

## The Theory of the Glass Electrode. III Statistical Explanation of the Alkaline Solution Behavior

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# The Theory of the Glass Electrode. III

## Statistical Explanation of the Alkaline Solution Behavior\*

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The application of Gurney's quantum and statistical mechanical theory of electrochemistry to the glass electrode results in an equation for the alkaline solution behavior identical with one previously obtained by the author except that the constants of the equation have a more reasonable significance. A qualitative explanation of the inability of negative ions to affect the glass electrode potentials is also given.

THE behavior of the glass electrode in alkaline solutions has been interpreted in a number of different ways by Hughes, Horovitz, Lengyel, Michaelis, Quittner, MacInnes and Belcher, Gross and Halpern and the author,<sup>1</sup> but as yet no physically satisfactory picture of the glass electrode has been presented. The first quantitative treatment of the glass electrode was that of the author<sup>2</sup> who applied liquid junction theory equations to the glass electrode and obtained the following equation

$$\Delta E = \frac{RT}{F} \ln \left\{ \frac{(u_{\text{Na}}/u_{\text{H}})c_{\text{Na}} + c_{\text{H}}}{c_{\text{H}}} \right\}, \quad (1)$$

where  $\Delta E$  is the error of the glass electrode,  $u_{\text{Na}}$ ,  $u_{\text{H}}$ ,  $c_{\text{Na}}$  and  $c_{\text{H}}$  the mobilities and concentrations of the sodium and hydrogen ions, respectively. Eq. (1) agreed with the data provided a suitable choice of the constants  $u_{\text{Na}}$  and  $u_{\text{H}}$  was made; but the assumptions made in the derivation of Eq. (1) namely, that the hydrogen ion has a mobility  $10^{11}$  times that of any other ion and that negative ions have zero mobility in the liquid junction could not be defended in any reasonable way on the basis of liquid junction theory. Statistical mechanics, however, seems to

offer a more satisfactory explanation of the glass electrode behavior. Gurney<sup>3</sup> has developed a quantum and statistical mechanical theory of electrochemistry which gives a new viewpoint with which to picture electrode mechanisms. This theory, which will not be described here, has been applied by Gurney to resolve the Volta potential difference controversy, to derive equations for interface and electrode potentials, to explain overvoltage and in some unpublished work to describe the plating out of alloys. Since the plating out of alloys consists in the deposition of two kinds of ions, Gurney's mathematical treatment for alloys is particularly applicable to the glass electrode where we have in alkaline solutions two kinds of ions affecting the observed e.m.f. The following theoretical treatment of the glass electrode is based on Gurney's mathematical theory of the plating out of alloys. Because the two mathematical treatments are similar, one must not infer that we conceive glasses to be similar physically to alloys. In alloys the positive ions maintain fixed positions while the negatively charged electrons are mobile and carry the electrical current. In glasses on the contrary, it is the negative silicate ions that are fixed, the electrical conduction being due to the positive ions. To apply Gurney's theory to the glass electrode it is only necessary to assume that the positive ions in the glass occupy positions of equilibrium and that the distribution of ions in the different energy levels of these equilibrium positions follows the Boltzmann distribution law.

\* Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at Chicago, September, 1933.

<sup>1</sup> See the author's first paper, *J. Am. Chem. Soc.* **53**, 4260 (1931) for bibliography up to 1931. More recent papers are Buchböck, *Zeits. f. physik. Chemie* **A156**, 232 (1931); MacInnes and Belcher, *J. Am. Chem. Soc.* **53**, 3315 (1931); S. I. Ssokolov and A. H. Passynsky, *Zeits. f. physik. Chemie* **A160**, 366 (1932); M. Dole, *J. Am. Chem. Soc.* **54**, 3095 (1932); P. Gross and O. Halpern, *J. Chem. Phys.* **2**, 136 (1934).

<sup>2</sup> M. Dole, *J. Am. Chem. Soc.* **53**, 4260 (1931).

<sup>3</sup> R. W. Gurney, *Proc. Roy. Soc.* **A136**, 378 (1932); **A134**, 137 (1931).

## APPLICATION OF GURNEY'S THEORY TO THE GLASS ELECTRODE

The hydrogen electrode function of glass may be explained according to statistical mechanics by imagining the hydrogen ion making transitions from its position of equilibrium in the neighborhood of a water molecule in the solution to a position of equilibrium on the surface of the glass; this latter position of equilibrium being at a level of equal or lower potential energy than the level in the solution. While some hydrogen ions are depositing on the glass, i.e., making  $d$ -transitions, other hydrogen ions on the surface of the glass having high enough energies will be dissolving, i.e., making  $s$ -transitions. At equilibrium the number of  $s$ -transitions must equal the number of  $d$ -transitions, and to obtain an equation for the interfacial potential it is only necessary to write down the number of  $s$ - and  $d$ -transitions and equate the two quantities. Let  $U_{\text{H}}^{\text{os}}$  be the energy of the lowest quantum level of the hydrogen ion on the glass surface,  $U_{\text{H}}^{\text{os}}$  the energy of the lowest quantum level of the hydrogen ion in the aqueous solution,  $U_{\text{Na}}^{\text{os}}$  and  $U_{\text{Na}}^{\text{os}}$  similar quantities for the sodium ion. We shall now suppose that owing to the interaction of neighboring molecules all energies above the ground level are possible vibration levels, in other words, all values of  $U$  between  $U^{\circ}$  and infinity are possible. We shall also assume that the distribution of the surface ions in their vibration levels is given by the Boltzmann law.

We shall first calculate the number of  $s$ -transitions, or rather the number of  $s$ -situations which is the number of situations or configurations that gives rise to an  $s$ -transition. Of the total number of surface ions per unit area of the glass, a fraction

$$(1/kT) \exp \{(U_{\text{H}}^{\text{os}} - U)/kT\} dU \quad (2)$$

will have energies between  $U$  and  $U + dU$  providing no interfacial potential exists. If an interfacial potential  $V$  does exist, the energy levels of the ions on the glass surface will be shifted relatively to those of the solution by the amount  $\epsilon V$  where  $\epsilon$  is the unit positive charge. Taking the potential of the electrolyte as the zero of potential, expression (2) becomes

$$(1/kT) \exp \{(U_{\text{H}}^{\text{os}} + \epsilon V - U)/kT\} dU. \quad (3)$$

The number of  $s$ -situations will also be proportional to  $N_w$ , the number of water molecules in contact with unit area of surface,

$$(N_w/kT) \exp \{(U_{\text{H}}^{\text{os}} + \epsilon V - U)/kT\} dU. \quad (4)$$

However, part of the surface may be covered by sodium ions; this has the effect of diminishing the number of  $s$ -situations for the hydrogen ion. If we let  $\gamma$  represent the fraction of unit surface covered by hydrogen ions the number of  $s$ -situations now is

$$\gamma(N_w/kT) \exp \{(U_{\text{H}}^{\text{os}} + \epsilon V - U)/kT\} dU. \quad (5a)$$

Similarly, the number of  $s$ -situations for the sodium ions is

$$(1 - \gamma)(N_w/kT) \exp \{(U_{\text{Na}}^{\text{os}} + \epsilon V - U)/kT\} dU. \quad (5b)$$

Up to this point we have assumed that the sodium and hydrogen ions can occupy the same number of lattice points on the surface of the glass; that is, we have assumed that a sodium ion can occupy any point occupied by a hydrogen ion and *vice versa*. But it is unnecessary to make this assumption. Let  $a$  equal the number of lattice points per unit surface which the hydrogen ion can occupy, then  $a\gamma$  is the fraction of total possible lattice points occupied by hydrogen ions. The number of lattice points not occupied by hydrogen ions is equal to  $a - \gamma a$  and of these we shall suppose that the sodium ions can occupy a fraction  $\delta$ ;  $(a - \gamma a)\delta$  being the actual number of lattice points per unit surface occupied by the sodium ion. The quantity  $\delta$  is independent of the concentration of the solution, but  $\gamma$  varies with the concentration. Eqs. (5a) and (5b) now become

$$a\gamma(N_w/kT) \exp \{(U_{\text{H}}^{\text{os}} + \epsilon V - U)/kT\} dU, \quad (6a)$$

$$\text{and } (a - \gamma a)\delta(N_w/kT) \exp \{(U_{\text{Na}}^{\text{os}} + \epsilon V - U)/kT\} dU. \quad (6b)$$

The number of  $d$ -situations depends upon the number of ions in the solution  $N_{\text{H}}$  or  $N_{\text{Na}}$ , upon the energy of the ions and upon the number of lattice points on the glass surface that the ions can occupy; thus for the hydrogen and sodium ions we have

$$a(N_H/kT) \exp \{(U_H^{os} - U)/kT\} dU \quad (7a)$$

$$\text{and } a\delta(N_{Na}/kT) \exp \{(U_{Na}^{os} - U)/kT\} dU. \quad (7b)$$

It will be noticed that this treatment assumes that an ion can deposit on any of the possible lattice points whether or not the lattice point is already occupied. At equilibrium the number of  $s$ -situations multiplied by the probability of an  $s$ -transition must be equal to the number of  $d$ -situations multiplied by the probability of a  $d$ -transition. If the ratio of the latter probability to that of the former be  $\beta$ , then

$$a\gamma(N_w/kT) \exp \{(U_H^{oo} + \epsilon V - U)/kT\} dU \\ = \beta_H a(N_H/kT) \exp \{(U_H^{os} - U)/kT\} dU, \quad (8a)$$

$$(a - \gamma a)\delta(N_w/kT) \exp \{(U_{Na}^{oo} + \epsilon V - U)/kT\} dU \\ = \beta_{Na} a\delta(N_{Na}/kT) \exp \{(U_{Na}^{os} - U)/kT\} dU. \quad (8b)$$

Letting  $Q_H$  equal  $(U_H^{os} - U_H^{oo})$  and  $Q_{Na}$  equal  $(U_{Na}^{os} - U_{Na}^{oo})$  and setting  $N_H/N_w$  and  $N_{Na}/N_w$  equal to  $c_H$  and  $c_{Na}$ , respectively, Eqs. (8a) and (8b) become

$$\gamma = c_H \beta_H \exp (Q_H - \epsilon V)/kT, \quad (9a)$$

$$1 - \gamma = c_{Na} \beta_{Na} \exp (Q_{Na} - \epsilon V)/kT. \quad (9b)$$

The quantity  $\gamma$  is easily eliminated from Eqs. (9a) and (b) by addition; we obtain

$$c_H \beta_H \exp (Q_H - \epsilon V)/kT + c_{Na} \beta_{Na} \exp (Q_{Na} - \epsilon V)/kT = 1. \quad (10)$$

If there were no sodium ions present in the solution, the potential would depend solely on the concentration of hydrogen ions; from Eq. (10) we have, on setting  $c_{Na}$  equal to zero

$$V_0 = Q_H/\epsilon + (kT/\epsilon) \ln c_H \beta_H. \quad (11)$$

Eq. (11) is the usual hydrogen electrode potential equation since  $\beta_H$  is a factor of the order of magnitude of unity. The author originally defined the error of the glass electrode as being equal to  $V - V_0$ . This quantity may be obtained by dividing Eq. (10) (first putting it in its exponential form) by Eq. (11) and rearranging, the result being

$$V - V_0 = (kT/\epsilon) \ln [(\beta_{Na}/\beta_H) c_{Na} \exp \{(Q_{Na} - Q_H)/kT\} + c_H]/c_H. \quad (12)$$

It is interesting to compare Eq. (12) with the previously derived Eq. (1). They are identical except that the constant factor multiplying the sodium ion concentration term has a different meaning in the two cases.

#### RESOLUTION OF THE GLASS ELECTRODE PROBLEMS

This statistical treatment of the glass electrode immediately obviates the necessity of making any assumptions concerning the mobility of the hydrogen and sodium ions. Gurney's theory also provides us with a plausible explanation of the negligible effect of negative ions upon the glass electrode potentials. According to Zachariasen,<sup>4</sup> glass consists of a network of oxygen tetrahedra which surrounds the silicon atoms. The holes which necessarily exist in this framework are bounded by oxygen atoms or perhaps we should say by negative oxygen ions and offer excellent positions for positive ions. However, it is obvious that large repulsive forces would come into play if the attempt is made to introduce negative ions into these holes. Negative ions are also generally larger than positive ions which is another reason why it would be difficult to deposit negative ions on the glass surface. If we plot the potential energy of a negative ion as a function of distance along a line perpendicular to the glass surface, a figure similar to Fig. 1 would probably be obtained. By an inspection of Fig. 1 it is readily seen that negative ions in solution cannot make transitions to the glass surface because they do not have sufficiently high energies. Thus negative ions have no effect upon the glass electrode potentials, not because they have zero mobility, but because the energy relationships are not favorable.

From the experimental data it is possible to calculate that the order of magnitude of the constant which multiplies the concentration of the sodium ion in Eq. (1) is  $10^{-11}$ , a figure which is not easily explained by the liquid junction theory.<sup>5</sup> This difficulty is fortunately considerably minimized if not entirely overcome by the statistical mechanical theory. Referring to Eq.

<sup>4</sup> W. H. Zachariasen, J. Am. Chem. Soc. **54**, 3841 (1932).

<sup>5</sup> Particularly since it is probably the hydrated proton and not the proton which moves across the glass-aqueous solution boundary.

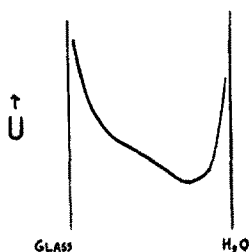


FIG. 1.

(12) it can be readily seen that the magnitude of the constant depends upon the magnitude of the term

$$\exp (Q_{\text{Na}} - Q_{\text{H}}) / kT, \quad (13)$$

since  $\beta_{\text{Na}}/\beta_{\text{H}}$  is of the order of magnitude of unity. Calculation shows that expression (13) has the order of magnitude  $10^{-11}$  when  $Q_{\text{H}}$  is greater than  $Q_{\text{Na}}$  by 15,000 calories per mole, an entirely plausible result. If experimental values of  $Q_{\text{H}}$  and  $Q_{\text{Na}}$  were known, it would be possible to test Eq. (12) quantitatively.

The final difficulty which is a stumbling block in the former liquid junction theory is due to the observation that the constant of Eq. (1) varies with the pH of the solution. It is hard to see why the mobility across the boundary should vary with the concentration of the aqueous solution. But let us examine the corresponding quantity in Eq. (12). Instead of the ratio of the mobilities we have the expression (13) whose magnitude is quite sensitive to the exponent  $(Q_{\text{Na}} - Q_{\text{H}}) / kT$ . If the glass were a metal, all ions of one kind on the metal surface would have the same value of  $U^0$ , but we would not expect this to be true for glass. Glasses in contrast to metals do not melt sharply but gradually soften over a range of temperature which indicates that ions in the glass do not have identical energies. To quote Zachariasen, "Since all atoms in glass are structurally unequivalent, the energy required to detach an atom from the net-work will be different for each individual atom." In acid solution the glass surface will be covered with hydrogen ions to the exclusion of sodium ions, but as the alkalinity of the solution increases some of the hydrogen ions will leave the glass surface; their places being taken by sodium ions. In all probability the remaining hydrogen ions will not have the same value of  $U_{\text{H}}^{00}$ . A small change in  $U_{\text{H}}^{00}$

or in  $U_{\text{Na}}^{00}$  would be sufficient to produce an appreciable change in the constant term of Eq. (12).

It should be emphasized, however, that until values of  $U_{\text{H}}^{00}$  and  $U_{\text{Na}}^{00}$  can be estimated this theory cannot be tested quantitatively.<sup>6</sup> Yet this new explanation seems to be much better than the former liquid junction theory.

#### CRITIQUE OF GROSS AND HALPERN'S THEORY

Gross and Halpern have recently interpreted the author's experimental data by assuming that glass may be treated as a difficultly soluble salt which forms with water a saturated solution and that the water dissolves in the glass until the glass becomes saturated with the water. They also assume that the mass action law holds for such strong electrolytes as sodium hydroxide and sodium acetate both in the water and glass phases, that water, glass, acids, bases, etc., distribute themselves between the glass and aqueous phases in accordance with the well-known distribution law and that the activity coefficients of all ions are the same. For alkaline solutions their equation reduces to

$$\Delta E = (RT/2F) \ln (1 + c_{\text{Na}}^0 / c_{\text{H}}^0), \quad (14)$$

where  $c^0$  represents the ionic concentration in the glass. By assuming the validity of the distribution laws mentioned above it is possible to rearrange Eq. (14) into the form of Eq. (1) except that the factor  $RT/F$  of Eq. (1) is replaced by the factor  $RT/2F$ . For acid solutions Gross and Halpern succeed in deriving an equation identical with the acid solution equation previously derived by the author<sup>7</sup> with the exception that once again their equation contains the factor  $RT/2F$  instead of the author's factor  $RT/F$ . Gross and Halpern claim that their equations agree with the author's data better than do the author's equations. Let us consider the acid solution data first. Gross and Halpern tested their Eq. (12) solely with the errors of the glass

<sup>6</sup> Eq. (12) may be tested quantitatively by measuring the temperature coefficient of  $V - V_0$ . Since the temperature appears in the exponential term multiplying the constant, the value of the glass electrode error should vary definitely with variation of temperature, the magnitude of the variation being quantitatively predicted by Eq. (12). Measurements of the temperature coefficient of the glass electrode are now in progress.

<sup>7</sup> M. Dole, J. Am. Chem. Soc. **54**, 3095 (1932).

electrode obtained in the ethanol solutions up to 66 percent ethanol and found slightly better agreement with their equation than with the author's. As a matter of fact, the alcohol experiments were not as accurate as the experiments, for example, measuring the error of the glass electrode in 4.4*N* lithium chloride. Over twenty measurements of the error of the glass electrode in 4.4*N* lithium chloride were obtained; one experiment yielded the following values of  $\Delta E$  over the pH range 4.600 to 0.308, 5.1, 5.1, 7.4, 6.5, 9.3, 8.7, 7.6, 7.4, 7.2, 6.9, 7.2, 7.5 mv. From these and other data the best value of the error in 4.4*N* lithium chloride was taken as 6.7 mv. The error theoretically calculated by the author's equation is 7.0 mv. while Gross and Halpern's equation gives 3.5 mv. Gross and Halpern limited the test of their Eq. (12) to solutions having a water activity of 0.79 or greater. The activity of the water in 4.4*N* lithium chloride is 0.77. The experimental data for solutions in which the activity of the water is less than 0.77 also agree better with the author's equation than with the equation of Gross and Halpern.

Gross and Halpern's equation for the high pH range does not agree with the data as well as the author's unless the slope of the function is fixed at unity. This fact is made clear by reference to Fig. 2 where Gross and Halpern's function  $\log [(\exp 2F\Delta E/RT) - 1]$  and the author's function  $\log [(\exp F\Delta E/RT) - 1]$  are plotted against the pH. If one draws a straight line through the lowest three points in each case, the values of the functions at the higher pH values deviate farther from the straight line in the case of Gross and Halpern's function than in the case of the author's. However, if comparison is made with a line drawn with unit slope as demanded by former theory, dotted line of Fig. 2, it is evident that Gross and Halpern's function is superior, yet far from perfect. Fortunately the statistical

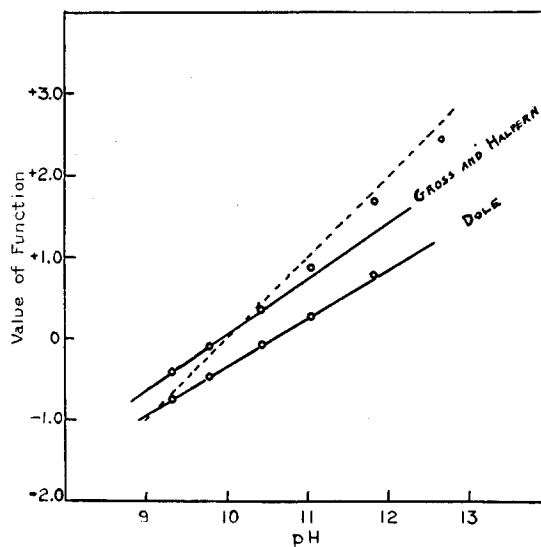


FIG. 2.

mechanical theory of the glass electrode does not demand a unit slope of the curves of Fig. 2.

Gross and Halpern's theory fails to give any explanation of the inability of negative ions to affect the glass electrode. Our new theory is decidedly superior in this respect.<sup>8</sup>

In conclusion the author wishes to acknowledge the kindness of Dr. R. W. Gurney in making available his unpublished treatment of the plating out of alloys and in discussing with the author the problems of the glass electrode.

<sup>8</sup> An interesting paper by Lengyel and Blum has recently appeared (Trans. Faraday Soc. 30, 461 (1934)). They point out the significant relation between glass electrode behavior and composition of the glass. The ability of the glass electrode to act as a sodium electrode for certain types of glasses may be explained on the basis of our statistical theory by assuming that  $Q_H - Q_{Na}$  has a negative or very small positive value. The  $Q$  values of this paper are not, however, the same as the  $Q$  values calculated by Lengyel and Blum. The latter represent the "heat of liberation" of the sodium ion in the glass whereas the author's  $Q$  values may be considered as being the difference between "the heat of liberation" in the aqueous solution and on the glass surface.