A Proposed Interpretation of the ZetaPotential

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(33) with $\alpha=0$ are given in the last column of Table III. We conclude that either

(a) Dissociation is nearly complete or

(b) Dissociation is not complete, but the mobility of dissociated centers is much greater than that of undissociated centers.

As far as our results go, they are in complete accord with Wagner's. It is interesting to note that the numerical agreement between calculated and observed activities is obtained without introducing any empirical constants and without reference to any absolute values for diffusion coefficients or conductivities. The shape of the concentration curve is determined entirely by the mechanisms assumed for the oxidation reaction and for the self-diffusion of radioactive Cu^+.

A Proposed Interpretation of the Zeta-Potential

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(Received September 21, 1946)

The method used by Gurney and Fowler in explaining the interfacial potential at a metal-solution boundary is applied to the zeta-potential. This gives the ζ-potential as a straight line function of the logarithm of the concentration, in agreement with the shape of the curves as found experimentally. To obtain exact agreement between theory and experiment, it is proposed that the dielectric constant of the electrical double layer is about 0.6 that of the value for pure water. This assertion can be checked by accurate measurements on the surface conductance of solution of electrolytes.

INTRODUCTION

A SATISFACTORY theory correlating the zeta-potential with the concentration of the electrolyte in an aqueous solution has not been devised. Most of the recent attempts at constructing a theory[1] have been used on the idea of the Gouy double layer. The mathematical treatment utilizes solutions of the Poisson-Boltzmann equation

$$\nabla^2\psi = -\frac{4\pi\epsilon}{D}\sum_{i=1}^{s} n_i z_i \exp\left(-\frac{z_i\epsilon\psi}{kT}\right), \qquad (1)$$

with special boundary conditions. Insufficient and unreliable experimental information has been largely responsible for the failure of most of the attempts. Below, attention is called to a method which is believed to be more fruitful than previous approaches to the problem. Improvements and modifications of this method, in the light of additional experimental information, will probably yield an adequate theory. The method employed here has been used by Gurney[2] and Fowler[3] in explaining the metallic electrode potential, and by Dole[4] in explaining the glass electrode potential.

Recently significant gains have been made in regard to the experimental knowledge concerning the potential existing at the interface between vitreous silica and aqueous solutions of electrolytes. Hitherto there has been no agreement among the various experimenters[5] in this

[1] G. Gouy, J. Phys. [4], **9**, 457 (1910); D. L. Chapman, Phil. Mag. **25**, 475 (1913); O. Stern, Z. Electrochem. **30**, 508 (1924); A. March, Trans. Faraday Soc. **31**, 1468 (1935); A. J. Rutgers and Ed. Verlende, Proc. Kon. Akad. v. Wetensch. Amsterdam **42**, 71 (1939).

[2] R. W. Gurney, Proc. Roy. Soc. **A134**, 137 (1931); **A136**, 378 (1932); R. W. Gurney, *Ions in Solution* (Cambridge University Press, Cambridge, 1936), pp. 85–88.

[3] R. H. Fowler, Proc. Roy. Soc. **A136**, 391 (1932); Trans. Faraday Soc. **28**, 368 (1932).

[4] M. Dole, J. Chem. Phys. **2**, 862 (1934); M. Dole, *Experimental and Theoretical Electrochemistry* (McGraw-Hill Book Company, Inc., New York, 1935), pp. 512–515; M. Dole, *The Glass Electrode* (John Wiley and Sons, New York, 1941), pp. 261–276.

[5] H. Lach and J. Kronman, Bull. Int. de L'Acad. Polonaise d. Sci. d. Let. [A], Sci. Math. 289 (1925); H. Freundlich and G. Ettish, Zeits. f. physik. Chemie **116**, 401 (1925); H. R. Kruyt and van der Willigen, Kolloid Zeits. **45**, 307 (1928); Furutani, Kurokochi, and Asoda, Jap. J. Gastroent. **2**, 148 (1930); H. Lachs and J. Biczyk, Zeits. f. physik. Chemie **A148**, 441 (1930); R. duBois and

field, and the reliability of much of the data is open to question. Many experimenters have not characterized their methods and instruments adequately, and, therefore, a valid evaluation of their results is difficult. A hopeful indication that reliable information has been obtained concerning these potentials is furnished in the work of Rutgers and deSmet[6] at Ghent (Belgium) and Jones, Wood, and Robinson[7] at Harvard. This is perhaps the first time that systematic agreement has been obtained by different investigators, using different experimental techniques. Rutgers and deSmet, using the method of electro-endosmosis, studied the ζ-potential of solutions of metallic nitrates in contact with Jena 16 III glass, whereas the Harvard experimenters studied solutions of metallic chlorides in contact with quartz. The latter group used the streaming potential method. It is remarkable that the results were practically identical.

An interesting regularity was observed in both sets of data. Instead of the curves passing through maxima, as shown in most textbooks,[8] the potentials decreased in a more or less linear fashion with the logarithm of the concentration. Both groups of workers found out that thorium salts did not fit the general behavior pattern. Hydrolysis and other effects with thorium salts give their solutions properties not common to the other electrolytes. In developing a theory, one must look for a method of making the zeta-potential a straight-line function of the concentration.

METHOD OF GURNEY AND FOWLER

The assumptions used in this discussion are not entirely those used by Gurney, and the mathematical description is largely that employed by Fowler. Ions in solution are assumed to be affected by electrostatic and thermal forces, whereas the ions adsorbed at the surface are acted upon by specific adsorption forces in addition to the aforementioned types. This concept has been used before by A. March,[9] among others. Let U_m be the lowest energy level of anions adsorbed on the silica surface; it is assumed that the phase boundary is impervious to cations to the extent that no cations are adsorbed on the quartz surface. Let U_a be the lowest energy level of anions in the bulk of solution i.e., energy of the anions without thermal motion. The corresponding energy for cations is U_c but is uninteresting at the moment. The anions are able to make transitions from equilibrium positions in solution to equilibrium positions on the surface of vitreous silica. At the same time anions already deposited on the surface, having high enough energies, are able to make reverse transitions and resume equilibrium positions near water molecules. When kinetic equilibrium is established, the number of ions depositing on the surface is equal to the number leaving the surface dissolving in solution (per unit time). It is assumed that the Boltzmann distribution prevails both in solution and on the quartz surface.

The problem to be discussed is that of the equilibrium between anions in solution and on the vitreous silica surface. The anions in solution are not entirely free but are bound to water molecules or to groups of water molecules. The partition function for the anions in solution is

$$Q_{\text{solution}} = Ww(T) \sum_{i=0}^{\infty} p_i \exp\left[-U_i/kT\right], \quad (2)$$

where W represents the number of water molecules available for each anion and $w(T)$ represents the partition function for each water molecule. p_i is the statistical weight of each state of energy U_i; it is quite likely that the perturbation resulting from interacting levels makes each p_i equal to unity. In the absence of any interfacial potential ζ, the partition function for an anion on the vitreous silica surface would be

$$Q_{\text{silica}}(\zeta=0) = \sum_{j=0}^{\infty} p_j \exp\left[-U_j/kT\right], \quad (3)$$

A. H. Roberts, J. Phys. Chem. 40, 543 (1936); A. J. Rutgers, Ed. Verlende, and M. Moorkens, Proc. K. Ned. Akad. Wetensch. Amsterdam 41, 763 (1938); A. J. Rutgers, Trans. Faraday Soc. 36, 69 (1940).

[6] A. J. Rutgers and M. deSmet, Trans. Faraday Soc. 41, 768 (1945).

[7] G. Jones and L. A. Wood, J. Chem. Phys. 13, 106 (1945); L. A. Wood and L. B. Robinson, J. Chem. Phys. 14, 251 (1946); L. B. Robinson, Ph.D. Thesis, Harvard University, Cambridge 38, Mass., May 1946, p. 125 and p. 162.

[8] H. A. Abramson, *Electrokinetic Phenomena* (Chemical Catalogue Co., 1934), p. 203; S. Glasstone, *Text-Book of Physical Chemistry* (D. Van Nostrand, 1940), p. 1201; S. Glasstone, *Introduction to Electrochemistry* (D. Van Nostrand, 1942), p. 534.

[9] A. March, Trans. Faraday Soc. 31, 1468 (1935).

where the symbols have the same meaning as before. The existence of an interfacial potential ζ shifts each energy level by an amount $z\epsilon\zeta$ with respect to the condition given in (3). Consequently the correct partition function for the ions on the surface is

$$Q_{\text{silica}} = \sum_{j=0}^{\infty} p_j \exp\left[-(U_j + z\epsilon\zeta)/kT\right]. \quad (4)$$

The assumption is also made that the specific adsorption forces holding the ions on the surface are of the same nature as those which hold the units of the vitreous state. Evidence shows that the forces existing between particles in the vitreous state are similar to those which exist in the crystalline state. Hence the adsorbed ions may be treated as units of a crystal; the problem is now the same as that of a metallic crystal and its ions in solution. The additional assumption is made that the number of adsorbed anions, on the surface of the silica, is a constant independent of the concentration of the solution (in the limited concentration range in question), i.e. the adsorbed ions are fixed to a finite number of adsorbing centers. Gurney, Fowler, and Dole with their models, assumed that the probability of a transition from the surface to the solution depended only on the number of water molecules in the vicinity of the surface. Here the additional assumption is used that the number of transitions in a given time depends also on the number of adsorbed ions. This, however, is a constant and contributes nothing to the form of the partition function.

Fowler[10] shows that the equilibrium condition in terms of the partition functions is

$$n = W\frac{Q_{\text{solution}}}{Q_{\text{silica}}}. \quad (5)$$

Equation (2) may be written as

$$Q_{\text{solution}} = Ww(T)(p_0 \exp\left[-U_0/kT\right] + p_1 \exp\left[-U_1/kT\right] + \cdots). \quad (6)$$

This may be rewritten as

$$Q_{\text{solution}} = Ww(T)p_0 \exp\left[-U_0/kT\right]$$
$$\times (1 + p_1/p_0 \exp\left[-(U_1 - U_0)/kT\right] + \cdots). \quad (7)$$

[10] R. H. Fowler, *Statistical Mechanics* (Cambridge University Press, Cambridge, 1929), p. 117.

Another way of writing (7) is

$$Q_{\text{solution}} = Q'(T) \exp\left[-U_a/kT\right], \quad (8)$$

where $U_0 = U_a$ and $Q'(T)$ contains the rest of the expression. Likewise (4) may be written

$$Q_{\text{silica}} = Q''(T) \exp\left[-(U_m + z\epsilon\zeta)/kT\right]. \quad (9)$$

Rewriting (5), one obtains

$$\frac{n}{W} = \frac{Q'(T) \exp(-U_a/kT)}{Q''(T) \exp\left[-(U_m + z\epsilon\zeta)/kT\right]}, \quad (10)$$

where n/W is, for all practical purposes, the concentration of the anions in solution.

From (10), it is immediate that

$$kT\left\{\ln c - \ln \frac{Q'(T)}{Q''(T)}\right\} = z\epsilon\zeta + (U_m - U_a). \quad (11)$$

Equation (11) is derived by assuming that each water molecule is available as a potential equilibrium position for an adsorbed anion. However, each anion in solution puts out of action, say q water molecules, and, consequently, the number of water molecules available as equilibrium positions is $(W - qn)$, and (11) takes a more rigorous form and becomes

$$\zeta = \frac{\bar{U}_a - \bar{U}_m}{zF} + \frac{RT}{zF} \ln\left\{\frac{c}{1 - qc}\frac{Q'(T)}{Q''(T)}\right\}, \quad (12)$$

where $\bar{U}_a$ and $\bar{U}_m$ are molar quantities instead of the molecular quantities in (11); R is the molar gas constant, and F is the Faraday constant. For this type of model, Fowler suggests that $Q'(T)/Q''(T)$ is very nearly unity, but need not be for a more general model. Consequently a simplification of (12) yields the approximate formula for the ζ-potential

$$\zeta = \frac{\bar{U}_a - \bar{U}_m}{zF} + \frac{RT}{zF} \ln c. \quad (13)$$

COMPARISON WITH EXPERIMENT

In calculating the zeta-potential from streaming potential data, one uses the formula,

$$\zeta = (4\pi\eta/D)(\kappa E/P), \quad (14)$$

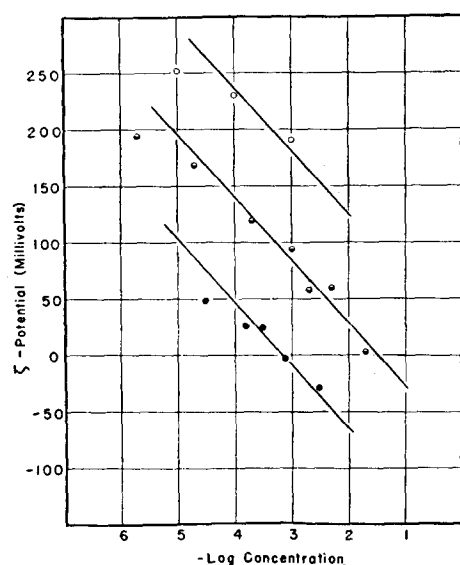and from electro-endosmosis,

$$\zeta = (4\pi\eta/D)(l/E), \quad (15)$$

FIG. 1. The newly defined zeta-potential (1.7 times the conventional values) *versus* concentration. The ·points represent the data of Jones, Wood, and Robinson; the solid lines give the slope of the lines in the proposed theory. Potassium chloride, ○; barium chloride, ◐; lanthanum chloride, ●.

where D is the dielectric constant of the electric double layer, η is the viscosity coefficient of the liquid in the double layer, κ is the specific conductance of the solution in the capillary tube, l is the length of the capillary, P is the pressure, and E is the measured potential. In both cases all of the quantities are measured except η and D. These are, in general, taken as the same as for pure water. Some authors[11] have pointed out that this assumption may be in error, especially in connection with the dielectric constant. Consequently, the values of the zeta-potential (Helmholtz-Perrin) as calculated are probably erroneous because of the uncertainty in the value of the dielectric constant. Thus, exact agreement between this theory and the data of Jones, Wood, Robinson, Rutgers, and deSmet is not expected. The dipole moment per unit area of the electrical double layer is the quantity actually measured by the experiments, and further assumptions must be made in order to convert the moment

into potential. However, one should expect the slopes of the lines representing the experimental data to be the same for the various salts. Such was actually observed for most of the salts.

A formula similar to (13) was proposed by Rutgers and deSmet in which C referred to the concentration of the *cation*, in contrast to the C of (11) and (13) in this article which refers to the *anion* concentration. Their data, with divalent cations, was practically the same as that reported by Wood and Robinson.[7] The factor 2.303 RT/zF gives a slope of 29 mv for the $\zeta - \log C$ curve in agreement with both groups of investigators. If C in (13) referred to the concentration of the cation, then one would expect the slope of the curve for the uni-univalent electrolytes to be greater than any of the others. Previously, Rutgers and Verlende[1] had derived the formula, and their last statement in the article is precisely: ". . . für 1–1, 2–1, 3–1, 4–1-wertige Elektrolyten sind die $\zeta - \log C$ Kurven also Geraden, deren Neigung bzw. 58, 29, 19.3 und 14.5 mV. beträgt." But the above assertion was not substantiated by either Rutgers and co-workers or Jones, Wood, and Robinson.

This writer believes that the slope of 29 mv (actually about 34 mv by Wood and Robinson) bears no relation to the factor 2.303 $RT/2F$. The theory proposed in this article makes the slope of each line about 58 mv. Therefore, it is proposed that the data should be multiplied by a factor of about 1.7. This proposal means that the dielectric constant (or the ratio of D to η) for the electric double layer is only 0.6 that of the value for pure water. This assertion could be tested experimentally by determining the number of ions at the surface (not adsorbed on the surface) from surface conductance measurements. Verification of the theory would result if the number of ions calculated in this manner would be about five times the number calculated from the Helmholtz-Perrin zeta-potential.

A graph is given of the newly defined zeta-potential (1.7 times the Helmholtz-Perrin zeta-potential) *versus* concentration (see Fig. 1). The value for water is greater than that of any of the salts.[12]

[11] H. B. Bull and R. A. Gortner, Physics 2, 21 (1932); J. W. McBain and M. E. L. McBain, Zeits. f. physik. Chemie 161, 279 (1932); E. A. Guggenheim, Trans. Faraday Soc. 36, 5 (1940); L. A. Wood, J. Am. Chem. Soc. 68, 432 (1946).

[12] L. A. Wood, J. Am. Chem. Soc. 68, 437 (1946).