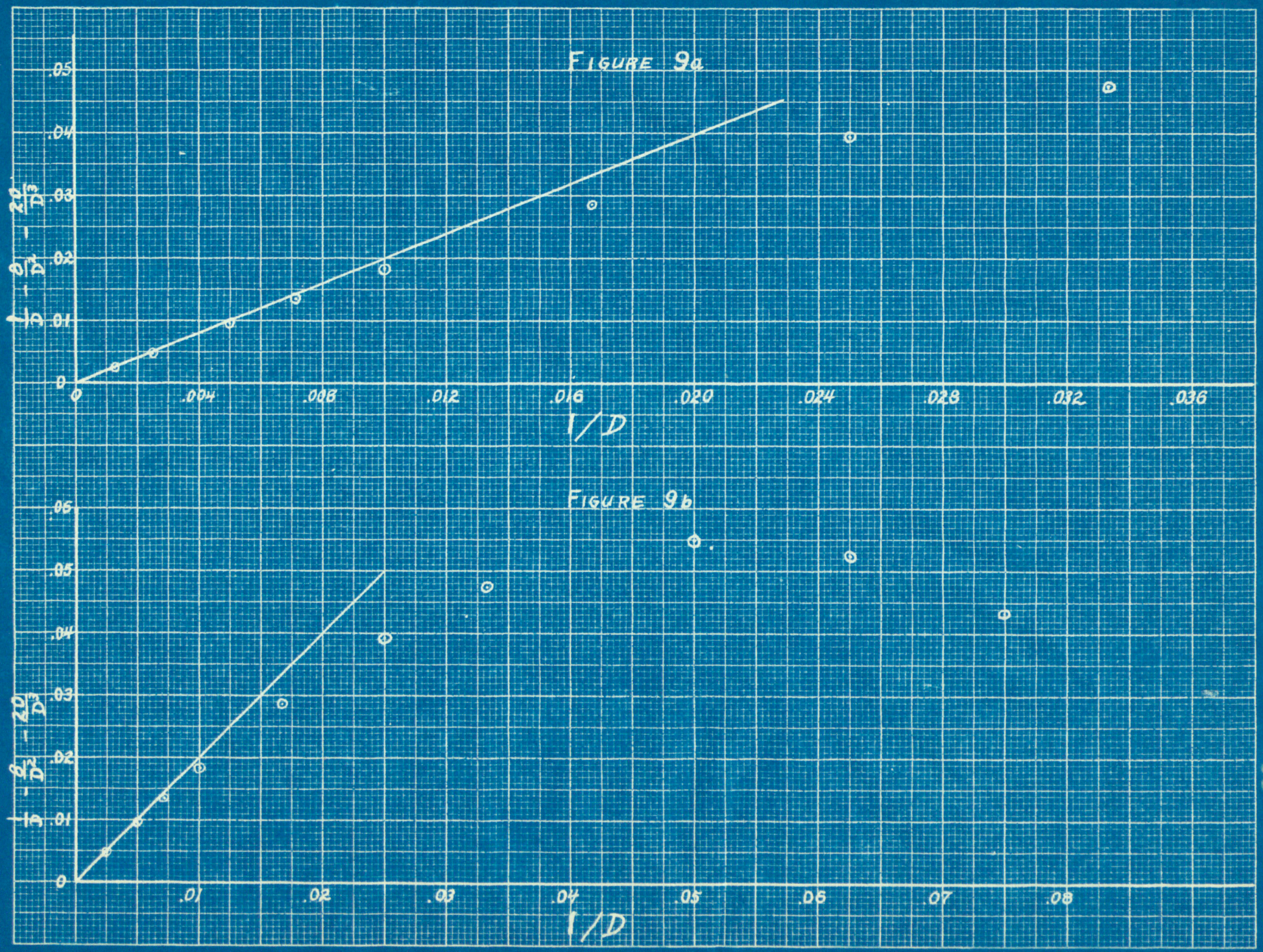
FIGURE 8



that the first apparent deviation from a straight line appears with a ratio of d/D of about 0.015. The experimental data in Figure 6 show a deviation from a straight line when 1/D is greater than 0.04, indicating a double layer thickness of approximately 2 to 3 microns. This value for the double layer thickness is clearly too large. Previous investigators (1, 14, 17, 21) have reported that the thickness is of the order of $10^{-6}$ cm., which is smaller than the above values by a factor of 100 . Also, the thickness of the double layer would hardly be $10^4$ molecular diameters as required by the figure of 2 or 3 microns.

However, the interference of the double layers may be the same as though they were actually this thick. The charges on the walls would supplement each other in reducing the motion of ions in the liquid even beyond the double layer and thus enlarge the apparent area of contact. There is no way of calculating the magnitude of this effect, but it could easily produce the given results.

The hypothesis of the interference of the double layers will also explain the discrepancies between streaming potential and resistance measurements. At first glance, reduction in conductivity should mean a corresponding reduction in values of P/E. However, consider that the streaming potential is produced by a balance of the electrical current, due to charges in the double layer being carried along by the moving liquid, and the reverse current dependent on the conductivity. The double layer interference reduces the surface



conductivity, but it also reduces the number of charges in the double layer which can be carried along by the moving liquid. These two effects apparently balance each other, and the resulting streaming potential is almost the same as though there had been no double layer interference.

Because of this effect, the use of the measured resistance across a cell in computing electrokinetic potentials is liable to give incorrect results, and is apparently the basis for claims of electro-osmotic back pressures of appreciable magnitude. Calculations of electro-osmotic back pressures made correctly, that is, taking account of the surface conductivity, indicate that it is negligible for capillaries of the size used in this investigation, and could not possibly account for the obseved discrepancies between streaming potential and resistance.

The data of Bull and Gortner (4) , as shown in table XI, also give results indicating this ''double layer interference''. If only the larger particles are considered, plotting of P/E vs. 1/D gives $K_S = 3.67 \times 10^{-9}$ ohms$^{-1}$. However, if values of P/E for the two smallest sizes are included in the plot, surface conductivity is obtained as $0.9 \times 10^{-9}$ ohms$^{-1}$, which is considerably lower. Even on the basis of this lower value, the effective conductivity in the filter bed should be changed from $K_B = 2.89 \times 10^{-5}$ ohms$^{-1}$ cm.$^{-1}$ to $K_E = 13.2 \times 10^{-5}$ ohms$^{-1}$cm.$^{-1}$ for particles 4.6 microns in diameter. The conductivity based on measured resistance was reported as $3.58 \times 10^{-5}$ ohm$^{-1}$cm.$^{-1}$, indicating that there was also considerable ''double layer inter-

ference!' Ahd as mentioned before, use of this measured resistance would tend to give incorrect results in calculating the kineitc potential.

TABLE XI.

Streaming potential data from Bull & Gortner (4)

| D(microns) | 1/D($cm^{-1}$) | E/P*($\frac{mv.}{cm.Hg}$) | P/E | K($ohms^{-1}cm.^{-1}$) |
|---|---|---|---|---|
| 214 | 46.7 | 30.15 | 0.0332 | $2.89 \times 10^{-5}$ |
| 163 | 61.4 | 29.31 | 0.0342 | " |
| 128 | 78.2 | 26.62 | 0.0375 | " |
| 98 | 102 | 24.19 | 0.0413 | " |
| 74.9 | 133 | 22.93 | 0.0456 | " |
| 31.1 | 323 | 20.12 | 0.0497 | " |
| 4.6 | 2180 | 6.25 | 0.1600 | $3.58 \times 10^{-5}$ |

*Little significance can be given to the thifd and fourth figures in these values of E/P since the average residual may be as high as 1.22 from a series of 5 measurements.

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The hypothesis of ''double layer interference'' is also supported by the changes observed in the resistance of the packed cells after forcing liquid through at high pressure. The particles were thoroughly washed with the solution to be used and then allowed to stand, covered with the solution, for 24 hours or longer; this same solution was used in washing out the cell and in transferring the sand. Therefore, the change in resistance could not be caused by a change in the bulk conductivity of the solution.

The elctrical resistance of the cell packed with fine sand varied considerably in the gravity packed condition, the resistance being always lower than that obtained after flow of liquid under high pressure. No measurable change

in the volune of the packed bed was observed after forcing liquid through, but the resistance was increased by an appreciable amount; especially with the smallest particle sizes. This would be caused by the compacting of the sand bed to cause ''double layer interference''.

Only a few measurements were taken of the electrical resistance of the freshly packed cell because of the extreme variability, but these are shown in table XII to indicate the changes observed.

TABLE XII.

Effect of liquid flow on cell conductivity.

| Test No. | Particle size | Resistance (megohms) | |
|---|---|---|---|
| | | Gravity pack | After flow at 40 cm.Hg |
| 61 | 57 | 7.5 | 8.1 |
| 62 | 31.5 | 5.7 | 6.7 |
| 63 | 14.5 | 2.1 | 6.6 |
| 46 | 14.5 | 0.46 | 1.52 |

A possible cause for this change in electrical resistance would be a change in the porosity of the sand bed. Muskat (13) reports that the porosity in packed beds of fine particles may vary between 40 and 90%. But change in porosity, sufficient to have an appreciable effect on the electrical resistance, would also cause a noticeable change in the volume of the packed bed.

Another explanation, suggested by McBain and Foster (8), is that low values of surface conductivity are obtained when liquid is forced through a capillary because the double

layer is fragile, and the excess mobile ions are swept away by the streaming liquid. Then, when flow of liquid is stopped, the liquid in the body of the capillary is lowered in concentration through migration of ions to the double layer; and the effective donductivity is decreased. However, if the capillaries were allowed to stand in contact with a large volume of solution, ions would diffuse into the capillaries to build up this decreased concentration; there would then be an increase in conductivity. In the present case, no increase in conductivity was noted when the cell was allowed to stand after it had been packed by flow at high pressure.

Thus, the hypothesis of a ''double layer resistance'' seems to be the only logical explanation for the observed discrepancies between measurements of resistance and streaming potential across packed sand beds.

Discussion of Results:

The measurements of the rate of flow of solutions of different concentrations through filter beds, prepared from various sizes of graded sand, show it to be proportional to the square of the average particle diameter, However,no indication was observed of a lower flow rate than that computed from the above proportionality for beds of the smaller particles, as reported by Ruth (19), although a possible explanation may be found in the data in table II. In section e of this table, values of $Q/D^2$ as based on average diameters from screen analysis and from microscopic measurements are reported. For the same samples, values of $Q/D^2$ , based om screen analysis, are more than double those based on microscopic measurements. Now consider the results obtained from tests on a number of beds of graded particles if screen analysis were used to determine the average diameter only for those particles below the range of screen analysis. Then, it is evident that values of $Q/D^2$ would be much lower for the smaller sizes, but only because of the difference in the methods of size analysis and not because of an electro-osmotic back pressure.

The electro-osmotic back pressure also has been cited as the cause for the gradual decrease in the rate of flow with time for filter beds of fine particles (19). The data in table IV could be used as an example of this, since the rate of flow gradually decreases as though an electro-

osmotic back pressure were building up. However, measurements of streaming potential indicated that the full value appeared immediately on starting flow, and that there was no ''building up'' or increase in the potential with time. Also, the data in table V indicate that the decrease in rate observed in table IV must have been caused by clogging of the capillaries, since pre-filtering should have no effect on the electrical properties and therefore should not prevent a decrease in rate of flow caused by electro-osmotic back pressure.

An electro-osmotic back pressure was detected in the course of this investigation, but it was of measurable magnitude only for very pure distilled water flowing through a filter bed of the very finest sand. The calculations carried out for the flow of tap water through capillaries show that this electro-osmotic effect would be negligible for filtrations with ferric hydroxide, which is a typical example of a very compressible slurry. Also, these calculations did not take into account the effect of using a filter-aid, which would have the effect of increasing the capillary size and decreasing any electro-osmotic effects. However, it must be admitted that the use of organic solvents having very low electrical conductivity might lead to the production of an appreciable electro-osmotic back pressure in filtration.

Measurements of the streaming potential produced by NaCl solutions flowing through packed beds of sand, as reported in table IX and figure 5, are in agreement with the

hypothesis that the lower potential observed in small capillaries is entirely due to the effect of surface conductance and not to any electro-osmotic back pressure. The surface conductivitgies for solutions of NaCl and sand have been calculated from these measurements and also from the measurements of the resistance across the packed beds. For purposes of comparison, the surface conductivitges, as determined from the different methods of measurement, are tabulated in table XIII.

TABEE XIII.

Surface conductivity, mhos x $10^{-9}$.

| | Method of measurement | Distilled water | 1 x $10^{-4}$ M NaCl | 2 x $10^{-4}$M NaCl | 5 x $10^{-4}$M NaCl |
|---|---|---|---|---|---|
| Sand packing | Streaming potential | 1.1 | 5.3 | 4.9 | 8.1 |
| | Resistance | 11.1b | 4.76<br>3.1a | | |
| Quartz packing | Resistance (D from screen analysis) | 1.7b | 5.1a | 4.7a | |
| | Resistance (D from microscopic meas.) | 2.5b | 4.8a | 7.5a | |

a. Resistance measured by A.C. bridge .
b. Resistance measured by D.C. bridge.

There is fair agreement in the values calculated by different methods, with a definite increase in the surface conductivity accompanying an increase in the concentration of the solutions. These results are in agreement with those reported for KCl solutions by Urban, White and coworkers (19, 20, 21, 22, 23) as contrasted with those of McBain and his associates

(8, 9, 10) and Rutgers, Verlende and Moorkens (16) who report values approximately twenty times as large. Surface conductivities calculated from the streaming potential measurements of Bull and Gortner (4) also agree with those presented in this report. For purposes of comparison, the surface conductivities determined by these different investigators are tabulated in table XIV.

There has been considerable discussion based on the differences in results referred to above, but no agreement has been reached. However, theoretical calculations by both groups of investigators (10, 16, 20), do agree with the experimental work of Urban, White et al. and with the present results. Because of the discrepancies in the published experimental measurements of surface conductivity and the lack of correlation between measurements of resistance and streaming potential noted in this work, this should be a fruitful field for additional research.

TABLE XIV.

| Author | Nature of surface | Method of meas. | Solution | Surface conductivity (mhos x $10^9$) |
|---|---|---|---|---|
| McBain, Peaker and King (10) | Polished glass | A.C. | 1 x $10^{-3}$ M KCl | 43 |
| | | | 1 x $10^{-2}$ M KCl | 93 |
| McBain and Peaker (9) | Pyrex | A.C. | 1 x $10^{-3}$ M KCl | 130 |
| | | | 1 x $10^{-2}$ M KCl | 207 |
| McBain and Foster (8) | Pyrex | A.C. | 1 x $10^{-3}$ M KCl | 99.6 |
| | | | 1 x $10^{-2}$ M KCl | 608 |
| White, Urban and Van Atto (24) | Pyrex | D.C. | 5 x $10^{-4}$ M KCl | 2.2 |
| Urban, Feldman and White (19) | Fractured Pyrex | D.C. | 5 x $10^{-4}$ M KCl | 2.0 |
| White, Monaghah and Urban (22) | Pyrex | D.C. | 5 x $10^{-4}$ M KCl | 1.7 |
| | | | 1 x $10^{-4}$ M KCl | 1.5 |
| Urban, Feldman and White (19) | Fractured Pyrex | A.C. | 1 x $10^{-3}$ M KCl | 7.9 |
| | | | 5 x $10^{-4}$ M KCl | 4.1 |
| | | | 1 x $10^{-4}$ M KCl | 2.1 |
| White, Monaghan and Urban (23) | Pyrex | A.C. | 1 x $10^{-3}$ M KCl | 6.3 |
| | | | 5 x $10^{-4}$ M KCl | 3.7 |
| | | | 2 x $10^{-4}$ M KCl | 4.1 |
| Bull & Gortner(4) | Quartz | Stream. Potential | 2 x $10^{-4}$ M NaCl | 3.7 |
| Rutgers, Verlende and Moorkens (14) | Jena glass | Stream. Potential | 4 x $10^{-5}$ M KCl | 18 |
| | | | 8 x $10^{-5}$ M KCl | 32 |
| | | | Dist. water | 10 |

Summary;

1. The electro-osmotic back pressure posulated by Ruth (18) is shown to be negligible for commercial filtrations A decrease in the value of $Q/D^2$ for beds of progressively finer particles, reported as due to electro-osmotic back pressure (19), is shown to be due to the use of different methods of size analysis; and a decrease in rate of flow with time, also reported as due to electro-osmotic effects, is caused by mechanical clogging of the capillaries. The possible exception, where an electro-osmotic back pressure might be appreciable, is for filtrations involving organic solvents of very low electrical conductivity.

2. The surface conductivities of NaCl solutions on sand particles have been calculated and agree with the experimental work of Urban, White and coworkers. These measurements also agree with theoretical calculations, but are smaller by a factor of twenty than those of McBain et al.

3. The electrical resistance across packed beds of fine particles was found to be much higher than that to be expected on the basis of surface conductivity calculations; this higher resistance being due to a decrease in the effective surface area of the particles caused by ''double layer interference''. It is shown that the use of the measured resistance in electrokinetic calculations with beds of fine particles may be a serious source of error.

## Symbols.

A, B = constants in equation relating P/E and 1/D.

A', B' = constants in equation relating $1/R_c$ and 1/D.

C, $C_1$, $C_2$ = constants.

$\mathfrak{D}$ = dielectric constant.

D = average particle diameter.

$D_m$ = average particle diameter from microscopic measurements.

$D_s$ = average particle diameter from screen analysis.

d = thickness of the electrical double layer.

E = electrical potential across the ends of a capillary.

G = constant relating surface area and particle size.

I = electrical current.

K = electrical conductivity.

$K_B$ = specific conductance of a solution.

$K_s$ = surface conductance at a phase interface.

$K_c$ = electrical conductivity of a packed cell.

l = length of capillary.

N = number of capillaries.

P = pressure causing flow through capillaries.

Q = quantity of liquid flowing through capillaries.

R = electrical resistance.

$R_c$ = electrical resistance of a packed cell.

r = capillary radius.

S, S' = surface area

u = velocity of fluid in capillaries.

V = volume of liquid flowing through a capillary.

Symbols(continued).

$y$ = distance from the capillary wall.

$\epsilon$ = electro-osmotic factor.

$\eta$ = coefficient of viscosity.

$\zeta$ = electrokinetic potential.

$\phi$ = electrical potential at a point.

$\psi$ = electro-osmotic back pressure.

$\sigma$ = density of electrical charge.

$\mu$ = microns.

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# Appendix

# APPENDIX

## A. Capillary radius for filter cake.

The equivalent capillary radius for a compressible slurry can be estimated by making use of two assumptions; these assumptions being that the equivalent cross-sectional area of the capillaries is 25% of the cake area (based on the experimental work in this paper) and that the length of the capillaries is equal to the thickness of the filter cake. On this basis, the following filtration data for a ferric hydroxide slurry (5) can be combined with Poiseuille's equation to calculate an equivalent capillary radius.

Filter cloth area -- 4.40 sq. dcm.

Kg. of solute-free solids per $dcm.^3$ of wet cake -- 0.0838

Grams of suspended solids per gram of water -- 0.00645

Temperature -- 25 C

Viscosity-- 0.936 centipoises

For a filtration run with 19.6 psi., $\frac{d\theta}{dV} = 9.57$ min./liter when the filtrate volume equals 2 liters.

$$Q = \frac{1000}{9.57 \times 60 \times 440} = 0.00396 \frac{cm.^3}{sec.\ cm.^2}$$

$$l = \frac{0.00645 \times 1000 \times 2}{0.0838 \times 400} = 0.35 \text{ cm.} = \text{thickness of cake.}$$

$$P = 19.6 \text{ psi} = \frac{454 \times 19.6 \times 980.6}{(2.54)^2} = 1.38 \times 10^6 \frac{dynes}{cm^2}$$

$$N\pi r^2 = 0.25 \text{ cm}^2$$

$$0.00396 = \frac{0.25r^2 \times 1.38 \times 10^6}{8 \times 0.00936 \times 0.35} \quad ; \quad r = 1.7 \times 10^{-5} \text{cm.} = 0.17 \text{ microns}$$

B. Summary of Experimental Data (Only those tests on freshly packed cells with solutions of the same conductivities have been included in this table)

$5 \times 10^{-4}$ M NaCl, $K_B = 7.5 \times 10^{-5}$ mhos, T = 30°C

| Test No. | Dm Microns | r Microns | E/P mv./cm.Hg | Q/P gms./cm.Hg.min. | $R_C$ megohms |
|---|---|---|---|---|---|
| 27 | 6 | 0.83 | 5.9 | 0.0030 | 0.31 |
| 25 & 26 | 8.2 | 0.98 | 6.2 | 0.0042 | 0.40 |
| 22 & 24 | 10.7 | 1.65 | 7.4 | 0.012 | 0.42 |
| 20 & 21 | 50 | 7.45 | 9.45 | 0.244 | 0.47 |
| 16 & 19 | 71 | 9.88 | 9.52 | 0.428 | --- |
| 12* | 108 | 14.3 | 10.8 | 0.900 | |

$2 \times 10^{-4}$ M NaCl, $K_B = 2.6 \times 10^{-5}$ mhos, T = 25°C

| Test No. | Dm | r | E/P | Q/P | $R_C$ |
|---|---|---|---|---|---|
| 40 | 6 | 0.81 | --- | 0.0026 | --- |
| 39 | 10.7 | 1.54 | 17.3 | 0.0094 | 0.935 |
| 38 | 12 | 1.59 | 18.6 | 0.0100 | 0.94 |
| 36 | 31.5 | 4.75 | 23 | 0.0895 | 0.95 |
| 41 | 50 | 6.52 | 28.4 | 0.168 | |
| 35 | 57 | 8.27 | 28.5 | 0.270 | .945 |
| 33 | 71 | 10.37 | 27.5 | 0.425 | 1.00 |
| 34 | 72.5 | 10.41 | 28.5 | 0.430 | .96 |
| 31 | 108 | 14.8 | 30.0 | 0.865 | .95 |
| 30 | 134 | 16.4 | 29.8 | 1.07 | 1.005 |
| 37 | 160 | 21.0 | 26.7 | 1.75 | --- |

$1 \times 10^{-4}$ M NaCl, $K_B = 1.2 \times 10^{-5}$ mhos, T = 25°C

| Test No. | Dm Microns | r Microns | E/P mv./cm.Hg | Q/P gms./cm.Hg.min. | $R_C$ megohms |
|---|---|---|---|---|---|
| 45 | 6 | .675 | 17.1 | 0.0018 | 1.15 |
| 46 | 14.5 | 2.03 | 38 | 0.0163 | 1.52 |
| 44 | 31.5 | 4.57 | 46.3 | 0.083 | 1.65 |
| 43 | 57 | 8.50 | 54.7 | 0.287 | 1.79 |
| 42 | 72.5 | 9.45 | 55.7 | 0.355 | 1.97 |
| 47 | 108 | 14.7 | 66.1 | 0.860 | 2.10 |
| 48 | 160 | 19.2 | 59.5 | 1.46 | 2.44 |

* At $7.1 \times 10^{-5}$ mhos

Distilled water, $K_B = 2 \times 10^{-6}$ mhos, T = 25°C

| Test No. | Dm | r | E/P | Q/P | $R_C$ |
|---|---|---|---|---|---|
| 65 | 6 | .83 | 62 | 0.00273 | 5.67 |
| 63 | 14.5 | 1.94 | 132 | 0.0150 | 6.65 |
| 62 | 31.5 | 4.23 | 169 | 0.0706 | 6.72 |
| 61 | 57 | 7.52 | 211 | 0.224 | 8.1 |
| 60 | 72.5 | 10.3 | 241 | 0.416 | 9.25 |
| 64 | 134 | 16.7 | 290 | 1.11 | 10.3 |

Distilled water, $K_B = 2 \times 10^{-6}$ mhos, T = 25°C

| Test No. | Dm, microns Screen Analysis | (Micro-scopic Measure-ments) | r Microns | C/P mv./cm.Hg | Q/P gms/cmHgmin | $R_C$ megohms |
|---|---|---|---|---|---|---|
| 49&59 | 63 | 102 | 13.9 | 258 | 0.77 | 8.05 |
| 50&58 | 96 | 141 | 18.4 | 280 | 1.34 | 8.4 |
| 51 | 135 | 195 | 27.4 | 335 | 2.95 | 9.05 |
| 52 | 177 | 321 | 35.3 | 346 | 4.94 | 9.8 |
| 53 | 251 | 510 | 53.9 | 332 | 11.5 | 10.1 |
| 54 | 356 | 670 | 61.7 | 353 | 15.1 | 11.0 |
| 55 | 503 | 910 | 82.5 | 342 | 26.9 | 11.1 |
| 56 | 611 | 1440 | 106 | 366 | 44.9 | 11.65 |
| 57 | 1000 | 1860 | 133 | 316 | 69.5 | 12.1 |

Results of size analysis on crushed quartz

| Screen size | Minimum Screen Opening | Maximum Screen Opening | Avg. Screen Opening $D_S$ | Avg. Diameter (micro. meas.) Dm |
|---|---|---|---|---|
| 200-270 | 52 | 74 | 63 | 102 |
| 150-170 | 88 | 104 | 96 | 141 |
| 100-115 | 124 | 147 | 135 | 195 |
| 65-100 | 147 | 208 | 177 | 321 |
| 48-65 | 208 | 295 | 251 | 510 |
| 35-48 | 295 | 417 | 356 | 670 |
| 28-35 | 417 | 589 | 503 | 910 |
| 20-28 | 589 | 833 | 611 | 1440 |
| 14-20 | 833 | 1168 | 1000 | 1860 |

C. Sample Calculations:

Cell resistance from shunted E/P for test No. 1.

Average E/P = 112.5 mv./cm.Hg.

With 2.44 megohm shunt, avg. E/P = 39.2 mv./cm.Hg.

With 5.25 megohm shunt, avg. E/P = 60.0 mv./cm.Hg.

$$R_C = \left[\frac{(E/P)_o}{(E/P)_S} - 1\right] R_S$$

$R_C$ = cell resistance

$R_S$ = shunt resistance

$(E/P)_o$ = potential, no shunt

$(E/P)_S$ = potential with shunt

$$R_C = \left(\frac{112.5}{39.2} - 1\right) 2.44 = 4.56 \text{ megohms}$$

$$R_C = \left(\frac{112.5}{60.0} - 1\right) 5.25 = 4.59 \text{ megohms}$$

Average $R_C$ = 4.57 megohms

Electrokinetic potential for $5 \times 10^{-4}$ M NaCl, for table IX.

$K_B = 7.5 \times 10^{-5}$ mhos

(P/E) = .0964 cmHg/mv when $1/D \rightarrow 0$

T = 30°C, $\eta$ = .00798 poises

$\mathfrak{D}$ = 80

$$\zeta = \frac{E\, 4\pi\eta K}{PD}$$

$$\zeta = \frac{4\pi \times .00798 \times 9 \times 10^{11} \times 7.5 \times 10^{-5}}{0.0964 \times 13.6 \times 980.6 \times 80} = 66 \text{ mv.}$$

Equivalent capillary radius for test No. 40

$$Q/P = \frac{r^2}{8\eta} \frac{K_C}{K_B}$$

$\eta$ = 0.798 poises at 25°C

$K_C/K_B$ = 0.035

Q/P = 0.0026 gms/cm.Hg.min.

$$r^2 = \frac{0.0026 \times 8 \times 0.00798}{13.6 \times 980.6 \times 60 \times 0.035} = 0.66 \times 10^{-8}$$

$$r = 0.81 \times 10^{-4} \text{ cm}$$

## D. Detailed Experimental data

Run No. 1 — May 30
Cell packed with 108 micron sand (170-200 mesh)
Distilled water, $K_B = 4.1 \times 10^{-6}$ mhos, T = 30°C
$R_C = 4.57$ megohms, (calc. from shunted E/P)

| Pressure P, cmHg | Potential E, mv. | Rate Q, gms/min | E/P | Q/P |
|---|---|---|---|---|
| 20.4 | 2250 | 16.5 | 110 | .81 |
| 12.0 | 1375 | 10.0 | 114 | .83 |
| 28.6 | 3195 | 23.3 | 112 | .82 |
| 16.5 | 1870 | --- | 113 | --- |
| 20.3b | 795 | 16.4 | 39.2 | .81 |
| 28.6b | 1120 | 23.1 | 39.2 | .81 |
| 28.5a | 1710 | --- | 60.0 | --- |
| 16.5a | 990 | --- | 60.0 | --- |

Run No. 2 — June 3
Same cell packing as No. 1
$1 \times 10^{-4}$ M NaCl, $K_B = 1.4 \times 10^{-5}$ mhos, T = 30°C
$R_C = 2.0$ megohms, (calc. from shunted E/P)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 9.0 | 460 | 6.1 | 51.2 | .67 |
| 17.5 | 865 | 14.4 | 49.5 | .82 |
| 24.4 | 1195 | 20.1 | 49.0 | .83 |
| 32.1 | 1560 | 26.1 | 48.6 | .81 |
| 32.4a | 1165 | --- | 36.0 | --- |
| 19.7a | 715 | --- | 36.3 | --- |

Run No. 3 — June 4
Same cell packing as No. 1 & 2
$3 \times 10^{-4}$ M NaCl, $K_B = 3.9 \times 10^{-5}$ mhos, T = 30°C
$R_C = 1.02$ megohms, (calc. from shunted E/P)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 20.7 | 380 | 16.4 | 18.4 | .79 |
| 31.7 | 575 | 24.9 | 18.1 | .79 |
| 11.0 | 200 | 8.8 | 18.2 | .80 |
| 14.5b | 210 | --- | 14.5 | --- |
| 30.6b | 490 | --- | 16.0 | --- |

a 5.25 megohm shunt across cell electrodes.
b 2.44 megohm shunt across cell electrodes.
c 0.98 megohm shunt across cell electrodes.

Run No. 4 — Same cell packing as No. 1, 2, & 3
June 5 — $5 \times 10^{-4}$ M NaCl, $K_B = 6.9 \times 10^{-5}$ mhos, T = 30°C
$R_C$ = 0.47 megohms, (calc. from shunted E/P)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 16.2 | 165 | 12.7 | 10.2 | .78 |
| 32.9 | --- | 25.5 | --- | .78 |
| 33.5 | 345 | --- | 10.3 | --- |
| 16.4b | 140 | --- | 8.5 | --- |
| 28.3b | 245 | --- | 8.7 | --- |

Run No. 5 — Cell packed with 95 micron sand (200-270 mesh)
June 26 — Distilled water, $K_B = 3.7 \times 10^{-6}$ mhos; T = 30°C
$R_C$ = 5.93 megohms, (calc. from shunted E/P)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 11.7 | 1150 | 6.9 | 98.5 | .59 |
| 21.8 | 2070 | 12.8 | 95.0 | .59 |
| 30.7 | 2870 | 18.1 | 93.5 | .59 |
| 16.6 | 1540 | 9.6 | 92.7 | .58 |
| 16.6a | 750 | --- | 45.2 | --- |
| 7.4a | 330 | --- | 44.7 | --- |
| 26.0a | 1150 | --- | 44.3 | --- |
| 33.2a | 1445 | 19.3 | 43.5 | .58 |
| 13.4a | --- | 7.6 | --- | .57 |

Run No. 6 — Same cell packing as No. 5
June 27 — $1 \times 10^{-4}$ M NaCl, $K_B = 1.1 \times 10^{-5}$ mhos, T = 30°C
$R_C$ = 2.37 megohms (calc. from shunted E/P)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 17.0 | 665 | 9.3 | 39.1 | .55 |
| 31.9 | 1270 | 18.0 | 39.8 | .565 |
| 41.5 | 1650 | 23.7 | 39.8 | .57 |
| 10.1 | 406 | 5.75 | 40.2 | .57 |
| 22.5 | 885 | 12.7 | 39.4 | .565 |
| 22.9b | 460 | 12.8 | 20.1 | .56 |
| 34.9b | 705 | 19.8 | 20.2 | .57 |

Run No. 7 — Same cell packing as No. 5 & 6
June 27 — $3 \times 10^{-4}$ M NaCl, $K_B = 3.7 \times 10^{-5}$ mhos, T = 30°C

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 17.7 | 225 | 9.5 | 12.7 | .535 |
| 27.9 | 360 | 15.2 | 12.9 | .545 |
| 38.4 | 495 | 21.3 | 12.9 | .55 |
| 13.4 | 170 | 7.4 | 12.7 | .55 |
| 21.2 | 270 | 11.6 | 12.7 | .55 |

Run No. 8 — Cell packed with 95 micron sand
July 4 — $5 \times 10^{-4}$ M NaCl, $K_B = 6.5 \times 10^{-5}$ mhos, T = 30°C

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 15.7 | 128 | 11.8 | 8.15 | .753 |
| 21.6 | 172 | 17.4 | 7.98 | .806 |
| 32.1 | 258 | 23.6 | 8.03 | .736 |
| 40.6 | 324 | 29.8 | 7.98 | .734 |
| 10.8 | 87 | 8.1 | 8.07 | .749 |
| 21.3 | 169 | 15.5 | 7.94 | .728 |
| 30.9 | 243 | 22.3 | 7.87 | .723 |
| 21.8 | 174 | 15.8 | 8.00 | .728 |
| 32.4 | 255 | 23.3 | 7.87 | .719 |

Run No. 9 — Same cell packing as No. 8
July 6 — $5 \times 10^{-4}$ M NaCl, $K_B = 6.8 \times 10^{-5}$ mhos, T = 30°C

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 21.1 | 153 | 13.9 | 7.21 | .66 |
| 36.5 | 271 | 24.1 | 7.42 | .66 |
| 14.5 | 103 | 9.3 | 7.10 | .63 |

Run No. 10 — Cell packed with 71 micron sand
July 6 — $5 \times 10^{-4}$ M NaCl, $K_B = 6.8 \times 10^{-5}$ mhos, T = 30°C

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 20.15 | 248 | 9.82 | 12.3 | .487 |
| 13.50 | 161 | 6.50 | 11.9 | .482 |
| 30.70 | 368 | 14.86 | 12.0 | .484 |
| 41.10 | 487 | 19.90 | 11.9 | .485 |
| 13.80 | 161 | 6.54 | 11.8 | .483 |
| 17.55 | 204 | 8.40 | 11.6 | .478 |
| 25.70 | 298 | 12.12 | 11.6 | .472 |

Run No. 11 — Same cell packing as No. 10
July 7 — $5 \times 10^{-4}$ M NaCl, $K_B = 7.1 \times 10^{-5}$ mhos, T = 30°C

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 19.1 | 209 | 8.76 | 10.9 | .458 |
| 28.6 | 308 | 13.06 | 10.8 | .456 |
| 38.5 | 413 | 17.72 | 10.7 | .460 |
| 11.8 | 130 | 5.40 | 11.0 | .457 |
| 25.45 | 272 | 11.74 | 10.7 | .461 |

Run No. 12 — Cell packed with 108 micron sand
July 7 — $5 \times 10^{-4}$ M NaCl, $K_B = 7.1 \times 10^{-5}$ mhos, T = 30°C

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 15.65 | 172 | 14.2 | 11.0 | .91 |
| 20.70 | 225 | 18.8 | 10.9 | .91 |
| 25.4 | 275 | 23.2 | 10.8 | .91 |
| 30.55 | 329 | 27.7 | 10.8 | .91 |
| 36.6 | 394 | 33.3 | 10.8 | .91 |
| 12.5 | 134 | 11.1 | 10.7 | .89 |
| 17.0 | 181 | 15.1 | 10.7 | .89 |
| 25.2 | 269 | 22.4 | 10.7 | .89 |
| 35.45 | 377 | 31.8 | 10.6 | .90 |

Run No. 13 — Same cell packing as No. 12
July 8 — $5 \times 10^{-4}$ M NaCl, $K_B = 7.1 \times 10^{-5}$ mhos, T = 30°C

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 18.0 | 186 | 15.6 | 10.3 | .87 |
| 22.8 | 237 | 19.9 | 10.4 | .87 |
| 30.05 | 310 | 26.5 | 10.3 | .88 |
| 37.2 | 385 | 32.9 | 10.4 | .88 |

Run No. 14 — Same cell packing as No. 12 & 13
July 9 — $5 \times 10^{-4}$ M NaCl, $K_B = 7.35 \times 10^{-5}$ mhos, T = 30°C

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 19.5 | 190 | 17.0 | 9.74 | .872 |
| 29.55 | 287 | 25.9 | 9.74 | .878 |
| 37.15 | 361 | 32.6 | 9.73 | .878 |
| 11.75 | 115 | 10.4 | 9.88 | .882 |

Run No. 15 Same cell packing as No. 12, 13 & 14
July 10 $5 \times 10^{-4}$ M NaCl, $K_B = 7.35 \times 10^{-5}$ mhos, T = 30°C

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 16.75 | 156 | 13.9 | 9.32 | .830 |
| 27.85 | 261 | 23.9 | 9.44 | .864 |
| 35.05 | 324 | 29.9 | 9.22 | .854 |
| 10.52 | 98 | 8.6 | 9.33 | .822 |
| 20.57 | 188 | 17.4 | 9.14 | .844 |
| 33.55 | 314 | 28.3 | 9.36 | .846 |

Run No. 16 Cell packed with 71 micron sand
July 10 $5 \times 10^{-4}$M NaCl, $K_B = 7.5 \times 10^{-5}$ mhos, T = 30°C

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 19.05 | 192 | 8.30 | 10.1 | .436 |
| 24.3 | 246 | 10.62 | 10.13 | .437 |
| 33.0 | 326 | 14.44 | 9.87 | .437 |
| 12.4 | 132 | 5.46 | 10.65 | .441 |
| 24.95 | 245 | 10.88 | 9.83 | .435 |

Run No. 17 Same cell packing as No. 16
July 11 $5 \times 10^{-4}$M NaCl, $K_B = 7.5 \times 10^{-5}$ mhos, T = 30°C

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 20.85 | 195 | 8.64 | 9.35 | .414 |
| 34.80 | 318 | 14.32 | 9.15 | .412 |
| 13.03 | 123 | 5.36 | 9.44 | .412 |
| 24.73 | 229 | 10.30 | 9.26 | .417 |
| 33.55 | 309 | 14.02 | 9.22 | .418 |
| 12.93 | 120 | 5.28 | 9.28 | .408 |

Run No. 18 Same cell packing as No. 16 & 17
July 13 $5 \times 10^{-4}$ M NaCl, $K_B = 7.5 \times 10^{-5}$ mhos, T = 30°C

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 18.35 | 163 | 7.28 | 8.89 | .398 |
| 27.6 | 248 | 11.26 | 8.98 | .408 |
| 35.1 | 315 | 14.38 | 8.97 | .409 |

Run No. 19 Cell repacked with 71 micron sand
July 13 $5 \times 10^{-4}$ M NaCl, $K_B = 7.5 \times 10^{-5}$ mhos, T = 30°C

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 18.7 | 175 | 8.00 | 9.36 | .427 |
| 26.6 | 246 | 11.56 | 9.25 | .434 |
| 34.5 | 323 | 15.02 | 9.36 | .436 |
| 9.65 | 91 | 4.12 | 9.42 | .427 |

Run No. 20 Cell packed with 50 micron sand
July 14 $5 \times 10^{-4}$ M NaCl, $K_B = 7.5 \times 10^{-5}$ mhos, T = 30°C

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 41.65 | 397 | 10.38 | 9.52 | .249 |
| 13.55 | 128 | 3.32 | 9.46 | .245 |
| 28.8 | 275 | 7.04 | 9.54 | .244 |
| 29.15 | 274 | 7.12 | 9.41 | .244 |
| 41.3 | 390 | 10.12 | 9.44 | .245 |
| 21.65 | 203 | 5.30 | 9.37 | .245 |

Run No. 21 Cell repacked with 50 micron sand
July 16 $5 \times 10^{-4}$ M NaCl, $K_B = 7.5 \times 10^{-5}$ mhos, T = 30°C
$R_C$ = 0.47 megohms (calc. from shunted E/P)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 12.55 | 120 | 2.62 | 9.56 | .208 |
| 26.15 | 246 | 5.48 | 9.42 | .210 |
| 35.55 | 338 | 7.50 | 9.53 | .211 |
| 18.0 | 169 | 3.82 | 9.39 | .212 |
| 22.8 | 216 | 4.80 | 9.47 | .211 |
| 26.5 | 252 | 5.60 | 9.49 | .211 |
| 32.15 | 303 | 6.78 | 9.43 | .211 |
| 29.8c | 205 | --- | 6.87 | --- |
| 37.45c | 260 | --- | 6.94 | --- |
| 26.0c | 170 | --- | 6.53 | --- |
| 18.0c | 115 | --- | 6.38 | --- |
| 12.1c | 75 | --- | 6.22 | --- |
| 26.65c | 170 | --- | 6.38 | --- |
| 36.65c | 240 | --- | 6.58 | --- |
| 17.15c | 108 | --- | 6.30 | --- |

Run No. 22
July 17

Cell packed with 10.7 micron sand
$5 \times 10^{-4}$ M NaCl, $K_B = 7.5 \times 10^{-5}$ mhos, T = 30°C
$R_C$ 0.42 megohms, (Calc. from shunted E/P)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 33.6 | 258 | .432 | 7.68 | .0129 |
| 23.3 | 174 | .300 | 7.47 | .0129 |
| 11.7 | 87 | .149 | 7.44 | .0127 |
| 27.6 | 215 | --- | 7.78 | --- |
| 29.7 | 229 | .380 | 7.72 | .0128 |
| 14.75 | 115 | .190 | 7.79 | .0129 |
| 10.35 | 80 | .133 | 7.73 | .0128 |
| 10.35c | 52 | .132 | 5.03 | .0128 |
| 19.40c | 102 | .247 | 5.27 | .0127 |
| 30.15c | 162 | .385 | 5.37 | .0128 |
| 18.1c | 101 | --- | 5.57 | --- |
| 25.0c | 142 | --- | 5.68 | --- |

Run No. 23
July 18

Same cell packing as No. 22
$5 \times 10^{-4}$ M NaCl, $K_B = 7.5 \times 10^{-5}$ mhos, T = 30°C
$R_C$ = 0.39 megohms (calc. from shunted E/P)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 29.65c | 162 | .375 | 5.45 | .0126 |
| 18.35c | 100 | .232 | 5.44 | .0126 |
| 18.45 | 135 | .232 | 7.34 | .0125 |
| 10.9 | 225 | .390 | 7.27 | .0126 |
| 35.55 | 257 | --- | 7.24 | --- |
| 23.9 | 176 | --- | 7.36 | --- |
| 14.6 | 107 | --- | 7.33 | --- |

Run No. 24
July 20

Cell packed with 10.7 micron sand
$5 \times 10^{-4}$ M NaCl, $K_B = 7.5 \times 10^{-5}$ mhos, T = 30°C
$R_C$ = 0.42 megohms, (calc from shunted E/P)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 30.5 | 222 | .326 | 7.27 | .0107 |
| 20.85 | 151 | .239 | 7.25 | .0115 |
| 11.85 | 86 | .129 | 7.26 | .0109 |
| 16.4 | 119 | .184 | 7.26 | .0112 |
| 24.6 | 175 | .270 | 7.12 | .0110 |
| 34.7 | 253 | .380 | 7.29 | .0109 |
| 34.7c | 185 | --- | 5.32 | --- |
| 13.4c | 66 | --- | 4.93 | --- |
| 22.2c | 110 | --- | 4.96 | --- |
| 32.2c | 164 | --- | 5.08 | --- |

Run No. 25
July 22

Cell packed with 8.2 micron sand
$5 \times 10^{-4}$ M NaCl, $K_B = 7.5 \times 10^{-5}$ mhos, T = 30°C

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 29.1 | 122 | .121 | 4.20 | .00417 |
| 28.9 | 183 | .120 | 6.34 | .00417 |
| 35.8 | 220 | .149 | 6.15 | .00417 |
| 14.8 | 102 | --- | 6.90 | --- |

Run No. 26
July 23

Same cell packing as No. 25
$5 \times 10^{-4}$ M NaCl, $K_B = 7.5 \times 10^{-5}$ mhos, T = 30°C
$R_C$ = 0.50 megohms, (calc. from shunted E/P)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 29.0 | 176 | .1184 | 6.28 | .00408 |
| 13.35 | 82 | .0545 | 6.15 | .00409 |
| 22.35 | 136 | .0934 | 6.08 | .00418 |
| 35.4 | 216 | .1494 | 6.10 | .00422 |
| 35.4c | 145 | .1488 | 4.10 | .00420 |
| 18.55c | 75 | --- | 4.05 | --- |
| 23.35c | 95 | --- | 4.07 | --- |

Run No. 27
July 24

Cell packed with 6 micron sand
$5 \times 10^{-4}$ M NaCl, $K_B = 7.5 \times 10^{-5}$ mhos, T = 30°C
$R_C$ = 0.31 megohms, (calc. from shunted E/P)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 39.25 | 222 | .1210 | 5.65 | .00308 |
| 14.10 | 82 | .0426 | 6.10 | .00302 |
| 19.0 | 113 | .0574 | 5.93 | .00303 |
| 24.75 | 143 | .0754 | 5.77 | .00305 |
| 33.85 | 198 | .1026 | 5.84 | .00309 |
| 13.5 | 81 | .0404 | 6.00 | .00299 |
| 21.2 | 123 | .0646 | 5.80 | .00305 |
| 35.5 | 204 | .1090 | 5.74 | .00307 |
| 30.3c | 130 | .0930 | 4.30 | .00306 |
| 39.25c | 167 | .1204 | 4.26 | .00307 |
| 35.7c | 155 | --- | 4.34 | --- |
| 14.6c | 67 | --- | 4.59 | --- |
| 22.45c | 97 | --- | 4.33 | --- |
| 13.15c | 60 | --- | 4.57 | --- |

Run No. 28
July 25

Cell packed with 8.2 micron sand
$5 \times 10^{-4}$ M NaCl, $K_B = 7.5 \times 10^{-5}$ mhos, T = 30°C
$R_C$ = 0.28 megohm, (calc. from shunted E/P)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 36.0 | 163 | .1306 | 4.53 | .00363 |
| 12.6 | 62 | .0450 | 4.83 | .00375 |
| 21.4 | 98 | .0772 | 4.58 | .00361 |
| 33.35 | 146 | .1236 | 4.43 | .00371 |
| 13.65 | 65 | .0508 | 4.77 | .00373 |
| 43.25 | 195 | .1574 | 4.50 | .00374 |
| 35.14c | 125 | .1222 | 3.56 | .00348 |
| 14.6c | 53 | .0528 | 3.36 | .00361 |
| 24.6c | 87 | .0878 | 3.54 | .00357 |

Run No. 29
July 27

Cell packed with 92 micron sand
$5 \times 10^{-4}$ M NaCl, $K_B = 7.5 \times 10^{-5}$ mhos, T = 30°C
$R_C$ = 0.58 megohms, (calc. from shunted E/P)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 27.45 | 229 | 13.72 | 8.35 | .500 |
| 34.7 | 290 | 16.88 | 8.36 | .514 |
| 41.0 | 342 | 20.64 | 8.34 | .503 |
| 13.1 | 109 | 6.46 | 8.32 | .493 |
| 19.4 | 162 | 9.42 | 8.36 | .485 |
| 13.55c | 70 | --- | 5.17 | --- |
| 21.15c | 110 | --- | 5.20 | --- |
| 28.95c | 155 | --- | 5.35 | --- |
| 36.95c | 210 | --- | 5.67 | --- |
| 16.25c | 80 | --- | 4.91 | --- |

Run No. 30
August 26

Cell packed with 134 micron sand
$2 \times 10^{-4}$ M NaCl, $K_B = 2.67 \times 10^{-5}$ mhos, T = 25°C
$R_C$ = 1.00 megohms, (Calc. from shunted E/P)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 36.2 | 1090 | 39.2 | 30.1 | 1.08 |
| 26.2 | 800 | 28.4 | 30.5 | 1.08 |
| 13.5 | 410 | 14.6 | 30.4 | 1.08 |
| 18.6 | 558 | 20.1 | 30.1 | 1.08 |
| 31.5 | 930 | 34.0 | 29.6 | 1.08 |
| 10.7c | 160 | 11.5 | 14.95 | 1.08 |
| 18.2c | 275 | 19.6 | 15.1 | 1.08 |
| 27.7c | 415 | 29.9 | 15.0 | 1.08 |
| 32.1c | 485 | --- | 15.1 | --- |
| 32.35 | 955 | --- | 29.5 | --- |

Run No. 31 August 27

Cell packed with 108 micron sand
$2 \times 10^{-4}$ M NaCl, $K_B = 2.63 \times 10^{-5}$ mhos, T = 25°C
$R_C$ = 0.95 megohms, (calc. from shunted E/P)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 37.0 | 1123 | 32.4 | 30.4 | .876 |
| 24.45 | 747 | 21.3 | 30.6 | .872 |
| 13.6 | 423 | 11.9 | 31.1 | .874 |
| 18.65 | 575 | 16.2 | 30.8 | .869 |
| 28.7 | 875 | 24.9 | 30.5 | .868 |
| 14.55c | 220 | --- | 15.1 | --- |
| 21.5c | 335 | --- | 15.6 | --- |
| 32.05c | 505 | --- | 15.7 | --- |
| 33.15 | 985 | --- | 29.7 | --- |

Run No. 32 August 27

Cell packed with 92 micron sand
$2 \times 10^{-4}$ M NaCl, $K_B = 2.64 \times 10^{-5}$ mhos, T = 25oC
$R_C$ = .99 megohms, (clac. from shunted E/P)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 32.25 | 806 | 18.16 | 25.0 | .563 |
| 11.2 | 278 | 6.18 | 24.8 | .552 |
| 17.05 | 422 | 9.40 | 24.7 | .552 |
| 25.2 | 633 | 14.08 | 25.1 | .558 |
| 37.2 | 927 | 21.02 | 24.9 | .565 |
| 12.15c | 145 | 6.56 | 11.9 | .541 |
| 24.0c | 300 | 12.28 | 12.5 | .553 |
| 33.05c | 423 | 18.38 | 12.8 | .555 |
| 16.9c | 210 | --- | 12.4 | --- |
| 19.7 | 485 | --- | 24.6 | --- |

Run No. 33 August 27

Cell packed with 71 micron sand
$2 \times 10^{-4}$ M NaCl, $K_B = 2.62 \times 10^{-5}$ mhos, T = 25°C
$R_C$ = 1.00 megohms, (calc. from shunted E/P)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 34.95 | 958 | 14.80 | 27.4 | .424 |
| 12.75 | 343 | 5.20 | 26.9 | .408 |
| 17.90 | 488 | 7.36 | 27.2 | .411 |
| 24.20 | 660 | 10.06 | 27.3 | .416 |
| 30.2 | 830 | 12.66 | 27.5 | .419 |
| 10.95c | 142 | --- | 12.9 | --- |
| 20.55c | 270 | --- | 13.1 | --- |
| 31.60c | 430 | --- | 13.6 | --- |

Run No. 34
August 28

Cell packed with 72.5 micron sand
$2 \times 10^{-4}$ M NaCl, $K_B = 2.62 \times 10^{-5}$ mhos, T = 25°C
$R_C$ = 0.96 megohms, (calc. from shunted E/P)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 36.5 | 1053 | 15.68 | 28.9 | .429 |
| 9.75 | 273 | 4.04 | 28.0 | .414 |
| 17.2 | 488 | 7.28 | 28.4 | .423 |
| 23.55 | 662 | 10.00 | 28.1 | .425 |
| 30.0 | 840 | 12.86 | 28.0 | .428 |
| 13.75c | 190 | --- | 13.8 | --- |
| 23.5c | 330 | --- | 14.0 | --- |
| 33.0c | 475 | --- | 14.4 | --- |
| 33.2 | 945 | --- | 28.5 | --- |

Run No. 35
August 28

Cell packed with 57 micron sand
$2 \times 10^{-4}$ M NaCl. $K_B = 2.62 \times 10^{-5}$ mhos, T = 25°C
$R_C$ = 0.94 megohms, (calc. from shunted E/P)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 36.8 | 1050 | 9.96 | 28.5 | .270 |
| 10.75 | 301 | 2.80 | 28.0 | .260 |
| 15.95 | 446 | 4.14 | 28.0 | .260 |
| 22.35 | 638 | 5.90 | 28.5 | .264 |
| 29.15 | 822 | 7.72 | 28.2 | .264 |
| 12.0c | 175 | --- | 14.6 | --- |
| 21.2c | 308 | --- | 14.5 | --- |
| 31.75c | 455 | --- | 14.3 | --- |

Run No. 36
August 29

Cell packed with 31.5 micron sand
$2 \times 10^{-4}$ M NaCl, $K_B = 2.62 \times 10^{-5}$, T = 25°C
$R_C$ = 0.95 megohms, (calc. from shunted E/P)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 37.65 | 865 | 3.36 | 23.0 | .0892 |
| 9.35 | 215 | .814 | 23.0 | .0872 |
| 15.15 | 337 | 1.330 | 22.3 | .0878 |
| 22.4 | 505 | 1.974 | 22.5 | .0882 |
| 28.9 | 653 | 2.564 | 22.9 | .0888 |
| 10.9c | 120 | --- | 11.0 | --- |
| 21.3c | 245 | --- | 11.5 | --- |
| 32.6c | 380 | --- | 11.7 | --- |

Run No. 37 August 29 — Cell packed with 160 micron sand
$2 \times 10^{-4}$ M NaCl, $K_B = 2.62 \times 10^{-5}$, T = 25°C

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 31.4 | 845 | 52.70 | 26.9 | 1.68 |
| 10.5 | 290 | 18.16 | 27.6 | 1.73 |
| 17.35 | 464 | 30.26 | 26.7 | 1.74 |
| 25.15 | 663 | 43.46 | 26.4 | 1.73 |

Run No. 38 August 30 — Cell packed with 12 micron sand
$2 \times 10^{-4}$ M NaCl, $K_B = 2.60 \times 10^{-5}$ mhos, T = 25°C
$R_C = 0.94$ megohms, (calc. from shunted E/P)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 39.1 | 725 | .388 | 18.55 | .0099 |
| 11.75 | 221 | .117 | 18.8 | .0099 |
| 17.7 | 331 | .175 | 18.7 | .0099 |
| 25.25 | 475 | .252 | 18.8 | .0100 |
| 32.85 | 620 | .329 | 18.9 | .0100 |
| 11.9c | 110 | --- | 9.2 | |
| 32.55c | 310 | --- | 9.5 | |

Run No. 39 August 31 — Cell packed with 10.7 micron sand
$2 \times 10^{-4}$ M NaCl, $K_B = 2.60 \times 10^{-5}$ mhos, T = 25°C
$R_C = 0.94$ megohms, (calc. from shunted E/P)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 12.45 | 215 | .115 | 17.3 | .00926 |
| 19.95 | 343 | .186 | 17.2 | .00932 |
| 28.85 | 495 | .269 | 17.2 | .00934 |
| 36.15 | 614 | .340 | 17.0 | .00942 |
| 36.15c | 320 | --- | 8.85 | --- |

Run No. 40 August 31 — Cell packed with 6 micron sand
$2 \times 10^{-4}$ M NaCl, $K_B = 2.60 \times 10^{-5}$ mhos, T = 25°C

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 34.05 | 280 | .0878 | 8.2 | .00258 |
| 11.65 | 105 | .0308 | 9.0 | .00265 |
| 17.95 | 175 | .0470 | 9.75 | .00262 |
| 24.6 | 217 | .0646 | 8.8 | .00262 |
| 29.7 | 260 | .0780 | 8.75 | .00263 |

The values of E/P from this run were discarded because a leak developed which prevented the complete stoppage of liquid flow through the cell and made it impossible to read the electrode polarization correctly.

Run No. 41 Cell packed with 50 micron sand
September 1 $2 \times 10^{-4}$ M NaCl, $K_B = 2.59 \times 10^{-5}$ mhos, T = 25°C

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 38.2 | 1089 | 6.40 | 28.4 | .168 |
| 13.05 | 370 | 2.14 | 28.3 | .164 |
| 19.3 | 547 | 3.06 | 28.4 | .159 |
| 30.2 | 867 | 4.96 | 28.7 | .164 |

Run No. 42 Cell packed with 72.5 micron sand
September 2 $1 \times 10^{-4}$ M NaCl, $K_B = 1.21 \times 10^{-5}$ mhos, T = 25°C
$R_C$ = 2.15 megohms, (Calc. from shunted E/P)
$R_C$ = 1.97 megohms, (D.C. bridge)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 12.95 | 718 | 4.46 | 55.5 | .345 |
| 19.90 | 1110 | 6.98 | 55.8 | .351 |
| 27.95 | 1558 | 9.84 | 55.7 | .352 |
| 37.60 | 2098 | 13.34 | 55.8 | .355 |
| 15.9b | 464 | --- | 29.2 | --- |
| 23.25b | 706 | --- | 30.3 | --- |
| 34.0b | 830 | --- | 29.4 | --- |

Run No. 43 Cell packed with 57 micron sand
September 2 $1 \times 10^{-4}$ M NaCl, $K_B = 1.22 \times 10^{-5}$ mhos, T = 25°C
$R_C$ = 1.81 megohms, (Calc. from shunted E/P)
$R_C$ = 1.79 megohms, (D.C. bridge)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 12.7 | 692 | 3.58 | 54.5 | .282 |
| 19.4 | 1056 | 5.50 | 54.5 | .283 |
| 27.85 | 1532 | 8.10 | 55.1 | .291 |
| 35.45 | 1940 | 10.32 | 54.8 | .291 |
| 14.6b | 458 | --- | 31.3 | --- |
| 22.0b | 686 | --- | 31.1 | --- |
| 31.45b | 994 | --- | 31.6 | --- |

Run No. 44 Cell packed with 31.5 micron sand
September 2 $1 \times 10^{-4}$M NaCl, $K_B = 1.21 \times 10^{-5}$ mhos, T = 25°C
$R_C$ = 1.65 megohms, (D.C. bridge)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 11.55 | 528 | .960 | 45.7 | .0830 |
| 20.45 | 948 | 1.692 | 46.3 | .0828 |
| 29.75 | 1378 | 2.466 | 46.3 | .0829 |
| 38.4 | 1780 | 3.212 | 46.3 | .0834 |

Run No. 45
September 3

Cell packed with 6 micron sand
$1 \times 10^{-4}$ M NaCl, $K_B = 1.21 \times 10^{-5}$ mhos, T = 25°C
$R_C$ = 1.15 megohms, (D.C. bridge)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 43.6 | 758 | .0804 | 17.4 | .00184 |
| 12.5 | 204 | --- | 16.3 | --- |
| 21.5 | 366 | --- | 17.0 | --- |
| 32.2 | 562 | --- | 17.4 | --- |
| 44.0 | 776 | --- | 17.6 | --- |
| 21.9 | --- | .0400 | --- | .00183 |

Run No. 46
September 4

Cell packed with 14.5 micron sand
$1 \times 10^{-4}$ M NaCl, $K_B = 1.21 \times 10^{-5}$ mhos, T = 25°C
$R_C$ = 1.52 megohms, (D.C. bridge)
In gravity packed cell, $R_C$ = 0.46 megohms

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 14.1 | 562 | --- | 39.9 | --- |
| 23.4 | 894 | --- | 38.2 | --- |
| 32.6 | 1234 | --- | 37.9 | --- |
| 42.1 | 1600 | --- | 38.0 | --- |
| 24.2 | --- | .389 | --- | .0161 |
| 30.9 | --- | .494 | --- | .0160 |
| 35.9 | --- | .599 | --- | .0167 |

Run No. 47
September 5

Cell packed with 108 micron sand
$1 \times 10^{-4}$ M NaCl, $K_B = 1.21 \times 10^{-5}$ mhos, T = 25°C
$R_C$ = 2.10 megohms, (D.C. bridge)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 11.2 | 700 | --- | 62.5 | --- |
| 21.0 | 1390 | --- | 68.2 | --- |
| 32.65 | 2160 | --- | 66.2 | --- |
| 42.9 | 2832 | --- | 66.0 | --- |
| 43.5 | --- | 37.46 | --- | .862 |
| 22.1 | --- | 18.62 | --- | .845 |
| 33.35 | --- | 28.40 | --- | .862 |

Run No. 48 — Cell packed with 160 micron sand
September 6 — $1 \times 10^{-4}$ M NaCl, $K_B = 1.21 \times 10^{-5}$ mhos, T = 25°C
$R_C \doteq 2.44$ megohms, (D. C. bridge)
$R_C = 2.42$ megohms, (Calc. from shunted E/P)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 11.5 | 678 | --- | 59.0 | |
| 20.1 | 1218 | --- | 60.6 | |
| 32.1 | 1906 | --- | 59.3 | |
| 41.5 | 2468 | 60.54 | 59.5 | |
| 16.0 | --- | 23.32 | --- | |
| 25.4 | --- | 36.92 | --- | |
| 13.65b | 404 | --- | 29.6 | |
| 27.7b | 826 | --- | 29.8 | |
| 36.8b | 1092 | --- | 29.7 | |

Run No. 49 — Cell packed with 200-270 mesh quartz
November 26 — Distilled water, $K_B = 2.05 \times 10^{-6}$ mhos, T = 25 C
$R_C = 8.4$ megohms, (D.C. bridge)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 4.42 | 1204 | 3.56 | 273 | .804 |
| 7.66 | 2114 | 6.28 | 276 | .820 |
| 10.65 | 2914 | 8.82 | 273 | .828 |

Run No. 50 — Cell packed with 150-170 mesh quartz
November 26 — Distilled water, $K_B = 2.0 \times 10^{-6}$ mhos, T = 25°C
$R_C = 8.4$ megohms, (D.C. bridge)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 4.04 | 1200 | 5.30 | 297 | 1.31 |
| 6.35 | 1880 | 8.72 | 296 | 1.37 |
| 9.44 | 3124 | 12.54 | 330 | 1.33 |
| 9.22 | 2350 | --- | 255 | --- |
| 6.75 | 1720 | --- | 255 | --- |
| 4.54 | 1160 | --- | 255 | --- |
| 4.44 | 1330 | --- | 299 | --- |
| 5.64 | 1670 | --- | 293 | --- |
| 8.66 | 2610 | --- | 301 | --- |

Run No. 51 Cell packed with 100-115 mesh quartz
November 27 Distilled water, $K_B$ = 2.0 x $10^{-6}$ mhos, T = 25°C
$R_C$ = 9.05 megohms, (D.C. bridge)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 4.18 | 1376 | 12.2 | 329 | 2.92 |
| 6.03 | 1964 | 17.4 | 325 | 2.89 |
| 8.22 | 2680 | 23.8 | 325 | 2.89 |
| 39.9 | --- | 112.5 | --- | 2.82 |
| 1.68 | 540 | 4.8 | 322 | 2.86 |

Run No. 52 Cell packed with 65-100 mesh quartz
November 27 Distilled water, $K_B$ = 2.0 x $10^{-6}$ mhos, T = 25°C
$R_C$ = 9.8 megohms, (D.C. bridge)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 39.64 | --- | 171 | --- | 4.32 |
| 4.83 | 1640 | 23.0 | 334 | 4.76 |
| 7.47 | 2492 | 35.4 | 333 | 4.74 |
| 1.54 | 500 | 7.14 | 325 | 4.58 |
| 8.86 | 2950 | --- | 333 | |

Run No. 53 Cell packed with 48-65 mesh quartz
November 27 Distilled water, $K_B$ = 2.0 x $10^{-6}$ mhos, T = 25°C
$R_C$ = 10.1 megohms, (D.C. bridge)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 1.85 | 548 | --- | 297 | --- |
| 3.61 | 1090 | 38.0 | 310 | 10.53 |
| 4.90 | 1460 | 50.9 | 298 | 10.38 |
| 7.83 | 2320 | 78.8 | 296 | 10.07 |
| 3.15 | 970 | --- | 308 | --- |
| 5.11 | 1750 | --- | 342 | --- |
| 9.78 | 3070 | --- | 314 | --- |

Run No. 54 Cell packed with 35-48 mesh quartz
November 27 Distilled water, $K_B$ = 2.0 x $10^{-6}$ mhos, T = 25°C
$R_C$ = 11.0 megohms, (D.C.) bridge

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 1.68 | 520 | 22.4 | 310 | 13.3 |
| 4.43 | 1340 | 56.9 | 302 | 12.8 |
| 8.75 | 2550 | 116.1 | 291 | 13.3 |

Run No. 55 Cell packed with 28-35 mesh quartz
November 27 Distilled water, $K_B = 2.0 \times 10^{-6}$ mhos, T = 25°C
$R_C$ = 11.1 megohms, (D.C. bridge)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 1.91 | 510 | 43.0 | 267 | 22.5 |
| 5.54 | 1390 | 108.5 | 251 | 19.9 |
| 10.88 | 2640 | 196.8 | 243 | 18.0 |

Run No. 56 Cell packed with 20-28 mesh quartz
November 27 Distilled water, $K_B = 2.0 \times 10^{-6}$ mhos, T = 25°C
$R_C$ = 11.65 megohms, (D.C. bridge)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 1.65 | 422 | 51.8 | 256 | 31.4 |
| 6.74 | 1440 | 161 | 214 | 23.7 |

Run No. 57 Cell packed with 14-20 mesh quartz
November 27 Distilled water, $K_B = 2.0 \times 10^{-6}$ mhos, T = 25°C
$R_C$ = 12.1 megohms, (D.C. bridge)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 1.51 | 282 | 61.9 | 186 | 40.9 |
| 3.53 | 624 | 117.8 | 177 | 33.4 |

Run No. 58 Cell packed with 150-170 mesh quartz
November 28 Distilled water, $K_B = 2.0 \times 10^{-6}$ mhos, T = 25°C
$R_C$ = 8.3 megohms, (D.C. bridge)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 10.25 | 2696 | 13.8 | 263 | 1.34 |
| 6.89 | 1824 | 9.3 | 265 | 1.35 |
| 4.04 | 1076 | 5.48 | 266 | 1.36 |

Run No. 59 Cell packed with 200-270 mesh quartz
November 28 Distilled water, $K_B = 2.0 \times 10^{-6}$ mhos, T = 25°C
$R_C$ = 7.7 megohms, (D.C. bridge)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 4.26 | 1052 | 3.06 | 247 | .720 |
| 6.63 | 1590 | 4.74 | 240 | .714 |
| 9.91 | 2378 | 7.20 | 240 | .736 |

November 28 A test also was made with the unpacked cell placed in the streaming circuit to determine the pressure drop due to frictional resistance in the connecting tubing as a function of the rate of flow. This was then used to correct the pressure reading for coarse samples where the rate of flow was high enough to cause an appreciable frictional pressure drop.

| P. cm $H_2O$ | P cm Hg | Q |
|---|---|---|
| 27.2 | 2.00 | 179. |
| 19.7 | 1.45 | 139. |
| 12.5 | 0.92 | 92.5 |
| 5.3 | 0.39 | 47.8 |
| 2.8 | 0.21 | 22.3 |

Run No. 60 Cell packed with 72.5 micron sand
November 28 Distilled water, $K_B = 2.0 \times 10^{-6}$ mhos, T = 25°C
$R_C$ = 9.25 megohms, (D.C. bridge)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 13.50 | 3226 | 5.53 | 239 | .410 |
| 8.47 | 2040 | 3.54 | 241 | .418 |
| 5.33 | 1290 | 2.24 | 242 | .420 |

Run No. 61 Cell packed with 57 micron sand
November 28 Distilled water, $K_B = 2.0 \times 10^{-6}$ mhos, T = 25°C
$R_C$ = 8.1 megohms, (D.C. bridge)
In gravity packed cell, $R_C$ = 7.5 megohms.

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 15.45 | 3240 | 3.49 | 210 | .226 |
| 10.89 | 2294 | 2.44 | 211 | .224 |
| 5.66 | 1196 | 1.26 | 212 | .223 |

Run No. 62 Cell packed with 31.5 micron sand
November 29 Distilled water, $K_B = 2.0 \times 10^{-6}$ mhos, T = 25°C
$R_C$ = 6.7 megohms, (D.C. bridge)
In gravity packed cell, $R_C$ = 5.7 megohms.

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 17.93 | 3012 | 1.28 | 168 | .0713 |
| 12.65 | 2152 | 0.892 | 170 | .0706 |
| 7.70 | 1304 | 0.538 | 170 | .0698 |

Run No. 63 Cell packed with 14.5 micron sand
November 29 Distilled water, $K_B = 2.0 \times 10^{-6}$ mhos, T = 25°C
$R_C = 6.65$ megohms, (D.C. bridge)
In gravity packed cell, $R_C = 2.1$ megohms

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 23.47 | 3120 | .352 | 133 | .0150 |
| 15.86 | 2100 | .240 | 132 | .0151 |
| 8.39 | 1110 | .126 | 132 | .0150 |

Run No. 64 Cell packed with 134 micron sand
November 29 Distilled water, $K_B = 2.0 \times 10^{-6}$ mhos, T = 25°C
$R_C = 10.3$ megohms, (D.C. bridge)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 11.20 | 3246 | 12.44 | 290 | 1.11 |
| 7.54 | 2190 | --- | 290 | --- |
| 4.15 | 1206 | 4.63 | 290 | 1.11 |

Run No. 65 Cell packed with 134 micron sand
November 29 Distilled water, $K_B = 2.0 \times 10^{-6}$ mhos, T = 25°C
$R_C = 5.67$ megohms, (D.C. bridge)

| P | E | Q | E/P | Q/P |
|---|---|---|---|---|
| 44.00 | 2644 | .1255 | 60.0 | .00274 |
| 25.60 | 1614 | .0706 | 63.0 | .00276 |
| 12.35 | 728 | .0334 | 62.3 | .00271 |

Additional measurements were taken of the rate of flow and are listed in the body of the report in tables IV, V, VI, and VII. Also, additional resistance measurements are tabulated in tables IX and X.