Summary

Vanillin has been substantially quantitatively oxidized to vanillic acid by means of alkali and one-half mole of silver oxide. A Cannizzaro reaction mechanism for this reaction has been proposed. The alcohol product of the Cannizzaro reaction of vanillin has been identified as 4,4′-dihydroxy-3,3′-dimethoxydiphenylmethane.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

An Analysis of the Streaming Potential Method of Measuring the Potential at the Interface between Solids and Liquids

BY LLOYD A. WOOD

A previous publication[1] describes in detail an improved method of measuring the streaming potential produced by flow of water solutions through a capillary, and measurements with capillaries of vitreous silica and dilute solutions of potassium chloride are reported. It is the purpose here to inquire into the physical significance of the streaming potential measurements and to establish the criteria and assumptions necessary to convert them into reliable zeta-potentials.

The Helmholtz Concept of the Electric Double Layer, and Subsequent Modifications.—Helmholtz,[2] who originally formulated the concept of the electric double layer and the equations of electrokinetics, assumed that there is an immobile layer of electric charges on the solid at a solid–liquid interface, and another sharply defined mobile layer of charges of opposite polarity parallel to the interface a short distance away in the interior of the liquid. Movement of one phase relative to the other results in electrokinetic effects such as the streaming potential. It is now realized that the solution layer must be diffuse, and the revision of Helmholtz's reasoning to conform to a charge distribution according to an exponential law was first carried out by Gouy.[3] Smoluchowski[4] later generalized the electrokinetic equations and showed them to be applicable to any distribution of charges in the solution.

It appears, however, that some of the clarity of understanding of the electrokinetic effects demonstrated by Helmholtz has been lost in subsequent discussions. The first property of the double layer discussed by him is the moment, which he defined as the quantity σd (where σ is the charge density, or number of charges per unit area, on the solid surface, and d is the distance between the two layers), and this is equal to the potential difference $(\psi_1 - \psi_2)$, the zeta-potential, between the two layers divided by the constant 4π. (He did not take into account the dielectric constant, D, of the medium between the layers, and therefore the relation should be $\sigma d = (\psi_1 - \psi_2)D/4\pi$.) While it is true that he referred almost exclusively to the potential in his arguments in developing the theory, it is noteworthy that he frequently referred to the moment, particularly when discussing experimental measurements, in such a way as to show that to him the moment and potential were synonymous.[5] This was dimensionally correct because at that time it was conventional to express electrical quantities in three fundamental dimensions: mass, length and time. The charge density has the dimensions $\mathrm{M}^{1/2}\mathrm{L}^{-1/2}\mathrm{T}^{-1}$ which when multiplied by the length d gives the dimensions of potential $\mathrm{M}^{1/2}\mathrm{L}^{1/2}\mathrm{T}^{-1}$.

Subsequent writers on electrokinetics have generally ignored the moment and focussed their attention exclusively upon the zeta-potential, probably because potential theory has been well developed, and the potential seems more familiar and is generally easier to handle mathematically. Furthermore, since Helmholtz's time it has become conventional in electrostatics to assign four dimensions to fundamental quantities: if the dielectric constant is taken as the fourth dimension, then the potential has the dimensions $\mathrm{D}^{-1/2}\mathrm{M}^{1/2}\mathrm{L}^{1/2}\mathrm{T}^{-1}$ and the moment of the double layer the dimensions $\mathrm{D}^{1/2}\mathrm{M}^{1/2}\mathrm{L}^{1/2}\mathrm{T}^{-1}$. With this convention the moment and potential are not the same kind of quality. Guggenheim,[6] in a study of this question, expressed concern over the apparent neglect of fundamental units in the electrokinetic equations, but this is unwarranted and the result of an inconsistency in his own conventions. He chose four fundamental units: length, time, energy and charge, in which to express electrical units, and then defined the dielectric constant as a dimensionless measure-ratio. If the dielectric constant is dimensionless, then the dimension of charge can be expressed in terms of the other dimensions by means of the fundamental equation of electrostatics. The force f on a charge q exerted by another charge q' at a distance r in a medium of dielectric constant D is given by: $f = qq'/Dr^2$. Thus if D is dimensionless, the charge has the

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

[2] H. Helmholtz, *Wied. Ann.*, **7**, 337 (1879).

[3] L. Gouy, *J. phys.*, **9**, 457 (1910).

[4] M. Smoluchowski in Graetz, "Handbuch der Electrizität und des Magnetismus," Vol. II, Verlag Johann Barth, Leipzig, 1921, p. 374.

[5] For example, see ref. 2, pp. 358–359, 370, 382.

[6] E. A. Guggenheim, *Trans. Faraday Soc.*, **36**, 141 (1940).

dimensions $(\mathit{length})^{1/2} \times (\mathit{energy})^{1/2}$ in Guggenheim's units, or $\mathrm{M}^{1/2}\mathrm{L}^{3/2}\mathrm{T}^{-1}$ in Helmholtz's units. If it is desired to use four dimensions for electrical quantities, then it is necessary that D be assigned units, while if D is defined as a measure-ratio, then three fundamental units suffice for electrical quantities, and potential and moment have the same dimensions. Guggenheim attempted to extricate himself from his inconsistency by stating that the constant 4π has dimensions in the electrokinetic equations, but this renders the fundamental electrostatic equation above dimensionally incorrect.

The Electrokinetic Equation for the Streaming Potential.—It will now be shown that the quantity which is actually measured by a streaming potential measurement is the electric moment of the double layer, and that the computation of the zeta-potential requires additional assumptions and specification about the double layer beyond those necessary for computation of the moment. Consider a cylindrical tube of radius a and length L through which a liquid containing ions is flowing at constant velocity without turbulence. The velocity v of the liquid flow at a distance r from the axis of the cylinder (the z-axis) is given by the well-known equation

$$v = (P/4L\eta)(a^2 - r^2) \tag{1}$$

wherein P is the pressure producing the flow and η is the viscosity coefficient. It is assumed that η is a constant, which is the assumption of stream-lined flow. Let the volume of the tube be divided into n small elements of volume, $\Delta V_1, \Delta V_2, \cdots, \Delta V_n$, each element being taken as small as necessary for all portions of the liquid in it to be considered as moving at the same speed. Let ΔN_i be the net electrical charge in each ΔV_i. These charges are presumed to arise from the influence of a layer of fixed charges on the wall of the tube, so that a so-called electric double layer exists composed of the fixed charges and the neutralizing charges in the solutions. As the solution flows, these latter charges will be conveyed through the tube, resulting in a current I_s. To express this current in terms of the charges and their velocities, it should first be noted that each of the ΔN_i charges will move a distance v_i cm. per second. Thus the total movement of charges will be $\Sigma_i v_i \cdot \Delta N_i$. The resulting current is then the charge movement per cm. length of the tube.

$$I_s = (1/L) \sum_{i=1}^{n} v_i \Delta N_i \tag{2}$$

Combining (1) and (2)

$$I_s = (P/4L^2\eta) \sum_{i=1}^{n} (a + r_i)(a - r_i) \Delta N_i \tag{3}$$

Let the following assumptions be made about the electric charges: (1) that the system as a whole is electrically neutral; (2) that the thickness of the electric double layer is small compared to the radius of the tube, so that ΔN_i is zero except where r is very nearly as large as a.

Assumption (1) is probably true in general. Since in the most extreme case the thickness of the double layer is probably of the order of only a few microns, assumption (2) is certainly justified when the capillary tube has a radius of 0.01 cm. or larger, as would be used experimentally. Equation (3) may therefore be rewritten, substituting $2a$ for $(a + r_i)$

$$I_s = (Pa/2L^2\eta) \sum_{i=1}^{n} (a - r_i) \Delta N_i \tag{4}$$

Each term, $(a - r_i) \Delta N_i$, in the summation in equation (4) is an electric moment, or has the characteristics of an electric moment, since it is the product of the charge of an element and its distance from the oppositely charged wall. The question may be raised as to whether other charges on the wall and in the solution do not interact with that in a given element, but this is of no concern because there is no net effect resulting from these charges. The electric moment for the entire tube is then the summation of all the individual moments. It is convenient to define the moment so that it is independent of the extent of the wall surface, so the moment of the electric double layer is defined as M in the equation

$$2\pi aLM \equiv \sum_{i=1}^{n} (a - r_i) \Delta N_i \tag{5}$$

According to this definition M is positive when the solution charges are positive, so that the positive direction of M is inward away from the solid surface. It should be noted that if the solution charges are condensed in a Helmholtz-type layer, $M = \sigma d$. Combining equations (4) and (5)

$$I_s = \pi a^2 PM/L\eta \tag{6}$$

The continual transfer of electricity as the liquid flows creates a potential difference between the ends of the tube, called the streaming potential, E. However, since the solution itself is a conductor, a countercurrent, I_c, in effect, must result from the streaming potential such that at equilibrium with constant flow

$$I_s + I_c = 0 \tag{7}$$

because there can be no net current through the tube. Experimentally, when the liquid flow commences, the streaming potential will increase until the countercurrent, I_c, is equal and opposite to the streaming current, I_s. It is this resulting steady streaming potential which is measured. Let R be the electrical resistance of the liquid in the capillary, and if there is no path other than that through the liquid by which I_c may pass, then $I_c = -E/R$, by Ohm's law. (The sign is negative because the current will go in the opposite direction to the positive potential.) Thus, from equations (6) and (7)

$$M = \eta EL/\pi a^2 RP \tag{8}$$

If κ is the average specific conductance of the liquid in the capillary, then $R = L/\pi a^2\kappa$ and

$$M = \eta E\kappa/P \tag{9}$$

It should be noted that it was unnecessary to assume any particular distribution of the charges in the solution in obtaining equation (9). It is therefore immaterial whether the charges in the double layer are distributed according to Helmholtz's conception, or according to the Maxwell–Boltzmann law, or in any other manner. Furthermore, all mention of the dielectric coefficient has been avoided, which eliminates any difficult and uncertain theoretical considerations as to what it may be in such a microscopically thin layer. It is apparent that measurement of E, κ and P constitutes the measurement of the fundamental property of the electric double layer, provided that proper experimental precautions are taken.

The dielectric coefficient, D, which must be assumed to be constant for purposes of computation, is introduced when the moment is expressed in terms of the zeta-potential, which is equal to $-4\pi M/D$. This is apparent when equation (5) is interpreted in terms of the potential, but in order to do this further specifications about the system are required. In addition to assumptions (1) and (2) above, the assumptions to be accepted are: (3) the solution charges may be treated as continuously distributed over the volume of the tube, and the wall charges may be treated as uniformly distributed over the wall. (4) The volume charge density ρ is a function of r but is independent of the angle θ about the z-axis in a given cross section of the tube. (5) The potential ψ caused by the wall charges and the solution charges is additive to the streaming potential, so that the superposition of the streaming potential does not affect the distribution of charges in a given cross section of the tube. (6) Poisson's equation holds.

Let the volume ΔV_i approach zero, and equation (5) becomes

$$2\pi a L M = \iiint\limits_V (a - r)\mathrm{d}N \tag{10}$$

Substituting $\mathrm{d}N = \rho r \mathrm{d}z\mathrm{d}\theta\mathrm{d}r$, and recalling that ρ is a function of r only

$$M = (1/2\pi a L)\int_0^L \mathrm{d}z \int_0^{2\pi} \mathrm{d}\theta \int^a (a - r)\rho r \mathrm{d}r \tag{11}$$

$$= (1/a)\int_0^a (a - r)\rho r\mathrm{d}r \tag{11}$$

The potential ψ must also be a function of r only in a given cross section of the tube, and ρ and ψ are related by Poisson's equation. According to assumption (5) the two-dimensional Poisson's equation holds for a cross section of the tube, and it is conveniently written in circular coördinates

$$\nabla^2\psi = \frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r}\left(r\frac{\mathrm{d}\psi}{\mathrm{d}r}\right) = -\frac{4\pi\rho}{D} \tag{12}$$

Combining equations (11) and (12), and integrating by parts

$$M = (-D/4\pi a)\left\{\left[(a - r)r\frac{\mathrm{d}\psi}{\mathrm{d}r}\right]\Big|_0^a + \int_0^a r\frac{\mathrm{d}\psi}{\mathrm{d}r}\,\mathrm{d}r\right\} \tag{13}$$

From assumptions (1), (2) and (5), it follows that when $r = 0$, $\psi = 0$, and $\mathrm{d}\psi/\mathrm{d}r = 0$; and when $r = a$, $\psi = \zeta$ by definition, and $\mathrm{d}\psi/\mathrm{d}r$ is finite as is known from the electrostatic theory of charged surfaces.[7] Hence $r/(a - r)(\mathrm{d}\psi/\mathrm{d}r)\big|_0^a = 0$. Since the double layer is assumed to be thin, which means that r/a is essentially unity in the region where the integral is not zero, then

$$M = (-D/4\pi)\int_0^a (r/a)\mathrm{d}\psi = -D\zeta/4\pi \tag{14}$$

Thus it is established that

$$\zeta = -4\pi M/D \tag{15}$$

From equation (9)

$$\zeta = -4\pi\eta E\kappa/DP \tag{16}$$

Equation (16) is the conventional equation relating the zeta-potential to the streaming potential. The negative sign is not usually written, but its correctness is evident, because when the liquid is flowing in the direction of positive z and E is positive at the efflux end, ζ is negative.

Study of the Effect of Neglecting the Double Layer Thickness when Compared with *a*.—Let the moment M be considered as composed of ΔM_1, ΔM_2, ΔM_3, etc., where

$$\Delta M_i \equiv (a - r_i)\Delta N/_i 2\pi a L \tag{17}$$

From equations (3) and (17)

$$I_s = (\pi a P/2L\eta)\Sigma_i(a + r_i)\Delta M_i \tag{18}$$

Let $(a - r_i) \equiv d_i$ where d_i is then the distance of the element i from the wall of the tube, and let $d_i/a \equiv q_i$. Then $r_i = a(1 - q_i)$ and

$$I_s = (\pi a^2 P/L\eta)[M - (1/2)\Sigma_i q_i \Delta M_i] \tag{19}$$

Now it is evident that only when the sum of the $q_i\Delta M_i$ terms is small are equations (9) and (16) true. In other words, most of the elements of volume which contain excess charges must be relatively close to the wall for equations (9) and (16) to hold. However, on the basis of (19), equation (9) can be rewritten in the exact form

$$M - (1/2)\Sigma_i q_i \Delta M_i = \eta E\kappa/P \tag{20}$$

If a series of streaming potential experiments is performed with capillary tubes of different radii but of the same material and with the same solutions, it is evident that as the radius becomes smaller and smaller, the measured quantity $\eta E\kappa/P$ will diminish, provided that the moment (and consequently the zeta-potential) is unchanged. This occurs because the q_i's become larger, and the term $(1/2)\Sigma q_i \Delta M_i$, which is negligible with large tubes, becomes appreciable with sufficiently small capillaries. Therefore with very small capillaries, the measured quantity is no longer a measure of M.

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(7) See O. D. Kellogg, "Foundation of Potential Theory," Frederick Ungar Publishing Company, New York, N. Y., 1929, p. 167.

The precise deviation from M cannot be evaluated because the relationship between ΔM_i and r_i (or q_i) is unknown, but criteria can be established such that it is possible to determine whether large enough capillaries are being used in determining M from the streaming potential. Moreover, in addition to the above mentioned deviation, which will be termed the "radius effect," it seems probable that the double layer structure itself would depend on the radius of the capillary. The conditions of electroneutrality and symmetry require that at the center of the capillary, when $r = 0$, $\psi = 0$ and $\mathrm{d}\psi/\mathrm{d}r = 0$. This means that with small enough radius, the double layer would be more compressed simply because there is not sufficient space for it to extend as far into the solution as it could if the radius were larger, and this would result in a decreased moment. This "compression effect" is probably not as important as the radius effect as a cause of the deviation until capillaries of exceedingly small radius are used, of the order of a micron or less in radius, when a large fraction of the double layer is subject to the compression. The radius effect may then be considered to be the result of variation in q_i, and the compression effect to be the result of variation in ΔM_i, as experiments are performed with successively smaller capillaries.

The kind of deviation caused by the radius effect can be determined from equation (20) on the basis of the reasonable assumption that the compression effect is relatively unimportant. Substituting d_i/a for q_i in equation (20)

$$M - (1/2a)\Sigma_i\, d_i \Delta M_i = \eta E_\kappa/P \qquad (21)$$

If the compression effect is assumed negligible, then M, the d_i's, and the ΔM_i's are constant. It is thus evident that with variation in a, $\eta E_\kappa/P$ describes a hyperbola

$$\eta E_\kappa/P = M - A/a \qquad (22)$$

where $A \equiv (1/2)\Sigma d_i \Delta M_i$.

It is interesting to note that Bull and Gortner[8] have reported experiments which at least partially verify the conclusions of equation (22). They measured streaming potentials of quartz diaphragms which were made by sintering powdered quartz which had previously been fractionated according to particle size. The average particle diameter in the diaphragm of smallest particles was 4.6 microns, and that in the one of largest particles was 630 microns. They studied the streaming potentials when 2×10^{-4} M sodium chloride flowed through the diaphragms, and found that while E_κ/P was essentially constant for a given diaphragm, there was considerable variation among the different diaphragms. This variation can be adequately explained on the basis of equation (22) provided that two assumptions be admitted: First that the variation in the size of the pores between the particles is a linear function of the particle size of the diaphragms; secondly that the streaming potential is the same as would be obtained if the pores were cylindrical tubes rather than irregular passages. In Fig. 1 $\eta E_\kappa/P$ (from the data of Bull and Gortner) is plotted as a function of particle size. The solid line is that given by equation (22) with $M = 8.0$ and $A = 1.25 \times 10^{-4}$. It is evident that the curve is a good fit except in the region of smallest particle size, where good agreement is not to be expected because the compression effect is no longer negligible. This demonstrates that to obtain reliable measurements of the moment it is necessary to have a capillary or diaphragm of dimensions which are well out on the flat portion of the curve. Experimentally, this can be insured by obtaining the same results using two capillary tubes of widely differing radii and if the same value for E_κ/P is obtained from both, it necessarily follows that both are sufficiently large to be on the flat portion of the curve within the experimental error.

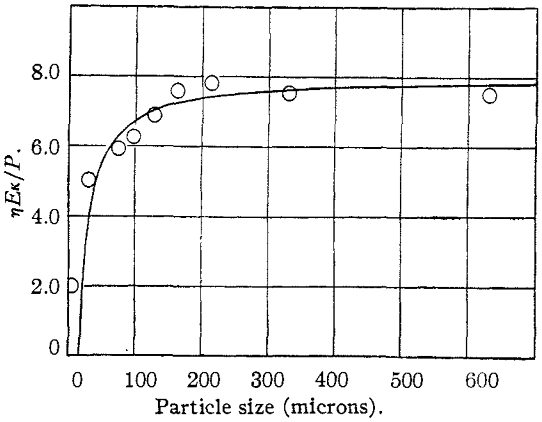

Fig. 1.—Variation of $\eta E_\kappa/P$ as a function of capillary radius. The solid line is from equation (27); the points are from the data of Bull and Gortner,[8] using $\eta = 0.00895$, and assuming a linear relation between the particle size of their quartz diaphragms and the radius of the capillaries between the particles.

The Computation of the Moment and the Zeta-potential from Experimental Data.—The above discussion has made it evident that the moment is the quantity which is most closely related to the experimentally measured quantities, because the streaming potential is determined for a given pressure, viscosity, and electrical resistance only by the location and number of charges in the fluid in the tube. The only assumptions required in relating the streaming potential to the moment are the assumptions of Poiseuillian flow in the capillary, and of electroneutrality of the system as a whole. These seem to be entirely reasonable assumptions. Furthermore, accepted criteria are available for verifying the conditions under which the flow is streamlined.[9] The assumption that the double layer is

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[8] H. B. Bull and R. A. Gortner, *J. Phys. Chem.*, **36**, 111 (1932).

[9] O. E. Reynolds, *Phil. Trans.*, **174**, 935 (1883); **A186**, 123 (1895).

thin compared with the capillary radius is also necessary, but can be experimentally verified. In previous work in this Laboratory,[1] it has been observed that when the streaming potentials were measured with capillaries of radii 0.0161 and 0.0084 cm., no detectable difference ascribable to the radius effect was observed. It is therefore certain that with capillaries of this size there is no possibility of experimental error as a result of the type of deviation shown in Fig. 1.

The conversion of the moment to the zeta-potential requires additional assumptions enumerated above, all of which seem reasonable. The computation of numerical values, however, involves an additional practical difficulty not involved for the moment, namely, assigning a value to the dielectric coefficient, D. This is conventionally assumed to be constant and equal to the dielectric constant of the bulk liquid, and this Abramson[10] states "is not altogether unjustified in dilute solutions," citing experimental evidence in support. On the other hand, Verwey[11] reasons that the dielectric constant is much smaller in the double layer than it is in the bulk liquid, because many of the molecules must be immobilized or oriented about ions and on the charged wall, and he presents evidence that the value of D is about 8 in the double layer of water solutions. These considerations are quite apart from the question of whether the dielectric constant has any meaning at all for such a microscopically thin layer. It is evident that the computation of values for the zeta-potential is based on a highly questionable assumption.

Guggenheim[6] has appreciated the greater generality of the moment and has suggested the adoption of the convention of reporting electrokinetic data as moments rather than as zeta-potentials, in terms of a new unit called the *Helmholtz*. This would have been a reasonable suggestion if made at the time of Perrin's publication[12] in which the dielectric constant was first introduced into the electrokinetic equations, but the vast literature now in existence with zeta-potentials reported in millivolts makes such a sweeping change inadvisable, because much confusion would arise from such a move. A more practical plan seems to be to accept frankly any conventional assumption about the dielectric constant, but to bear in mind that in any event it is the moment which is actually measured experimentally. The assumed value of D should of course be stated, although many previous investigators have not done so, so that revisions and new interpretations do not render the data useless.

It is worth mentioning that two groups of workers[13,14] claim to have developed static methods of measuring zeta-potentials by means of a single potential measurement in certain special cases. If the reliability of these methods can be established, then it may be possible to test the validity of the assumptions made in interpreting electrokinetic data.

Many investigators have apparently not realized how the specific conductance κ is introduced into equations (9) and (16). It is clear from equation (8) that the required experimental quantity is the resistance R of the capillary, together with the dimensions of the capillary. (Actually the dimensions themselves need not be accurately known, but only the ratio $L/\pi a^2$.) By substitution of $L/\pi a^2\kappa$ for R, it is found that the streaming potential is apparently independent of the dimensions of the capillary. This simplification is only illusory, however, because the specific conductance κ is that of the liquid in the capillary. It has been customary to measure the specific conductance of the same solution in the conventional type of conductance cell, and to use the value so obtained in equation (16). That this is not necessarily the correct value for κ is shown by much evidence[1,15] which indicates that the liquid in the region of the solid surface is a better conductor than the bulk liquid. In the conventional conductance cell any such effect is negligible, but in capillaries or diaphragms this surface conductance may be responsible for a large proportion of the total conductance of the capillary. Therefore, in order to use the bulk specific conductance, some proof must be provided that the surface conductance is negligible, and also that there is no other electrical path owing to electrical leakage over the outer surfaces of the capillary or through the measuring instrument. Such precautions have been neglected in almost every instance in the literature. The experimental means by which the capillary resistance and the "cell constant," $L/\pi a^2$, may be measured with precision has been previously described,[1] and the experimental precautions necessary for this and for the streaming potential measurement need not be described here.

The author wishes to express his gratitude and appreciation to Professor Grinnell Jones for his helpful suggestions and stimulating interest in this paper.

Summary

1. Attention is called to the fundamental property of the electric double layer, the moment, first defined by Helmholtz.

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[10] H. A. Abramson, "Electrokinetic Phenomena," Reinhold Publishing Corporation, New York, N. Y., 1934, p. 137.

[11] E. J. W. Verwey, *Chem. Rev.*, **16**, 335 (1931).

[12] J. Perrin, *J. chim. phys.*, **2**, 601 (1904).

[13] S. Lewina and W. Sarinsky, *Acta Physicochim. U. R. S. S.*, **7**, 485 (1937).

[14] H. R. Kruyt and H. de Bruyn, *Z. physik. Chem.*, **A186**, 282 (1940). Also see discussions of S. R. Craxford and J. J. Bikerman of Kruyt's method, *Trans. Faraday Soc.*, **36**, 718 (1940), in reference to the paper of Kruyt and J. T. G. Overbeek, *ibid.*, **36**, 110 (1940).

[15] J. W. McBain, C. R. Peaker and A. M. King, THIS JOURNAL, **51**, 3294 (1929); J. W. McBain and C. R. Peaker, *J. Phys. Chem.*, **34**, 1033 (1930); J. W. McBain and J. F. Foster, *ibid.*, **39**, 331 (1935); H. L. White, F. Urban and E. T. Krick, *ibid.*, **36**, 120 (1932); H. L. White, F. Urban and E. A. van Atta, *ibid.*, **36**, 3152 (1932); H. L. White, F. Urban and B. Monaghan, *ibid.*, **45**, 560 (1941); A. J. Rutgers, *Trans. Faraday Soc.*, **36**, 69 (1940); A. J. Rutgers, E. Verlende and M. Moorkens, *Proc. Koninkl. Akad. Wetenschappen Amsterdam*, **41**, 763 (1938).

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.

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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

BY LLOYD A. WOOD

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[1] 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[2] determined the streaming potentials of ordinary distilled water (specific conductance in bulk: 3.86×10^{-6} ohms^{-1} cm.$^{-1}$ 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 η 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[3] using the streaming potential method with Jena 16 III glass capillaries report several measurements with water of specific conductance 1.15×10^{-6} ohms^{-1} cm.$^{-1}$, giving values for ζ ranging from -64 to -80 mv. Lachs and Biczyk[4] 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[5] 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[1,6] 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-

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