On the Alkaline Error of the Glass Electrode *

NILS LANDQVIST

Rydboholms A.B., Rydboholm, Sweden

A theoretical treatment is given to the glass electrode alkaline behaviour, considering the influence of the state of adsorption on the adsorption energies. By expanding in series and approximating, the equation deduced has been transformed into earlier known, empirical expressions. Experimental results confirm the theoretical treatment. Finally a differential measuring method has been described, to be applied for correcting the alkaline error in glass electrode measurements when the activity of the sodium ion (or other) is unknown, comprising the use of two glass electrodes of different, but known, alkaline error functions.

Since Hughes¹ discovered the alkaline error of glass electrodes in 1922, several theories have been applied to the quantitative treatment of the difference between hydrogen and glass electrode behaviour. Important contributions in this field have been made by Dole *et al.*²⁻⁷, and also by Nicolsky⁸, Gross and Halpern⁹ and Tendeloo and Voorspuij^{10, 11}. For a more general review of the different theories, reference may be made to Kratz¹².

The theories of Dole and of Nicolsky give the same final equation, which can be written:

$$\log[\exp(F\Delta E/RT) - 1] = \text{pH} + \log C_{\text{Na}^+} + \text{constant} \quad (1)$$

(ΔE is the alkaline error, pH and C_{Na^+} refer to the solution surrounding the glass electrode.) If $\log[\exp(F\Delta E/RT) - 1]$ is plotted as a function of pH from experimental data, the linear agreement is good, except that the slopes of the lines are not unity, as demanded by eq. (1). Thus, for an electrode made of Corning 015 glass, a slope of 0.57 for 1 M Na⁺ at 25° C was found by Dole¹³. (It was also stated in the same paper that no quantitative explanation of the deviation of the slope from unity had been advanced at that time.)

The validity of the Gross and Halpern treatment has been discussed and criticised by Dole⁷, who concludes that their final equation is not as good as eq. (1) for explaining glass electrode behaviour in alkaline solutions.

* This paper is based on a lecture given by the author at the 8:th Congress of Scandinavian Chemists in Oslo, June 14—17, 1953.

The treatment by Tendeloo and Voorspuij gives the equation:

$$\log [\exp (F\Delta E/RT)-1] = \text{pH} + \log [(1 + K_2' \cdot C_{\text{Na}^+})/K_1'] \quad (2)$$

(ΔE is the alkaline error, pH and C_{Na^+} refer to the surrounding solution, K_1' and K_2' are electrode constants.) The equation is very similar to eq. (1), and for ordinary glass electrodes it fails as does eq. (1) in predicting a slope of unity. However, these authors used an electrode made of Al_2O_3 -containing glass with a very high alkaline error. At pH 11 and $C_{\text{Na}^+} = 0.1$ the error was about 50 times greater than that of an electrode made of Corning 015 glass. In this case eq. (2) is in good agreement with experimental results, but the lack of agreement occurs at low ΔE , which can be expected from the behaviour of said Corning 015 glass. This is also stated by the authors.

The basic ideas of the four different treatments referred to above, have been:

Dole: Ion exchange reactions take place between the glass electrode surface and the surrounding solution, and the equilibrium is treated mathematically by a statistical method used earlier by Gurney^{14,15} in studies on other electrode reactions.

Nicolovsky: The ion distribution on the glass surface and in the surrounding solution is treated by the law of mass action.

Gross and Halpern: "It is assumed that the electrode glass may be treated as a difficulty soluble salt, which forms with water a saturated solution, so that the water dissolves in the glass until the glass becomes saturated with water. It is also assumed that the mass action law holds for such strong electrolytes as sodium hydroxide and sodium acetate both in water and glass phases, that water, glass, acids, bases *etc.* distribute themselves between the glass and the aqueous phase in accordance with the well-known distribution law, and that the activity coefficients of all ions are the same." (Dole⁷).

Tendeloo and Voorspuij: Dissociation equilibria between the swollen glass surface and the surrounding solution are controlled by real constants of dissociation for the silicic acid in that surface.

In the following discussion a refined treatment of the glass electrode alkaline error will be given, and the influence of the state of adsorption on the adsorption energies will also be considered. This has not been made in the treatments mentioned above.

The *physical model* used for the mathematical treatment is in accordance with the ideas of Tendeloo and Voorspuij¹¹, the SiO_4 -network of the electrode glass being regarded as containing three dimensional interstices, offering room for metal ions such as Na^+ and Ca^{2+} . When the electrode surface is brought in contact with water the network on the surface and to some depth into the glass will pass into a swollen state, the aforesaid metal ions will be dissolved to a great extent and replaced by H^+ or H_3O^+ ions. In this way the *surface layer* is substantially free from other cations, and consists of silicic acid. The silicic acid is then able to take part in ion exchange reactions, so that all states from complete H^+ saturation to a more or less mixed composition of H^+ and other cations are possible. Under these conditions it may be anticipated that the adsorption energies, *i.e.* the forces between adsorbed ions and the adsorption sites, will be dependent on the state of adsorption, so that the energy will not be the same if an adsorbed ion has identical or dissimilar ions as neighbours

Fig. 1. Apparatus for hydrogen and glass electrode measurements.

on the surrounding adsorption sites. This seems to be reasonable, as the degree of "energy saturation" of each adsorption site may influence the surrounding sites, with regard to their available adsorption forces. As we are dealing with a network, *i.e.* a kind of a large molecule, the state of the internal resonance energies can to some extent be compared with that of a polybasic acid. However, in the case of glass the effect is more complex, as the glass is a solid acid, where the electrical forces outside the molecule have a large influence on the activity of the adsorbed ions.

EXPERIMENTAL

In the experiments a glass apparatus, Fig. 1, was used, with spaces for four glass electrodes C, a reference electrode A, a hydrogen electrode B and a temperature compensator D, used when measurements were made with instruments having an automatic temperature compensation device. During the measurements the whole system was enclosed in a Faraday cage, and the temperature of the surrounding room, 25° C, controlled by means of a radiant heating device to within 0.1° C, with a temperature change less than 0.1° C per hour. When hydrogen electrodes are used in alkaline solutions, it is of greatest importance that the hydrogen should be of a very high purity. An amount of oxygen exceeding 300 μg per litre can give mixed hydrogen-hydrogen ion and oxygen-hydroxyl ion potentials, disturbing the response of the electrode. The cylinder hydrogen used in this work was purified in the following manner, which gave excellent results. The gas was passed through a tube of stainless steel, with a diameter of 20 millimeters, con-

taining one layer of cut copper wires, and another of platinum deposited on porcelain. The height of each layer was 300 millimeters. The tube was heated by a 1 000 watt heating coil, controlled by an energy regulating device to maintain the temperature of the catalyst at $650 \pm 25^\circ \text{C}$. The gas was in contact with the catalyst for about 5 minutes. It was then passed through a copper pipe for air cooling and bubbled through concentrated sulphuric acid and then through a solution of sodium hydroxide (400 g per litre). Before entering the hydrogen electrode, the gas was passed through a large quantity of thermostated distilled water, in order to avoid temperature changes at the electrode and to attain approximate equilibrium with the vapor pressure of the solution to be investigated. This eliminated changes in concentration, caused by evaporation from the electrode solution. The efficiency of the purification was examined from time to time. The purified hydrogen was bubbled through a small volume of 0.1 M KCl, and after one hour of bubbling the oxygen was determined polarographically. The amount of oxygen was always found to be less than a few μg per litre, which was below the limit for side reactions. Anodic polarographic investigations in 0.1 M Na_2HPO_4 gave no detectable wave of H_2S , arising from the sulphuric acid and not completely removed by the sodium hydroxide solution. From this it can be concluded that the amount of hydrogen sulphide was less than a few μg per litre of solution.

The hydrogen electrode B was designed as a triple electrode with three separate platinum wires for measuring the response of the electrode. In every pH measurement the three electrodes were measured individually several times, and the agreement of the three potentials had to be within the accuracy of the instruments used for the determination, before the measurements were accepted. Experience has shown that oxygen impurities, bad platinum plating and other electrode errors do not give identical potentials. The platinum plating was prepared by electrolysis, using a Pt anode, area 200 mm^2 , at a distance from the cathodes of 20–30 mm, in 20% PtCl_4 at 4 volts for 15 sec. and at a temperature of 20°C . The cathodes, i. e. the three platinum wires of the hydrogen electrode, were each 0.5 mm in diameter and 7 mm in length. The platinum deposit was renewed when necessary, but at least every day. The old deposit was carefully removed and the electrode cleaned by means of sodium chromate in sulphuric acid and rinsed in distilled water before replating. The reference electrode was a 0.1 M calomel electrode, this concentration being used as it has a low temperature coefficient and seems, with the electrode design used here to be practically free from variations in diffusion potentials. The electrode was similar to the type introduced by Perley¹⁶.

The apparatus was operated in the following manner: With the cocks 2 and 6 (without grease) and 5 open, the test solution, buffer I or II, was introduced into the apparatus to cover the electrodes. (The reference electrode has a little hole, not shown, to allow the air to escape.) After closing the cocks 2 and 6 and opening 1 and 4, the hydrogen bubbling was started. As the hydrogen electrode space has a small volume, the oxygen in the solution was removed and hydrogen saturation quickly obtained. The minimum time of bubbling was of the order 10–15 minutes. The glass electrode potentials were measured at 5 minute intervals over a period of 30 minutes, thus giving 6 different determinations on each solution. The solution around the glass electrodes was stirred continuously by means of the bubbling hydrogen, introduced by means of the pipe E. After 30 minutes the hydrogen electrode potential was determined, and during this measurement, cock 5 was closed, and all the three electrodes tested for coincidence. In order to investigate if any liquid junction potentials arise at the cocks 2 and 6, these cocks were opened and the potential difference determined. To change the pH of the solution, the cocks 1 and 5 were opened and the hydrogen electrode tube and that containing the reference electrode drained by means of cocks 2, 3 and 6. A desired amount of "contrabuffer" II or I was added to the solution around the glass electrodes, which was then stirred violently by means of the hydrogen, and by using the cocks 2, 3 and 6 the hydrogen and reference electrodes were rinsed several times, and finally as much solution removed as was necessary to maintain constant liquid level. The next measurements could then be made. Before and after each series of measurements the apparatus was filled with a control buffer and hydrogen and reference electrodes and asymmetry potential changes checked. As a rule identical values were found, but if this was not the case, the whole series of measurements were rejected and repeated after careful checking of the electrode system. The average accuracy was $\pm 0.25 \text{ mV}$.

The buffer solutions used were: I. 0.010 M Na₂PO₄ + 0.010 M Na₂CO₃ + 0.050 M NaOH + NaCl to C_{Na⁺} = 0.10, 0.50, 1.00, 2.00 and 4.00. II. The same as I, but with 10 ml per litre 10 M HCl added. Control buffer: 0.025 M KH₂PO₄ + 0.025 M Na₂HPO₄; pH 6.86.

The instruments used for the potential determinations were a Radiometer PHM 3g and two different Leeds & Northrup instruments as secondary controls.

Measurements were made on two commercial glass electrodes, one of type A, and one of another type B, using the method described above. The investigated ranges were: pH 9–11.5 and C_{Na^+} 0.10–4.00 at a temperature of 25°C. The electrodes A and B have different, but unknown glass composition. For calculations in accordance with the theory presented later in this paper, data obtained by Dole *et al.*^{2-7, 12} have also been used. The object of this has been to include still another composition of glass, and also to include the effect of different temperatures, 10, 25 and 50°C, and of different ions, Na⁺ and Li⁺. (As the other ions investigated by Dole give a very low alkaline error, the accuracy is not sufficient for these calculations. Hence only the Na⁺ and Li⁺ results have been examined.)

In the present paper, the electrode used by Dole has been denoted by C. Figures for Na^+ at 25°C from the manufacturers' bulletins concerning two different electrodes D and E, having a very low alkaline error, were also used as a basis for mathematical calculations. In this case the data are of doubtful value, as nothing is known of the measuring technique and accuracy, the test solution composition and the activity changes at high pH values. The assumption has been made that NaCl was present in the solution and that the amount of buffer was low. The values have been included since they do give some additional indication of the low alkaline error electrode behaviour.

For the electrodes mentioned above, two functions have been plotted for all of them from experimental data, to be used in the theoretical treatment, namely:

$$F(\Delta E'' - \Delta E')/2 RT = f(F\Delta E/RT) \quad (3)$$

$$F\Delta E/RT = g(M.pH + \ln a_{\text{Na}^+}) \quad (4)$$

In these functions ΔE is the alkaline error at an activity of hydrogen ions corresponding to pH and a sodium activity of a_{Na^+} . $\Delta E''$ is the alkaline error at a pH 0.25 units above the pH value at ΔE , and $\Delta E'$ is that at a pH 0.25 below. M is the logarithm conversion figure. In the case of eq. (4) the sodium ion activity has to be estimated. This is, of course, a difficult task. In the measurements made by the author, the buffer concentration was kept low and most of the sodium ions are due to NaCl. This gives a simpler solution from the point of view of activity calculations. In all cases the mean activity coefficient of the electrolyte has been applied to Na^+ , and has been taken from different papers¹⁷⁻¹⁹. However, even if the accuracy of the activity figures is moderate, they are to be preferred to the concentration figures used in other treatments. In Figs. 2-13 plots of the functions (3) and (4) are shown, and the mean curve from them will be used later for further calculations.

THEORETICAL

Applied to a system where ions are distributed between different phases, the Boltzmann energy distribution law can be written:

$${}_iC_j = \exp(-{}_i\varepsilon_j/RT) \quad (5)$$

where ${}_iC_j$ = concentration of an ion i in a phase j ; ${}_i\varepsilon_j$ = total energy for an ion i in a phase j . If considering the physical model, and eq. (5) is applied to one of the two glass electrode surfaces, *i.e.* to the system solution — surface layer, then:

$${}_iC_s = \exp(-{}_i\varepsilon_s/RT) \quad (5a)$$

$${}_iC_g = \exp(-{}_i\varepsilon_g/RT) \quad (5b)$$

$${}_iC_g = {}_iC_s \cdot \exp[-({}_i\varepsilon_g - {}_i\varepsilon_s)/RT] \quad (6)$$

where: ${}_iC_s$ = concentration in the solution of an ion i , ${}_iC_g$ = concentration of an ion i in the *surface layer* of the glass, defined in accordance with the *physical model*, ${}_i\varepsilon_s$ = total energy in the solution for an ion i , ${}_i\varepsilon_g$ = total energy in the surface layer for an ion i .

Let: ${}_iU_s$ = equilibrium energy in the solution for an ion i , ${}_iU_g$ = equilibrium energy in the surface layer for an ion i .

Then:

$${}_i\varepsilon_s = {}_iU_s + \text{constant}$$

$${}_i\varepsilon_g = {}_iU_g + zFE + \text{constant}$$

where E is the difference in electrical potential between solution and surface layer, and z is the valency of i .

From this:

$${}_iC_g = {}_iC_s \cdot \exp [-({}_iU_g + zFE - {}_iU_s)/RT] \quad (6b)$$

As the logarithm of the activity coefficient gives the difference between actual and ideal energies in the solution, then if the ideal energy is written ${}_iU_{os}$:

$${}_iC_g = {}_ia_s \cdot \exp [-({}_iU_g + zFE - {}_iU_{os})/RT] \quad (7)$$

where ${}_ia_s$ is the activity of the ion in the solution.

If we define: ${}_iU_{os} - {}_iU_g = Q_i$
then

$$\Sigma {}_ia_s \cdot \exp [(Q_i - zFE)/RT] = \Sigma {}_iC_g \quad (8)$$

This can be regarded as the fundamental equation of the glass electrode.

In the following treatment we shall for simplicity select the ions H_3O^+ and Na^+ . In this case eq. (8) can be written:

$$E = \frac{RT}{F} \ln [a_{H_3O^+} \cdot \exp (Q_{H_3O^+}/RT) + a_{Na^+} \cdot \exp (Q_{Na^+}/RT)] - \frac{RT}{F} \ln \Sigma {}_iC_g \quad (9)$$

Let $X_i = {}_iC_g/\Sigma {}_iC_g$, and define $Q_i \rightarrow Q_{oi}$ ${}_iC_g \rightarrow {}_iC_{og}$ when $X_i \rightarrow 1$.
If $a_{Na^+} \cdot \exp (Q_{Na^+}/RT) \ll a_{H_3O^+} \cdot \exp (Q_{H_3O^+}/RT)$ eq. (9) can be written:

$$E' = Q_{oH_3O^+}/F - \frac{RT}{F} \ln \Sigma {}_iC_{og} - \frac{MRT}{F} pH \quad (10)$$

$$\text{Let } Q_{oH_3O^+}/F - \frac{RT}{F} \ln \Sigma {}_iC_{og} = e_o$$

$$\text{then } E' = e_o - \frac{MRT}{F} pH \quad (10a)$$

This is, except e_o , the equation for the hydrogen electrode. The differences in e_o for the two active surfaces of the glass electrode:

$$e_o'' - e_o' = \varphi \quad (11)$$

is an expression of the *asymmetry potential*, i.e. the deviation in E_o in comparison with the hydrogen electrode. If the electrode surfaces change their properties in different ways, this will cause a variation in φ . However, for short periods (of the order 100 hours) φ is a constant.

If it is not possible to neglect the Na^+ -term, and if we define:

$$\Delta E = E - E' \quad (12)$$

then, since

$$\begin{aligned} \Sigma {}_iC_g/\Sigma {}_iC_{og} &= X_{H_3O^+} + X_{Na^+} \\ (X_{H_3O^+} + X_{Na^+}) \cdot \exp [(Q_{oH_3O^+} - Q_{H_3O^+})/RT] \cdot \exp (F\Delta E/RT) &= \\ \frac{a_{Na^+}}{a_{H_3O^+}} \exp [(Q_{Na^+} - Q_{H_3O^+})/RT] + 1 & \end{aligned} \quad (13)$$

Applying the distribution law once more:

$$\frac{X_{\text{Na}^+}}{X_{\text{H}_3\text{O}^+}} = \frac{a_{\text{Na}^+}}{a_{\text{H}_3\text{O}^+}} \exp [(Q_{\text{Na}^+} - Q_{\text{H}_3\text{O}^+})/RT]$$

and
$$\frac{a_{\text{Na}^+}}{a_{\text{H}_3\text{O}^+}} \exp [(Q_{\text{Na}^+} - Q_{\text{H}_3\text{O}^+})/RT] + 1 = \frac{X_{\text{Na}^+} + X_{\text{H}_3\text{O}^+}}{X_{\text{H}_3\text{O}^+}}$$

Combining this with eq. (13) gives:

$$F \cdot \Delta E/RT = (Q_{\text{H}_3\text{O}^+} - Q_{\text{OH}_3\text{O}^+})/RT - \ln X_{\text{H}_3\text{O}^+} \quad (14)$$

So far nothing has been assumed concerning the *number* of points for cationic adsorption in the surface layer. Here the assumption will be made that *the number of points is constant*. The reason for this is that only a destruction of the surface layer will change that number, and the possibility of such a destruction seems to be remote. This can be concluded from the fact that the asymmetry potential remains constant, even if the electrode is alternately brought in contact with acid and alkaline solutions, and also from the reproducible alkaline behaviour.

From this assumption we get:

$$\Sigma_i C_g = \Sigma_i C_{\text{og}} = \text{constant} \quad (15)$$

and
$$X_{\text{H}_3\text{O}^+} + X_{\text{Na}^+} = 1 \quad (16)$$

It may be pointed out that eq. (16) contains *concentrations*, i.e. *numbers* of ions. However, the *activity* of the adsorbed ions may change with the state of adsorption, and this will be revealed by variations in U_g and Q_i . By applying eq. (16), eq. (13) is reduced to:

$$\exp [(Q_{\text{OH}_3\text{O}^+} - Q_{\text{H}_3\text{O}^+})/RT] \cdot \exp (F \Delta E/RT) = \frac{a_{\text{Na}^+}}{a_{\text{H}_3\text{O}^+}} \exp [(Q_{\text{Na}^+} - Q_{\text{H}_3\text{O}^+})/RT] + 1 \quad (17)$$

From the treatment given above it is possible to calculate $X_{\text{H}_3\text{O}^+}$, X_{Na^+} , $(Q_{\text{H}_3\text{O}^+} - Q_{\text{OH}_3\text{O}^+})/RT$ and $(Q_{\text{OH}_3\text{O}^+} - Q_{\text{Na}^+})/RT$ from experimental data on the alkaline error under different conditions. This can be done from two separate values of both ΔE and $a_{\text{Na}^+}/a_{\text{H}_3\text{O}^+}$ by means of eq. (14) and eq. (17). The first step is to determine $\exp [(Q_{\text{OH}_3\text{O}^+} - Q_{\text{H}_3\text{O}^+})/RT]$, keeping a_{Na^+} constant.

In practice it is not possible to attain these conditions, as the sodium ion activity changes with the ionic strength when pH is altered. However, errors from this source can be kept low if a suitable solution is used, containing a small amount of buffer with most of the sodium ions present as NaCl. We write:

$$\exp [(Q_{\text{OH}_3\text{O}^+} - Q_{\text{H}_3\text{O}^+})/RT] = \gamma$$

$$\exp [(Q_{\text{Na}^+} - Q_{\text{H}_3\text{O}^+})/RT] = \delta$$

From eq. (17)
$$\gamma \cdot \exp (F \Delta E/RT) = \delta \frac{a_{\text{Na}^+}}{a_{\text{H}_3\text{O}^+}} + 1$$

and for $\Delta E''$ and $\Delta E'$

$$\gamma \cdot \exp (F \Delta E'' / RT) = \delta \frac{a_{\text{Na}^+}}{a'_{\text{H}_2\text{O}^+}} + 1$$

$$\gamma \cdot \exp (F \Delta E' / RT) = \delta \frac{a_{\text{Na}^+}}{a'_{\text{H}_2\text{O}^+}} + 1$$

$$\text{i.e.} \quad \frac{\gamma \cdot \exp (F \Delta E' / RT) - 1}{\gamma \cdot \exp (F \Delta E'' / RT) - 1} = \frac{a''_{\text{H}_2\text{O}^+}}{a'_{\text{H}_2\text{O}^+}}$$

($\Delta E' < \Delta E''$ and correspondingly $a'_{\text{H}_2\text{O}^+} > a''_{\text{H}_2\text{O}^+}$)

With a pH difference of 0.50, which is adequate for over all accuracy in the measurements, we have: $a''_{\text{H}_2\text{O}^+}/a'_{\text{H}_2\text{O}^+} = 1/\sqrt{10}$ and

$$\frac{1}{\gamma} = \exp [(Q_{\text{H}_2\text{O}^+} - Q_{\text{OH}_2\text{O}^+})/RT] = \frac{3.16 \exp (F \Delta E' / RT) - \exp (F \Delta E'' / RT)}{2.16} \quad (18)$$

Putting as a first approximation $\Delta E = (\Delta E' + \Delta E'')/2$, which is equivalent to assuming that the alkaline error function is a straight line in the small interval between $\Delta E'$ and $\Delta E''$, and combining eq. (14) and eq. (18):

$$X_{\text{H}_2\text{O}^+} = \frac{1.46}{\exp (F(\Delta E'' - \Delta E')/2RT)} - 0.462 \cdot \exp [F(\Delta E'' - \Delta E')/2RT] \quad (19)$$

From the earlier equation:

$$\frac{X_{\text{Na}^+}}{X_{\text{H}_2\text{O}^+}} = \frac{a_{\text{Na}^+}}{a_{\text{H}_2\text{O}^+}} \exp [(Q_{\text{Na}^+} - Q_{\text{H}_2\text{O}^+})/RT]$$

and eq. (14) we get:

$$\ln X_{\text{Na}^+} + (Q_{\text{OH}_2\text{O}^+} - Q_{\text{Na}^+})/RT = \ln a_{\text{Na}^+} + M \cdot \text{pH} - F \Delta E / RT \quad (20)$$

As $X_{\text{H}_2\text{O}^+} + X_{\text{Na}^+} = 1$ we can derive X_{Na^+} and $(Q_{\text{OH}_2\text{O}^+} - Q_{\text{Na}^+})/RT$ from eq. (19) and eq. (20). As can be seen from above, it is convenient to plot the functions (3) and (4) from the experimental data, as this considerably reduces the calculation required.

In order to deduce an alkaline error equation, it is necessary to find the dependence of $(Q_i - Q_{\text{oi}})/RT$ on X_i . We will here start with the assumption earlier used for localized adsorption layers, *e.g.* by Fowler²⁰, that the energy of interaction can be expressed as the sum of contributions of pairs of nearest neighbours. If every adsorption point has n neighbours, and an ideal distribution is assumed, every site has a possibility X_i of being occupied by an ion i ; the number of pairs will be $\frac{n}{2} \cdot X_i$. As it is assumed that the change in interaction energy, for the whole system given as $X_i \cdot d_i U_g$, is proportional to the change in number of pairs, we get:

$$X_i \cdot d_i U_g = k_2 \cdot \frac{n}{2} dX_i \quad (21)$$

Or, if we write $\frac{2}{n k_2} = k_3$,

$$\frac{dX_i}{X_i} = k_3 \cdot d_i U_g \quad (22)$$

$$\text{and} \quad \ln X_i = k_3 \cdot d_i U_g + \text{constant} \quad (23)$$

As we defined ${}_i U_g \rightarrow {}_i U_{og}$ when $X_i \rightarrow 1$, the value of the constant is $-{}_i U_{og}$.
and $\ln X_i = k_3({}_i U_g - {}_i U_{og}) \quad (23a)$

Regarding the significance of Q_i and Q_{oi} and writing $k_3 \cdot RT = k_4$:

$$\ln X_i = k_4(Q_{oi} - Q_i)/RT \quad (24)$$

From the different experimental figures, plotted in accordance with eq. (3) and eq. (4), and by means of eq. (16), (18), (19) and (20) the functions

$$\begin{aligned} -\ln X_{H_2O+} &= f\left(\frac{Q_{H_2O+} - Q_{oH_2O+}}{RT}\right) \\ -\ln X_{Na+} &= f\left(\frac{Q_{oH_2O+} - Q_{Na+}}{RT}\right) \end{aligned}$$

have been calculated for the different electrodes at different conditions. As can be seen from the diagrams, Figs. 14—17, the requirements of eq. (24) are fulfilled, *i.e.* the experimental results are in agreement with the theoretical equation:

From the distribution law we have:

$$X_i = \frac{a_i}{\Sigma_i C_{og}} \exp [(Q_i - EF)/RT]$$

and from this and eq. (24):

$$X_i^{(1 + k_4)/k_4} = \frac{a_i}{\Sigma_i C_{og}} \cdot \frac{\exp (Q_{oi}/RT)}{\exp (FE/RT)} \quad (25)$$

$$\text{and} \quad X_{H_2O+} = \left(\frac{a_{H_2O+}}{\Sigma_i C_{og}} \cdot \frac{\exp (Q_{oH_2O+}/RT)}{\exp (FE/RT)} \right)^{k_{4H_2O+}/(1 + k_{4H_2O+})} \quad (25a)$$

$$X_{Na+} = \left(\frac{a_{Na+}}{\Sigma_i C_{og}} \cdot \frac{\exp (Q_{oNa+}/RT)}{\exp (FE/RT)} \right)^{k_{4Na+}/(1 + k_{4Na+})} \quad (25b)$$

Let $(1 + k_{4H_2O+})/k_{4H_2O+} = \vartheta$ and $(1 + k_{4Na+})/k_{4Na+} = \tau$; and we get from eq. (25a) and eq. (25b):

$$\frac{X_{H_2O+}^{\vartheta}}{X_{Na+}^{\tau}} = \kappa \cdot \frac{a_{H_2O+}}{a_{Na+}} \quad (26)$$

In this treatment eq. [26] is therefore the adsorption isotherm of the glass electrode. As $\Sigma X_i = 1$, the general equation for a system containing two different univalent ions can be written:

$$\Sigma \left(\frac{\exp (Q_{oi}/RT)}{\Sigma_i C_{og}} \cdot \frac{a_i}{\exp (FE/RT)} \right)^{k_{4i}/(1 + k_{4i})} = 1 \quad (27)$$

(This treatment probably cannot be applied in its simple form to multi-ion systems, as the adsorption sites not occupied by the ion i can be occupied by more than one kind of ion. This makes the treatment of the interaction energies more complicated. However, in practice the case of two univalent ions is of most interest.)

Applied to H_3O^+ and Na^+ eq. (27) will be, if $p = 1/\theta$ and $q = 1/\tau$:

$$\left(\frac{\exp(Q_{\text{OH}_3\text{O}^+}/RT)}{\Sigma_i C_{\text{og}}} \cdot \frac{a_{\text{H}_3\text{O}^+}}{\exp(FE/RT)} \right)^p + \left(\frac{\exp(Q_{\text{ONa}^+}/RT)}{\Sigma_i C_{\text{og}}} \cdot \frac{a_{\text{Na}^+}}{\exp(FE/RT)} \right)^q = 1 \quad (28)$$

This equation can be transformed:

$$-p \cdot \text{pH} + p \cdot Q_{\text{OH}_3\text{O}^+}/M \cdot RT - p \cdot F \cdot E/M \cdot RT - p \cdot \log \Sigma_i C_{\text{og}} = \log \left[1 - K \left(\frac{a_{\text{Na}^+}}{\exp(FE/RT)} \right)^q \right] \text{ where } K = \left(\frac{\exp(Q_{\text{ONa}^+}/RT)}{\Sigma_i C_{\text{og}}} \right)^q.$$

Since $-\text{pH} = FE'/MRT - Q_{\text{OH}_3\text{O}^+}/MRT + \log \Sigma_i C_{\text{og}}$; and as $\Delta E = E - E'$ therefore

$$\Delta E = -\frac{MRT}{pF} \cdot \log \left[1 - K \left(\frac{a_{\text{Na}^+}}{\exp(FE/RT)} \right)^q \right] \quad (29)$$

$$\text{or } \Delta \text{pH} = -\frac{1}{p} \cdot \log \left[1 - K \left(\frac{a_{\text{Na}^+}}{\exp(FE/RT)} \right)^q \right] \quad (30)$$

It is interesting to see that by expanding eq. (30) in

$$\log(1-x) \sim -x \dots \dots$$

we obtain

$$\Delta \text{pH} \sim \frac{K}{p} \left(\frac{a_{\text{Na}^+}}{\exp(FE/RT)} \right)^q$$

and from this:

$$\log \Delta \text{pH} = q \cdot (\text{pH}_{\text{measured}} + \log a_{\text{Na}^+}) + \text{constant} \quad (31)$$

and, with the approximation $a_{\text{Na}^+} = \text{constant} \cdot C_{\text{Na}^+}^a$:

$$\log \Delta \text{pH} = a \cdot \text{pH}_{\text{measured}} + b \cdot \log C_{\text{Na}^+} + \text{constant} \quad (32)$$

This is the same as Jordan's empirical equation ^{21, 22}.

Eq. (29) can also be written:

$$\frac{1}{\exp(pF\Delta E/RT)} = 1 - \left[\frac{\exp[(Q_{\text{ONa}^+} - Q_{\text{OH}_3\text{O}^+})/RT]}{\exp(F\Delta E/RT)} \cdot \frac{a_{\text{Na}^+}}{a_{\text{H}_3\text{O}^+}} \right]^q \quad (33)$$

As, in accordance with eq. (24)

$$k_4 = \frac{\ln X_i}{(Q_{\text{oi}} - Q_i)/RT}$$

is $k_4 = \infty$ if not the interaction is considered. In such a case $p = q = 1$, and from eq. (33):

$$\log [\exp(F\Delta E/RT) - 1] = \text{pH} + \log a_{\text{Na}^+} \cdot \exp[(Q_{\text{Na}^+} - Q_{\text{H}_3\text{O}^+})/RT] \quad (34)$$

This is the same as eq. (1) derived by Dole, neglecting interaction. (Eq. (1) contains C_{Na^+} as Dole starts from what has been defined as U_s in this paper, instead of the constant value U_{os} .) As mentioned earlier, the lack of agreement is that the experimental alkaline error figures do not give the slope of unity, as the equation requires.

As, in accordance with the following

$$\begin{aligned} \exp [(Q_{\text{Na}^+} - Q_{\text{H}_3\text{O}^+})/RT] \cdot \frac{a_{\text{Na}^+}}{a_{\text{H}_3\text{O}^+}} &= \beta \\ F \cdot \Delta E/RT &= x \end{aligned}$$

eq. (33) can be written:

$$\frac{1}{e^{px}} = 1 - \frac{\beta^q}{e^{qx}} \text{ or } e^{qx} - e^{(q-p)x} = \beta^q$$

and after expanding in series and approximating, we get:

$$e^{qx} - e^{(q-p)x} \sim p \cdot x$$

However, this is also the first member of the expression for $p(e^x - 1)$, and we get:

$$p(e^x - 1) \sim \beta^q$$

And from this

$$\begin{aligned} \frac{1}{q} \cdot \log[\exp(F\Delta E/RT) - 1] &= \text{pH} + \log a_{\text{Na}^+} \cdot \exp[(Q_{\text{Na}^+} - Q_{\text{H}_3\text{O}^+})/RT] + \\ &\frac{1}{q} \cdot \log p \end{aligned} \quad (35)$$

This equation is the same as eq. (1), except that it does not demand a slope of unity, and so can be brought into agreement with the experimental results.

Eq. (29) can also be written:

$$\frac{1}{q} \cdot \log[1 - \exp(-pF\Delta E/RT)] = \text{pH} + \log a_{\text{Na}^+} + \log K \quad (29a)$$

From the results obtained for the electrodes A and B, a check on the validity of eq. (29a), (31) and (35) can be obtained from Figs. 18–20. (The values of p are calculated from Fig. 14.) As can be expected from the approximations introduced, the agreement is good for low and moderate alkaline errors, but deviations appear at higher values. Deviations of the same kind can also be found in Dole's investigations, *e.g.* Dole¹², p. 271, Fig. 16.8. In the case of eq. (29a), where no mathematical approximations are introduced, it can be found that the equation is valid also at high alkaline errors, so that it describes the experimental behaviour of the glass electrodes in alkaline solutions.

DISCUSSION

In the treatment given above, it has been shown that when the interaction in the surface layer is taken into account, an alkaline error equation can be derived, which is in good agreement with experimental results. The equation can also be approximated to the empirical equation suggested by Jordan, and to an equation of the Dole type, but with a slope in accordance with experimental data. It has also been shown that the interaction can be expressed as the sum of contributions of nearest neighbours. An adsorption isotherm for the glass electrode has been deduced, and the asymmetry potential given thermodynamic significance.

A more exact treatment of the significance of "contributions of nearest neighbours" would of course be of great interest, but at present there is in-

sufficient theoretical and experimental background. The adsorption isotherm derived is probably of interest for ion exchange resins, where studies on different resins could give an indication of the interaction on a more general basis.

In the case of the glass electrode it would be of interest to determine the absolute amount of adsorbed ions, for example by means of radioactive isotopes. However, this approach is also difficult since it cannot be assumed that *e.g.* tritium is adsorbed to the same extent as protium, and furthermore the determination of tritium is very complicated. Other difficulties arise from the probable isotope equilibrium with water and the fact that the removal of excess solution from the glass will probably disturb the adsorption equilibrium.

However, some interesting figures can be obtained from the potential measurements. If in Figs. 15–17 an extrapolation is made to $-\ln \bar{X}_{\text{Na}^+} = 0$, *i.e.* $X_{\text{Na}^+} = 1$, it is possible to determine:

$$(Q_{\text{OH}_2\text{O}^+} - Q_{\text{ONa}^+})/RT$$

This quantity is essentially the energy involved in the dissociation, so that a kind of dissociation constant, K_o , can be found from the formula:

$$(Q_{\text{OH}_2\text{O}^+} - Q_{\text{ONa}^+})/RT = -\ln K_o$$

$$\text{or } pK_o = (Q_{\text{OH}_2\text{O}^+} - Q_{\text{ONa}^+})/M \cdot RT \quad (36)$$

It may be expected that pK_o will be of the same order as the pH at which the alkaline error appears. pK_o can be considered as a characteristic of the glass electrode. Other characteristics are the interaction constants $k_{\text{H}_2\text{O}^+}$ and k_{Na^+} in eq. (24) and these and pK_o will completely define the alkaline behaviour of the electrode. In Table 1 the values in question can be found for the electrodes studied. It would be of a great interest to determine these characteristics as functions of the electrode glass composition, and so facilitate the search for suitable glass electrode glasses.

A DIFFERENTIAL MEASURING METHOD

In the Swedish Patent 129833 a method is described for correcting the alkaline error in pH measurements when the activity of the sodium ion (or other) is unknown. The principle is that the measurements are made with two glass electrodes of different, but known, alkaline error functions. From the

Table 1. Characteristic constants of some glass electrodes.

Electrode and ion.	Temperature C°	pK_o	$k_{\text{H}_2\text{O}^+}$	k_{Na^+}
A Na ⁺	25	10.4	1.08	0.36
B Na ⁺	25	11.3	1.00	0.24
C Na ⁺	10	11.6	1.00	0.32
C Na ⁺	25	11.3	1.00	0.44
C Na ⁺	50	10.1	1.00	2.00
C Li ⁺	10	12.6	1.25	0.27
C Li ⁺	25	12.2	1.25	0.32
C Li ⁺	50	10.5	1.25	0.42
D Na ⁺	25	14.3	0.41	1.00
E Na ⁺	25	15.5	0.32	0.48

difference in measured pH for the two electrodes, $\text{pH}_1 - \text{pH}_2$, the alkaline error for each can be found from a predetermined diagram. If curves similar to Fig. 2 are plotted from experimental data for the electrodes, each value of $M \cdot \text{pH} + \ln a_{\text{Na}^+}$ corresponds to the alkaline errors ΔpH_1 and ΔpH_2 , and as $\text{pH}_1 - \text{pH}_2 = \Delta \text{pH}_2 - \Delta \text{pH}_1$ the required functions

$$\text{pH}_1 - \text{pH}_2 = f(\Delta \text{pH}_1) = g(\Delta \text{pH}_2)$$

can be determined. Such functions for the electrodes A and B are shown in Fig. 21.

The method seems to be valuable as highly stable low alkaline error electrodes seems to be rare, and for high temperature measurements, where even low alkaline error electrodes show a considerable deviation from ideal behaviour, and also when such electrodes are used for pH determinations in a range of high alkalinity. The method is also of interest when measuring at low temperatures, where the electrical resistance of some of said electrodes is rather high.

The author wishes to thank the board of *Rydboholms A. B.* for permission to publish this paper and Mr. A. Lindberg for his valuable assistance in the experimental work, and is also indebted to Professor N. Gralén, Dr. J. O'M. Bockris, Dr. T. Vickerstaff, Mr. E. Blomgren and Mr. A. Olofson for their kind interest.

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Received January 22, 1955.