

2. The equation relating the streaming potential to the moment of the double layer is developed for any distribution of charges in the double layer, and the conditions for its validity are established.

3. The equation relating the moment to the

zeta-potential is developed by the same approach, and the necessary assumptions are discussed.

4. Criteria to insure measurement and computation of reliable values for the moment and for the zeta-potential are developed and discussed.

CAMBRIDGE, MASS.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## The Measurement of the Potential at the Interface between Vitreous Silica and Pure Water

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It is the purpose here to report experimental measurements, obtained for the first time with some degree of precision, of the zeta-potential of vitreous silica in contact with water of high purity. Measurements have been reported<sup>1</sup> of the zeta-potential of silica with potassium chloride solutions as dilute as  $10^{-5}$  *N* and the apparatus and technique have now been modified for measurements with water.

**Previous Attempts to Measure the Zeta-Potential of the Silica-Water and Glass-Water Interfaces.**—Lachs and Kronman<sup>2</sup> determined the streaming potentials of ordinary distilled water (specific conductance in bulk:  $3.86 \times 10^{-6}$  ohms<sup>-1</sup> cm.<sup>-1</sup> at 18°) flowing through a silica capillary, and obtained a mean *E/P* of 310 mv. per cm. of mercury. Using the modern values of  $\eta$  and *D* at 18°, this gives a zeta-potential of -133 mv., assuming the capillary specific conductance is the same as the figure given for the conductance in bulk. They state that this value is only approximate, because the high resistance of the capillary made the measurement of the streaming potentials very difficult. They also obtained streaming potentials for a "Thuringian" glass capillary, which gave -117 mv. for the zeta-potential of this glass. The attempt of Lachs and Kronman to measure the zeta-potential of the silica-water interface is the only one reported in the literature, but several other measurements of the zeta-potentials of glass-water interfaces have been made. Kruyt and van der Willigen<sup>3</sup> using the streaming potential method with Jena 16 III glass capillaries report several measurements with water of specific conductance  $1.15 \times 10^{-6}$  ohms<sup>-1</sup> cm.<sup>-1</sup>, giving values for  $\zeta$  ranging from -64 to -80 mv. Lachs and Biczky<sup>4</sup> using the same method and the same glass report zeta-potentials as a function of the specific conductance of the water ranging from -146 mv. for  $\kappa = 0.72 \times 10^{-6}$  to -55 mv. for  $\kappa = 3.00 \times 10^{-6}$ . They do

not mention any variation in their values as Kruyt observed or as Lachs and Kronman observed earlier with solutions. Fairbrother and Varley<sup>5</sup> found a pronounced decrease with time in the zeta-potential of glass in contact with water as determined by electro-endosmosis through a sintered glass powder diaphragm. Similar variations in the value of the zeta-potentials were observed by the writer with all solutions measured<sup>1,6</sup> in silica capillaries and it was found that reliable values could only be obtained by studying the change of zeta-potential with time with two different sets of apparatus simultaneously until the potential approached an equilibrium value.

**The Variation in the Zeta-Potential.**—A wide variation is commonly observed in repeated experiments among the initial values obtained for the zeta-potential, which cannot be attributed to errors in measurement. If measurements with a given system are made over a period of time, a variation is also observed, although few investigators have concerned themselves with this. The author has attributed these observations to the presumption that the solid surface approaches equilibrium with the solution slowly, and that the different initial zeta-potentials are the results of observations made with surfaces at varying deviations from what may be termed the "equilibrium zeta-potential." There seem to be only two other possible explanations: firstly, that the zeta-potential is not a reproducible property of the surface and, secondly, that the observations are the results of varying amounts of impurities in the system. The first can be categorically denied, in the opinion of the author, because surface phases must obey thermodynamic laws as well as any other system, and it seems inconceivable that the zeta-potential could be independent of the constitution of the system or depend upon it in such a way that it could have many different equilibrium values in a given system. The second could be ruled out if sufficient care were taken to protect the system from contamination. This the author deems experi-

(1) Grinnell Jones and L. A. Wood, *J. Chem. Phys.*, **13**, 106 (1945).

(2) H. Lachs and J. Kronman, *Bull. intern. acad. polon. sci.*, A289 (1925).

(3) H. R. Kruyt and P. C. van der Willigen, *Kolloid-Z.*, **45**, 307 (1928).

(4) H. Lachs and J. Biczky, *Z. physik. Chem.*, **148A**, 441 (1930).

(5) F. Fairbrother and H. Varley, *J. Chem. Soc.*, 1584 (1927).

(6) L. A. Wood, *J. Chem. Phys.*, **13**, 429 (1945).

mentally practicable, and is convinced it has been done in this and previous work in this Laboratory. Then it is reasonable to ask what kind of process is so slow that many days are required in some instances for a final zeta-potential to be approached within the limit of the error of measurement. The answer must be in part speculation, because there is at present no generally accepted theory explaining the origin of the zeta-potential. This potential must obviously be the result of the acquisition of electric charges by the solid surface, and with solutions the charges may be acquired by the adsorption of ions. For example, with potassium chloride solutions, with which the potential of silica is negative, the charge may be attributed to chloride ions. The following process may then be imagined: a perfectly dry and uncontaminated silica surface, on which the potential must be zero, is brought in contact with the potassium chloride solution, and the adsorption of chloride ions commences. As

the potential becomes more negative, a resulting repulsive force is exerted at long range on the chloride ions in solution, which greatly decreases the probability that a negative ion will approach closely enough to the surface so that van der Waals or other short range adsorptive forces may act to bind the ion to the surface. Thus a credible postulate is possible by which the approach to final equilibrium is slow. However, in the present instance of the zeta-potential of silica with pure water, this hypothesis is untenable, because there are no ions other than those supplied by the water. Therefore another explanation must be sought, which with solutions would naturally be a concomitant phenomenon. With the silica-water system the

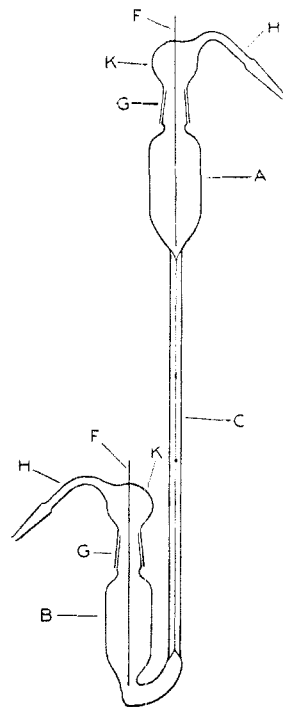


Fig. 1.—Vitreous silica apparatus for the production of streaming potentials.

charges on the silica surface may arise as a result of the adsorption of hydroxyl ions or by the formation on the surface of a monolayer of partly ionized silicic acid gel. In the writer's opinion no real distinction can be made between these. For examples of the swelling of silica and glass surfaces, attributed to gel formation, reference should be made to work already mentioned,<sup>2,5</sup> to Haber and Klemensiewicz,<sup>7</sup> and in particular to

(7) F. Haber and Z. Klemensiewicz, *Z. physik. Chem.*, **67**, 385 (1909).

Lenher.<sup>8</sup> Lenher stated that "the first thing which takes place when silica is wet is hydration," and described experiments by which this process was enormously speeded: when vitreous silica was heated in a bomb with water at 400°, it was partially converted after many days into hydrated silica gel. Such a gel layer would then throw off hydrogen ions, leaving behind a negatively charged structure. It seems probable that at 25° such a process would be extremely slow in approaching an equilibrium even insofar as the surface layers are concerned. Thus the hydration is the slow process which would explain the observations with the silica-water system. It is obviously possible in the experiments described below that this equilibrium might be approached from either direction, depending on whether more or less than an equilibrium amount of silicic acid gel was previously formed on the capillary surface in cleaning and filling the apparatus. If an excess of gel were formed the process would be similar to syneresis.

### Experimental

**Apparatus.**—In attempting to prepare and manipulate water of high purity, it is desirable to avoid bringing the water in contact with glass, which may introduce ionic impurities. Therefore, it was considered inadvisable to use the glass parts of the streaming potential apparatus developed for the accurate measurements with solutions of electrolytes. A new apparatus, shown in Fig. 1, was designed, which was made of vitreous silica, in so far as the parts which came in contact with the water were concerned. This consisted of two reservoirs, A and B, each about 15 cc. in volume, and a capillary C connecting them, which was about 19.6 cm. in length, and about 0.0138 cm. in internal diameter as computed from the cell constant (length/cross section). Some uncertainty as to the exact length was due to the flaring ends where the capillary was sealed to the reservoirs A and B. The top of each of the reservoirs was the inner part of a ground joint (G), over which fitted a cap (K) made of soft glass. During the manipulation of the apparatus, the glass parts never came in contact with the liquid in the reservoirs. Through the center of each cap was sealed a platinum wire (F) of gage no. 18 which extended to the bottom of the reservoir and served as an electrode. The outer end of each wire was connected to the electrical measuring instruments which were described previously. In the side of each glass cap was sealed a tube (H) which was connected by means of a ground joint to the tube leading to the pressure reservoirs of hydrogen. The simplicity of this design had the advantage of facilitating cleaning, and rapid and repeated thorough rinsing. There were two disadvantages as compared with the apparatus described earlier: first, that because of the small size of the reservoirs, the difference in the liquid level changed more rapidly so that it had to be determined quickly after the e. m. f. measurement to avoid error; and, second, since this difference was large (about 20 cm.) and had to be measured with the eye about 35 cm. from the reservoirs and the transparent scale, less accuracy was possible in determining it. It could be determined to about  $\pm 0.1$  cm. of solution, which was equivalent to less than  $\pm 0.01$  cm. of mercury, less than 1% of the total pressure. The measurement had to be completed too quickly to permit use of a cathetometer, because the level was continuously changing, since there was no way of stopping the flow. This difference in level gives rise to a hydrostatic pressure, which must be included in the pressure producing the streaming potential, and therefore the pressure is somewhat less accurately determined with this apparatus than with the type previously used for potas-

(8) V. Lenher, *This Journal*, **43**, 391 (1921).

sium chloride solutions. The uncertainty accordingly introduced was small, however, compared with others and was not the limiting factor in the precision of the measurements.

It was found that silver-silver chloride electrodes could not be used because the solubility of the silver chloride caused too great an increase in the ion concentration of the water. Therefore the bright platinum was used for the electrodes, and since the pressure was furnished by hydrogen gas, a hydrogen electrode presumably existed at the platinum-water interface. No difficulties were encountered as a result of polarization or asymmetry of the electrodes with pure water in the apparatus, but with a solution no more concentrated than  $10^{-4}$  *M* potassium chloride, the polarization was severe. No attempt was made to determine the critical ionic concentration at which the conductivity was sufficient to permit a current density great enough to cause appreciable polarization.

**Purification of Water.**—Ordinary conductivity water from a Barnstead still with block tin condensers was found to have a specific conductance, when carbon dioxide was removed, of about  $0.8 \times 10^{-6}$  ohm $^{-1}$  cm. $^{-1}$ , when measured in the capillary. This included the effect of surface conductance, if any, and might reasonably be expected to be larger than would be obtained with a conventional conductance cell of large cross section. When this water was redistilled and condensed in a silica tube, the specific conductance, measured in the capillary, was easily reduced to  $0.3 \times 10^{-6}$  ohm $^{-1}$  cm. $^{-1}$ , and in one instance to  $0.15 \times 10^{-6}$  ohm $^{-1}$  cm. $^{-1}$ . In order to obtain water of high purity, it must be protected not only from carbon dioxide, which can be removed, but also from other vapors and dust as well which may be present in the air and which cannot be removed. This was done by enclosing the exhaust end of the silica condenser tube in a glass hood, open at the bottom and by decreasing the flow of the cooling water in the condenser jacket so that the effluent was partly steam. Thus the water, which was run directly into reservoir A, was constantly in an atmosphere of steam and not exposed to air.

## Results

After thorough rinsing and steaming, about 10 cc. of water was collected and the electrode cap was replaced, with a small amount of previously washed paraffin as lubricant on the joint. During the streaming potential and conductance measurements the apparatus was maintained at  $25.00 \pm 0.03^\circ$ . It was impossible to avoid the introduction of some air while connections were being made to the pressure lines so that, after assembly, hydrogen was bubbled through the water for about twenty minutes to remove any traces of carbon dioxide. The hydrogen was passed through a tube of soda lime and then through a tube of glass wool, each about 20 cm. in length. In spite of all precautions the high purity of the water could not be long maintained, at most for a day or two, and often not even long enough for a measurement to be made, and frequent refilling with fresh water was necessary. As a result the change of the zeta-potential with time could not be studied, and the practice of observing the potential until it reached a constant and presumably equilibrium value could not be followed, as was done with the potassium chloride solutions previously reported.<sup>1</sup>

In making a streaming potential measurement, the procedure was as follows: (1) the resistance of the capillary was measured; (2) the potential difference *E* between the electrodes was determined; (3) the pressure *P* producing *E* was deter-

mined by measuring the difference in liquid level between the reservoirs A and B and by reading the mercury manometer across the hydrogen pressure lines; and (4) the resistance of the capillary was measured again. The direction of flow was reversed and the measurements (1) to (4) repeated, so that any asymmetry of the electrodes would be detectable if it were large, and would at least partially cancel out on averaging the measurements in any case. If the resistance of the capillary was the same in measurements (1) and (4), it was assumed that it was constant during the course of the measurements and the data were accepted for computing the zeta-potential, provided the same conditions held during the repetition with flow in the opposite direction. It was not considered necessary for the resistance of the capillary to be the same for each direction of flow as long as it was known to be constant during the *E* measurement. If the specific conductance was greater than  $0.5 \times 10^{-6}$ , the data were rejected. The data obtained in 24 accepted pairs of measurements out of a total of 118 attempts are given in Table I. The pressure *P* is given in cm., and is accurate to better than 0.02 cm. The streaming potential *E* is given in millivolts, and is accurate to about 10 mv. The resistance *R* is the resistance of the capillary, obtained with the D. C. bridge previously described.<sup>1</sup> The average specific conductance,  $\kappa$ , of the liquid in the capillary is  $32,345/R$ , where 32,345 is the cell constant of the capillary ( $L/\pi a^2$ ). The cell constant was determined by measuring the resistance with 0.1 *D* potassium chloride solution in the capillary, which has a specific conductance of  $0.012856$  ohm $^{-1}$  cm. $^{-1}$ , according to Jones and Bradshaw.<sup>9</sup> With this concentration of potassium chloride it was assumed that the surface conductance was negligible, an assumption which has been shown to be justified.<sup>10</sup> It will be noted that the resistance of the capillary with pure water is extremely high, between 74,000 and 161,000 megohms for the measurements reported. Since the null instrument responded appreciably to a variation of 1 ohm in the variable resistor with 250 volts imposed on the bridge, the higher figure is presumably accurate to better than 2%, and the lower to better than 1%. To make certain that paths for the electric current other than through the capillary were negligible, the water was frequently allowed to drain completely into reservoir B, so that the electrode in A was completely surrounded by hydrogen. Under these conditions, the bridge was balanced by setting the variable resistor at zero, which meant that the electrical path between the two electrodes then had a resistance greater than  $10^{18}$  ohms, since the residual resistance of the variable resistor was less than a tenth of an ohm. Therefore it is reasonable to suppose that  $\kappa$  is accurate to about  $0.004 \times 10^{-6}$

(9) Grinnell Jones and B. C. Bradshaw, *THIS JOURNAL*, **55**, 1780 (1933).

(10) Ref. 1, pp. 111-113.

TABLE I  
STREAMING POTENTIAL MEASUREMENTS

Time	Flow	P, cm. Hg	E, milli- volts	R × 10 <sup>-9</sup> , ohms	κ × 10 <sup>6</sup> , mhos/ cm.	ζ, milli- volts
0 <sup>a</sup>	A ← B	1.18	9,635	153.8	0.210	-166
	A → B	1.61	11,350	133.3	.243	-166
1 day	A ← B	2.00	11,611	111.1	.291	-163
	A → B	1.57	8,933	111.1	.291	-160
0 <sup>a</sup>	A ← B	1.55	11,270	101.0	.320	-228 <sup>d</sup>
	A → B	1.58	11,490	101.0	.320	-224
2 days	A ← B	1.65	11,670	111.1	.291	-199 <sup>d</sup>
	A → B	1.59	11,430	106.4	.304	-211
2 days	A ← B	1.57	11,180	106.4	.304	-209 <sup>d</sup>
	A → B	1.63	11,600	106.4	.304	-209
0 <sup>a</sup>	A ← B	1.68	10,470	91.7	.353	-213 <sup>c</sup>
	A → B	1.68	10,470	91.7	.353	-213
12 hr.	A → B	1.69	8,683	95.2	.340	-169 <sup>c</sup>
	A ← B	2.16	11,280	95.2	.340	-172
0 <sup>a</sup>	A ← B	1.86	11,160	104.2	.311	-180
	A → B	1.62	9,300	101.0	.320	-178
0 <sup>a</sup>	A ← B	1.66	11,630	125.0	.259	-175
	A → B	1.63	11,290	125.0	.259	-173
0	A → B	1.57	10,620	122.0	.265	-173
	A ← B	1.55	10,570	122.0	.265	-174
5 hr.	A ← B	1.78	9,555	101.0	.320	-166
	A → B	1.55	8,263	101.0	.320	-165
0 <sup>a</sup>	A ← B	1.90	7,870	85.5	.378	-151
	A → B	1.63	6,570	84.0	.385	-149
0	A ← B	2.12	7,480	74.1	.437	-149
	A → B	1.63	5,510	73.5	.440	-144
0 <sup>a</sup>	A ← B	2.06	8,900	78.7	.411	-172
	A → B	1.58	6,540	78.7	.411	-164
0 <sup>a</sup>	A → B	1.56	7,000	90.1	.359	-156
	A ← B	1.55	6,570	90.1	.359	-148
1 day	A ← B	2.14	10,360	93.5	.346	-162
	A → B	1.62	7,360	91.7	.353	-156
0 <sup>a</sup>	A ← B	2.07	12,060	117.6	.275	-155
	A → B	1.58	9,180	117.6	.275	-154
0 <sup>a</sup>	A → B	1.44	12,660	161.3	.201	-171
	A ← B	1.39	12,680	161.3	.201	-177
0	A ← B	1.48	12,380	147.1	.220	-178
	A → B	1.58	13,070	147.1	.220	-176
0 <sup>a</sup>	A → B	1.64	12,730	119.0	.272	-204 <sup>b</sup>
	A ← B	1.69	12,350	116.3	.278	-196
0	A ← B	1.63	13,080	125.0	.259	-201 <sup>b</sup>
	A → B	1.48	11,750	125.0	.259	-199
3 days	A ← B	0.86	4,610	91.7	.353	-183 <sup>b</sup>
	A → B	1.57	8,180	89.3	.362	-182
0 <sup>a</sup>	A → B	1.63	8,300	92.6	.349	-172
	A ← B	2.05	10,880	92.6	.349	-179
0	A ← B	2.06	10,170	88.5	.365	-174
	A → B	1.65	7,820	88.5	.365	-167

<sup>a</sup> Denotes that a new sample of water had been put in the apparatus preceding the designated measurement.  
<sup>b,c,d</sup> Explanation in text.

ohm<sup>-1</sup> cm.<sup>-1</sup>. In the computation of the zeta-potential  $D$  is taken as 78.49 and  $\eta$  is taken as

0.00895.<sup>11</sup> The values for the fundamental physical constants are according to Birge.<sup>12</sup>

The average value of the zeta-potential is  $-177$  mv., the P.E. of an individual measurement is  $\pm 14$  mv., and the P.E. of the mean is  $\pm 2.1$  mv., as computed by Bessel's formula. There is a difference of  $84$  mv. between the extremes, but there seems to be no valid reason for rejecting any of the measurements. Such variation is to be expected on the basis of the observations with dilute potassium chloride solutions,<sup>1</sup> when it was found that the initially observed potential was occasionally as much as  $30$  mv. away from the potential observed many days later which was presumed to be the equilibrium potential. Since the observations made with water were performed for the most part initial observations, it is reasonable to suppose that they deviated to a greater or lesser extent from the equilibrium potential upon which they would have converged if it were possible to maintain the purity of the water long enough to observe it. When  $\zeta$  is plotted as a function of  $\kappa$  (Fig. 2), two things are evident: firstly, that the six zeta-potentials with the water of  $\kappa$  less than  $0.25 \times 10^{-6}$  are close to  $-177$  mv.; and secondly, at higher values of  $\kappa$ , the spread was much greater among the zeta-potential values, with a high group of twelve ranging from  $-196$  to  $-228$  mv., and the main group in the range from  $-144$  to  $-183$  mv. The gap of  $13$  mv. between these two groups is not statistically reliable, and therefore it is unjustifiable to discard the high group. It might be argued that measurements with those samples of water which had the lowest conductance should be considered most reliable, and more attention should be given them. This would be correct if the surface conductance were negligible or could be assumed reasonably constant. However, it is possible that the larger part of the conductance of the capillary may be attributed to the surface conductance. For example, suppose the true bulk specific conductance  $\kappa_B$  of the water is  $0.100 \times 10^{-6}$ . The specific surface conductance  $\kappa_S$  necessary to give a measured  $\kappa$  of  $0.200 \times 10^{-6}$  is computed by the formula

$$\kappa_S = (\kappa - \kappa_B)a/2 = 7 \times 10^{-10} \Omega^{-1}$$

wherein  $a$  is the radius of the capillary. This value is smaller than anyone has claimed on the basis of existing information<sup>10,13</sup> about dilute solutions, and if it were subject to variation to as much as  $20 \times 10^{-10}$ , the entire variation of  $\kappa$  could be accounted for on the basis of the surface conductance. Therefore it does not necessarily follow that water with the lowest observed  $\kappa$  is the purest, although it seems more probable.

That the observed variation in the zeta-potential values cannot be ascribed to errors in the measurements is shown by consideration of the

(11) N. E. Dorsey, "Properties of Water-Substance," Reinhold Publishing Corp., New York, N. Y., 1940, p. 364 and p. 187, resp.

(12) R. T. Birge, *Rev. Mod. Phys.*, **13**, 233 (1941).

(13) See reference 15, preceding paper, p. 436.

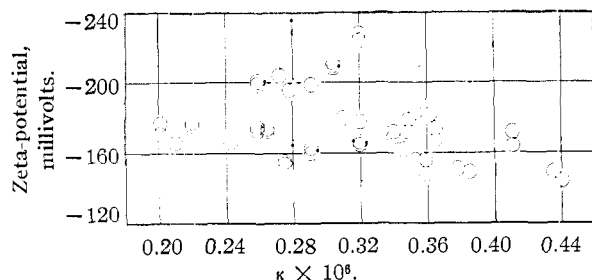


Fig. 2.—Observed zeta-potentials plotted as a function of the average specific conductance of the liquid in the capillary. (Each circle is 4 millivolts in radius; the P. E. is  $\pm 14$  millivolts.)

probable errors of  $E$ ,  $P$  and  $R$ . Assuming liberal P.E.:  $\pm 1\%$  for  $E$ ,  $\pm 2\%$  for  $P$ ,  $\pm 2\%$  for  $R$ , all of which are certainly larger than the actual values, it is found that the P.E. of a single  $\zeta$  value is  $\pm 6$  mv. or less, as compared with  $\pm 14$  mv. from Bessel's formula. This indicates that the observed variation in the zeta potential is for the most part real, as would be expected in view of the above-mentioned experience with dilute electrolyte solutions. The fact that in the twenty-four pairs of measurements given, the average difference between the two measurements of each pair is 4 mv. further justifies the belief that the precision is sufficient that the variation must be considered as real. Since other criteria are lacking, it seems best to rely upon statistical criteria, and to consider the mean value as the most probable equilibrium zeta-potential. In one instance, however, a sample of water remained at high purity for six days, so that the variation in the zeta-potential was observed for this limited time. The only measurements meeting all the acceptance criteria are indicated by  $b$  in Table I. These show a pronounced drop from  $-200$  mv., after the water was first added, to  $-182$  mv. three days later. On the sixth day one measurement was obtained, with flow  $A \rightarrow B$ ,  $P = 1.71$  cm.,  $E = 7,360$  mv.,  $R = 76.9 \times 10^9$  ohms before the  $E$  measurement and  $75.2 \times 10^9$  ohms after, giving an average  $\kappa = 0.425 \times 10^{-6}$ , all of which give  $\zeta = -177$  mv. It was impossible to get any further measurements on the sixth day, as the water became contaminated. In the measurements  $c$  a similar decrease was observed in thirteen hours, but in measurements  $d$  only a slight decrease occurred. These observations make it seem probable that the high values are not equilibrium values and give some measure of confidence in the mean value. No comparable increase was observed in any of the low values.

It is therefore reasonable to conclude that the equilibrium zeta-potential of vitreous silica in contact with pure water is within a few millivolts

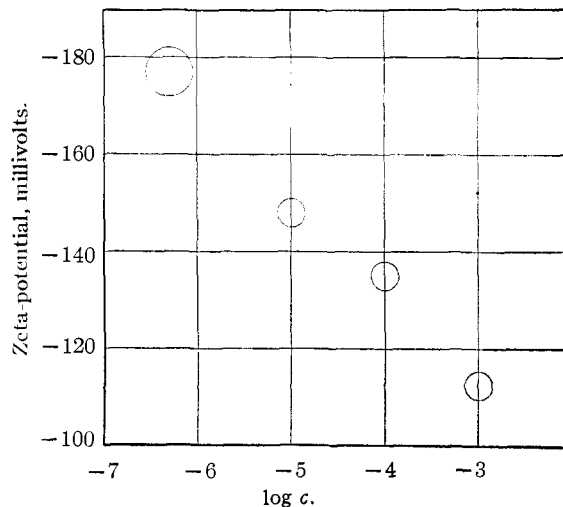


Fig. 3.—Zeta-potential of vitreous silica in contact with water and with potassium chloride solutions,<sup>1</sup> plotted as a function of positive ion concentration.<sup>14</sup>

of  $-177$  mv. That this is not inconsistent with the accurately determined zeta-potentials of silica in contact with dilute solutions of potassium chloride is evident in Fig. 3, where the observed zeta-potentials are plotted against the logarithm of the positive ion concentration. The three small circles (radius, 3 mv.) represent the potassium chloride solutions of  $10^{-3}$ ,  $10^{-4}$  and  $10^{-5}$   $M$  concentration, and the larger circle (radius, 5 mv.) represents the mean value for water of assumed concentration  $0.5 \times 10^{-6}$  (if  $\kappa_B$  is  $0.2 \times 10^{-6}$  and  $\Lambda$  is 400,  $c = 1000 \kappa_B / \Lambda = 0.5 \times 10^{-6}$ ). It is seen that the four points fall fairly well on a straight line.

### Summary

1. An apparatus for the production of streaming potentials is described in which the liquid is in contact only with silica and platinum, so that it is suitable for measurements with water of high purity.
2. The measurement of the zeta-potential of vitreous silica in contact with water of high purity is reported. It is probable that this potential is about  $-177$  millivolts.

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(14) It is evident from the conductance measurements (see Table II in ref. 1) that the positive ion concentrations of the  $10^{-4}$  and  $10^{-3}$   $M$  potassium chloride solutions are essentially determined by the potassium chloride concentrations, but with the  $10^{-5}$   $M$  potassium chloride the average  $\kappa_B$  is  $2.5 \times 10^{-6}$ , compared with the theoretical value of  $1.5 \times 10^{-6}$  from  $\Lambda_\infty$ , which means that the concentration of ions other than  $K^+$  and  $Cl^-$  is not negligible. Therefore it is apparent that the  $10^{-5}$   $M$  potassium chloride point should be moved slightly to the right by a distance roughly equal to its radius, in order to have  $c$  represent the total ion concentration.