

# ON THE THEORY OF THE ALKALINE ERROR OF THE GLASS ELECTRODE

By

Ch. OLÁH

Department for Physical Chemistry, Polytechnical University, Budapest

(Received November 20, 1959)

The glass electrode is a glass-diaphragm having a thin wall, which in an aqueous solution is electrically charged with respect to the solution. The building up potential difference is an unambiguous function within very wide limits of the ion concentration of hydrogen, namely the linear function of the pH. In an alkaline medium (depending on the sort of glass from 9–12 pH) the pH dependence differs from linearity, hereby setting a limit to its applicability. The behaviour of the glass electrode has been investigated by several persons and also different explanations are given to-day as regards the interpretation of the building up of the potential and also the alkaline error.

## The building up of the electrode potential

On studying the glass electrode the investigations of QUITNER [1] are of fundamental importance. He measured the transport number of different cations and anions electrolyzed through a thin glass wall with a high field strength. The result of his investigations may be summarized as follows:

1. Electrons do not contribute to the conduction (the Faraday law is valid within the limit of error).

2. Neither do the anions contribute to the conduction.

3. In an acid solution the transport number of hydrogen-ions is practically equal to 1. In an alkaline solution also other cations, first of all alkali ions might participate in the conduction. The transport number of polyvalent cations is also very small in an alkaline solution.

On the basis of the investigations of ZACHARIASEN [2] and others, the structure of glass is known: as a rigid silicate anion lattice with more or less mobile cations in the gaps of the lattice space structure. Besides that also swelling water [3] is contained in the glass electrode.

What has been said before is valid for any sort of glass used as electrodes.

From all these facts the process of the building up of potentials can be explained as follows: There are two phases: one of them, namely, the glass

contains hydrogen ions (+ alkali ions) and polysilicate anions (further on briefly silicate,  $\text{SiO}^-$ ). The other one the aqueous solution also contains  $\text{H}_3\text{O}^+$  cations and for instance  $\text{Cl}^-$  anions. If in the two phases the chemical potential of  $\text{H}_3\text{O}^+$  is different, than at the boundary of the phase it can go over into the other one. Either entering from the glass into the solution or diffusing from the solution into the glass (since, however, it cannot be followed by the anion), neither the silicate can be solved nor the  $\text{Cl}^-$  ion can enter into the spaces of the silicate structure (evidently owing to the repulsion of the silicate anion structure of negative charge), necessarily a charging takes place by which within a short time the further entering or emerging of  $\text{H}_3\text{O}^+$  ions is hindered. At the boundary a double layer is formed, the equilibrium sets in and thus an electrical potential difference equivalent to the chemical potential difference hydronium-ion can be measured between the two phases.

Generally one used to start for deriving the glass electrode potential from the general formula of the diffusion potential:

$$d\varepsilon_{\text{diff}} = - \frac{RT}{F} \sum \frac{n_i}{z_i} d \ln a_i$$

where  $n_i$  is the transport number of the  $i$ -th ion,  $z_i$  is the charge number and  $a_i$  is its activity. Since the transport number of the hydronium-ions is 1, we obtain by integration:

$$\varepsilon = \frac{RT}{F} \ln \frac{A_{\text{H}_3\text{O}^+}}{A'_{\text{H}_3\text{O}^+}} \quad (1)$$

Thus we obtain the empirically justified function, which is completely identical with the potential formula of the ordinary hydrogen-concentration cell. Hence the mental process of considering the potential building up on the glass electrode as the limiting case of a diffusion potential is not an incorrect one, but is by no means more justified as, for instance, considering the potential of any of the metal electrodes as the limiting case of the diffusion potential. (There is much more analogy between the glass electrode and metal electrodes of a primary kind as between the glass electrode and the diffusion potential building up between fluids.) The difference between metals and glass consists essentially in the fact that the metal is electronically conducting, whereas in the glass the current is conducted by cations moving in the rigid silicate structure, further on instead of the electrons compensating the charge of metal-ions of the metallic lattice, the anion structure of silicate is to be found in the case of glass.

In case of glass, in the process of building up the potential, a difference consists in that the boundary phase contributes and its composition differs

(as regards cations) by the internal phase of glass and no possibility is given for equalization owing to the very slight mobility of ions in the glass (high electrical resistance, act. energy = 16–20 Kcal/mol). This being a practical fixation of the  $\text{H}_3\text{O}^+$  ions in the glass phase is also similar to the rigid metal lattice. It is a common feature that the particles of negative charge (anions, silicate ions, and in the case of metals the electrons) cannot cross the phase boundary, only the cations can do so. The difference between the potential of the glass and the diffusion potential is a much more considerable one. It is characteristic for the latter that particles of both types of charges may go over at the boundary into the phase in which their chemical potential is smaller, and the reason for the electrical charging consists in the different mobility of the anions and cations. Here the electrical potential difference is not in equilibrium with the chemical potential difference which maintains the diffusion, the state is only a stationary one but not an equilibrium state and the whole process is irreversible.

Hence it is logical to consider the glass electrode as one kind of cation electrode, which differs from the others, for the potential of which, however, the potential expression of the former one is also valid.

According to what has been mentioned before, in the building up of the electrode potential only the surface of the glass participates. When the glass membrane on both sides is in contact with the electrolytic solution, the potential is building up at the two boundaries independent of each other.

In the following only the surface phase which is in contact with the solution can to be understood as a glass phase. The internal glass phase between two boundaries does not contribute to the building up of the potential, its role consists only in maintaining the conducting connection between the two interfaces. Its structure is mainly of interest from this point of view only. The alkaline error:

In a basic solution in the presence of alkali ions, the potential of the glass electrode differs from the hydrogen function to an extent which is the higher, the higher the pH and the alkali concentration is.

If the pH and the alkali concentration is high enough, not the hydrogen but practically the alkaline function is followed by the glass electrode. This phenomenon can be interpreted in several ways. According to one of the theories, -- there is in fact question of an adsorption potential in the case of glass --, which is the consequence of the selective adsorption of the hydronium ions. The alkaline error is explained by this theory in such a manner that  $\text{H}_3\text{O}^+$  ions are exchanged on the surface by alkali ions. According to the already above-mentioned interpretation of the diffusion potential, the alkaline error is due to the fact that the transport number of  $\text{H}_3\text{O}^+$  ions is reduced on account of the transport number of the alkali ions and for a high enough alkali concentration unity is approached by the latter. It is, however, the most simple

to extend the analogy of glass electrodes derived by metal electrodes when beside  $\text{H}_3\text{O}^+$  ions also the alkali ions are present. Thus the glass electrode is analogous to the mixture electrodes, and so can be considered as a hydrogen alkali mixture electrode.

The deduction carried out for the mixture electrode of the potential dependence is now valid as well.

In the following, the potential of the glass considered as a mixture electrode will be derived in function of the hydronium alkali concentration of the solution.

Let  $\varepsilon$  be the potential of the glass electrode.

Let  $\varepsilon_H$  be the normal potential of the glass as H-electrode.

Let  $\varepsilon_K$  be the normal potential of the glass as an alkali electrode.

Let  $a_H, a_K$  the activity of  $\text{H}_3\text{O}^+$  and the alkali cations in the solution

Let  $a'_H, a'_K$  the activity of  $\text{H}_3\text{O}^+$  in the glass phase.

Let  $\gamma_H, \gamma_K$  be the activity coefficients of  $\text{H}_3\text{O}^+$  and alkali cations in the solution

Let  $\gamma'_H, \gamma'_K$  be activity coefficients of cations in the solution in the glass.

Let  $X_H, X_K$  the mole fraction of  $\text{H}_3\text{O}^+$  and alkali cations in the solution.

Let  $X'_H, X'_K$  the mole fraction of  $\text{H}_3\text{O}^+$  in the glass.

Let  $X'_s$  the mole fraction of the  $\text{SiO}^-$  anions in the glass.

The condition of the thermodynamic equilibrium is the equality of the potentials of the two systems forming the mixture electrode:

$$\varepsilon = \varepsilon_H^\circ + \frac{RT}{F} \ln \frac{a_H}{a'_H} = \varepsilon_K^\circ + \frac{RT}{F} \ln \frac{a_K}{a'_K} \quad (2)$$

$$\varepsilon = \varepsilon_H^\circ + \frac{RT}{F} \ln \frac{x_H \cdot \gamma_H}{x'_H \cdot \gamma'_H} = \varepsilon_K^\circ + \frac{RT}{F} \ln \frac{x_K \cdot \gamma_K}{x'_K \cdot \gamma'_K}$$

$$\frac{x_H}{x'_H} = \frac{\gamma'_H}{\gamma_H} \cdot \exp\left(\frac{\varepsilon - \varepsilon_H^\circ}{RT} F\right); \quad x'_H = x_H \cdot \frac{\gamma'_H}{\gamma_H} \exp\left(\frac{\varepsilon_H^\circ - \varepsilon}{RT} F\right)$$

$$\frac{x_K}{x'_K} = \frac{\gamma'_K}{\gamma_K} \cdot \exp\left(\frac{\varepsilon - \varepsilon_K^\circ}{RT} F\right); \quad x'_K = x_K \cdot \frac{\gamma'_K}{\gamma_K} \exp\left(\frac{\varepsilon_K^\circ - \varepsilon}{RT} F\right)$$

Since because the electro-neutrality shall be valid

$$x'_H + x'_K = x'_s \quad (3)$$

Hence:

$$x_H \frac{\gamma_H}{\gamma'_H} \cdot e^{\frac{\varepsilon_H^\circ F}{RT}} \cdot e^{-\frac{\varepsilon F}{RT}} + x_K \frac{\gamma_K}{\gamma'_K} \cdot e^{\frac{\varepsilon_K^\circ F}{RT}} \cdot e^{-\frac{\varepsilon F}{RT}} = x'_s$$

and

$$x_H \frac{\gamma_H}{\gamma'_H} \cdot e^{\frac{\varepsilon_K^\circ F}{RT}} + x_K \cdot \frac{\gamma_K}{\gamma'_K} e^{\frac{\varepsilon^\circ F}{RT}} = x'_s \cdot e^{\frac{\varepsilon F}{RT}}$$

Hence the electrode potential of the mixture electrode is:

$$\varepsilon = \varepsilon_H^\circ + \frac{RT}{F} \ln \left[ \frac{1}{x'_s} \left( x_H \frac{\gamma_H}{\gamma'_H} + x_K \frac{\gamma_K}{\gamma'_K} e^{\frac{\varepsilon_K^\circ - \varepsilon_H^\circ}{RT}} e^{\frac{\varepsilon_K^\circ - \varepsilon_H^\circ}{RT}} F \right) \right] \quad (4)$$

The alkaline error is the deviation of the potential of the alkali hydrogen mixture electrode from the electrode merging into an ion of identical  $\text{H}_3\text{O}^+$  activity but free of alkali ion solution. The values referring to the latter case are denoted for discriminations sake by \*.

If there is no alkali present

$$x_K = 0 \quad \text{and} \quad x'_s = x_s^*$$

Hence

$$\varepsilon^* = \varepsilon_H^\circ + \frac{RT}{F} \ln \left( x_H \frac{\gamma_H}{\gamma'_H} \frac{1}{x_s^*} \right) \quad (5)$$

and from here the total formula of the alkaline error is:

$$\Delta\varepsilon = \varepsilon - \varepsilon^* = \frac{RT}{F} \ln \left[ \frac{x_s^*}{x'_s} \cdot \frac{\gamma_H^*}{\gamma'_H} \left( 1 + K \frac{a_K}{a_H} \cdot \frac{\gamma'_H}{\gamma'_K} \right) \right] \quad (6)$$

where

$$K = e^{\frac{\varepsilon_K^\circ - \varepsilon_H^\circ}{RT} F} \quad (7)$$

Let us assume for simplification's sake that:

1. The number of silicate anions is not influenced by the presence of alkali:

$$x_s^* = x'_s \quad (8)$$

2. The ratios of the activity coefficients do not considerably differ from unity:

$$\frac{\gamma'_H}{\gamma'_K} \approx 1; \quad \frac{\gamma_H^*}{\gamma'_H} \approx 1 \quad (9)$$

By these neglects the following simple form is obtained:

$$\Delta\varepsilon = \frac{RT}{F} \ln \left( 1 + K \frac{a_K}{a_H} \right) \quad (10)$$

or substituting the values of  $\frac{RT}{F}$  and going over to a common logarithm:

$$\Delta\varepsilon = 0.059 \cdot \log \left( 1 + K \frac{a_K}{a_H} \right) \quad (11)$$

or

$$1 + K \frac{a_K}{a_H} = e^{\frac{\Delta\varepsilon \cdot F}{RT}} = \exp = B \quad (12)$$

The expression of the right hand side will be shortened ( $B$ ) further on. This is nothing else as the well-known potential formula of the mixture electrodes. If the constant value of  $K$  is small, for instance of an order of magnitude

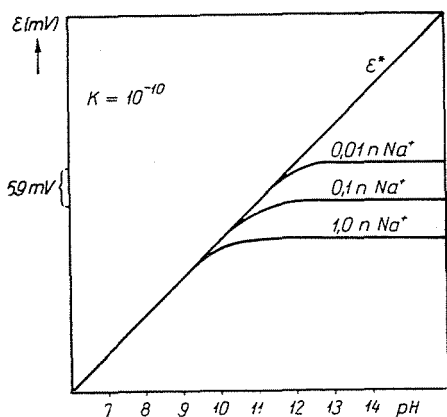


Fig. 1

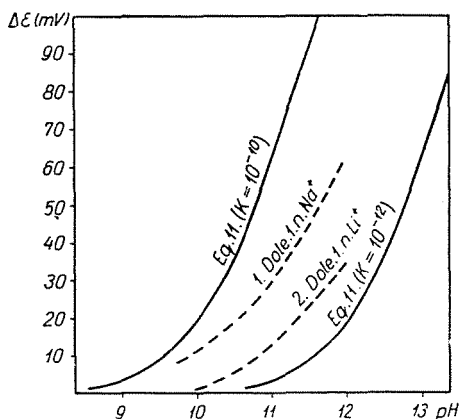


Fig. 2

$10^{-10}$ , than the alkaline error can be neglected in a very wide interval of concentration ratio  $a_H/a_K$ . If the value of the ration of concentration attains the order of magnitude of  $K$ , the alkaline error increases rapidly. If the so computed alkaline error was calculated in the function of pH for the value  $a_K = 1$  in case of values  $\log K = 10^{-10}$  and  $K = 10^{-12}$ , for instance (Fig. 2), then curves very similar to the obtained curves are attained. The value of  $K$  characteristic for glass and the type of alkali ions can be determined from the curves. These are namely going over in the direction of increasing values of pH into a straight line, the equation of which is:

$$\Delta\varepsilon = 0.059 \cdot pH - 0.059 (p a_K + pK) \quad (13)$$

Its abscissa section is:

$$pH = p a_K + pK$$

Hence the value of  $pK = -\log K$  can be graphically determined from the axial section. Assuming that this relation was valid for the glass electrode the value of  $K$  can be graphically computed from the experimental curves,  $pK$  values visible from experimental curves illustrated in Fig. 1., are shown in Table I. According by the characterization of the alkaline error of the glass electrode can be performed by giving a constant of a good approximation, by which the behaviour of the glass is obtained from the point of view of the alkaline error (as a matter of course for a given kind of ions.)

Table I

	pK
Corning 015, DOLE [6]. $1 \times n \text{ Li}^+$ .....	11.4
Corning 015, WIENER [7]. $1 \times n \text{ Na}^+$ .....	11.0
Cross-linked polymethacrylic acid [8] .....	6.0
Polystyrol, sulfonized [8] .....	1.5
Glass denoted by D .....	1.5
Glass denoted by $D_M$ .....	1.0

(Examined by B. LENGYEL) [9]

Examining the physical meaning of  $K$  constant the following result is obtained:

$$RT \ln K = F(\varepsilon_K^\circ - \varepsilon_H^\circ) = (\mu_K^\circ - \mu_K^{\circ'}) + (\mu_H^\circ - \mu_H^{\circ'}) = RT \ln \frac{a_H \cdot a_K'}{a_H' \cdot a_K}$$

The values  $\mu^\circ$  mean the standard chemical potentials of the corresponding ions, whereas the values  $a$  now signify the equilibrium activities. Hence:

$$K = \frac{a_H \cdot a_K'}{a_H' \cdot a_K} \quad (14)$$

Whereas this is nothing else but the equilibrium constant of the following process



Whereas the physical meaning of the product  $K \frac{a_K}{a_H}$  is:

$$K \frac{a_K}{a_H} = \frac{a_K'}{a_H'}$$

Therefore if the value of  $K$  is, for instance,  $10^{10}$ , then in order to obtain a proportion of hydrogen and alkali ions in the glass phase of 1 : 1, the alkali ion concentration should to be  $10^{10}$  times the  $H_3O^+$  ion concentration (for instance normal alkali ion and pH 10). Hence the process which is taking place here is an ion exchange between the glass phase and the solution in a quite analogous manner to synthetical polymers having an ion exchanging property. The physical analogy between the glass and materials of ion exchanging properties is otherwise also very considerable. There is also a rigid anion structure (at the cation exchanging the lattice space resin structure with the acidic  $-SO_3$  groups for instance) where in the gaps cations might be moving and exchanging. For comparison's sake the ion exchanging constant of some synthetical ion exchanging resins is visible.

This analogy was first pointed out by the Soviet researcher NICOLSKI [10] and the first thermodynamic interpretation of the alkaline error is also related to his name.

It should be noted that a completely similar relation is attained in form by deriving the influence exerted by the alkali ions on the hydrogen function by starting from the selective adsorption. In this case instead of the chemical potential differences for the  $K$  constant, the difference of the adsorption energies occur. By the validity of the attained relation the problem is not yet solved as to which one is the process and to which the building up of the potential is due, the adsorption taking place at the external surface or the ion penetration taking place in the interior of the surface phase. The most probable assumption is that both of them are taking place. It seems, however, very likely that the latter plays a decisive role in the building up of the potential. The fact why for glasses containing Li — the  $H^+$  ions bond on the surface cannot be interchanged by  $Na^+$  ions could hardly be explained by the external surface adsorption. The above assumption has an interesting consequence :

In solutions having a composition where no alkaline error is present (hence for smaller pH values for instance in neutral or acid solutions) the fact that the glass phase is completely alkali free corresponds to the ion exchange equilibrium. According to the assumption at least in the surface phase, in direct contact with the solution the alkali ion content of the glass becomes detached already at the dilution more exactly interchanged by hydrogen ions. The uptake of alkali ions takes place for high pH values only. Just the effect of this phenomenon appearing in the building up of the potential is the so-called alkaline error. If so, the composition of the surface phase, in general, differs from the composition of the interior phase, where this interchange cannot take place. Should the mobility of the hydrogen ion and the alkali ion be different, then also the building up of the diffusion potential may be caused hereby. Now there is the question of an electrode potential only building up at the boundary of glass electrolytic solution and the occasional further potential



differences are not taken into consideration by which very likely the measured potential differences are not considerably affected.

It is hardly to be expected that in the internal phase the water uptake, the dilation does not take place. It is namely empirically revised that at the dilation resp. drying, the resistance of the glass varies with many orders of magnitude. MacInnes for instance dried a glass in vacuo at 50 C° over P<sub>2</sub>O<sub>5</sub> and its resistance increased from 32 megohms to 40 000 megohms [11]. This would be incomprehensible if assuming that the dilation extends to the surface phase only and the interior of the glass phase remained intact.

If the agreement between the derived formula of the mixture electrodes with empirical values is thoroughly examined a quantitative, moreover a

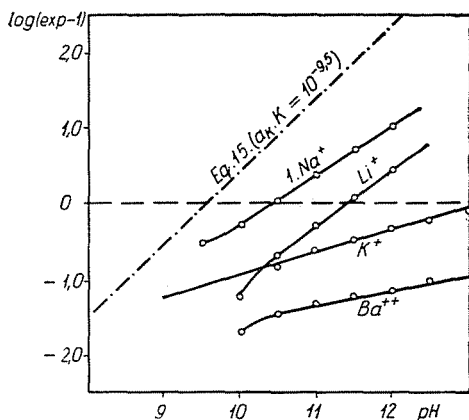


Fig. 3

qualitative agreement cannot be always found. With the Li-ion of the glass electrode investigated by LENGYEL, for instance, when the Li-ion concentration changes by 10 orders of magnitude no variation of 59 mV is shown but much less, approximately half of its value. The same is to be found for some glass electrodes investigated by DOLE and WIENER. (Fig. 3.)

The comparison with experience can be most practically carried out by transforming equation (12) in the following manner:

$$\log \left( e^{\frac{\Delta \epsilon F}{RT}} - 1 \right) = \log (B - 1) = \log (a_K K) + \text{pH} \quad (15)$$

Accordingly,  $\log(\exp-1)$  in the function of  $\text{pH}$  should give a straight line, the slope of which is 1. DOLE stated (Fig. 4) that the points computed from the experimental data are lying to a good approximation on a straight line. The angle of inclination of the straight lines, however, is in general smaller

than 45°. The values of the slopes in case of different ions are:

Li : 0.75

Na: 0.65

K : 0.31

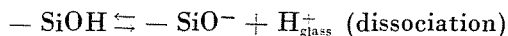
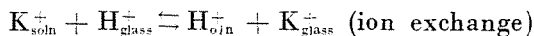
DOLE could give no explanation for this difference. The theory is therefore either incorrect or it has to be completed.

The reason for the differences can be searched for in the unjustified neglects used for equation 10. First of all let us revise the following assumption:

$$x_s^* = x'_s \quad (8)$$

The problem is: whether it is justified to assume that the number of silicate anions remain invariable from the very beginning to the end and that it is not influenced by the appearance of alkali ions not even by the appearance of alkali ions not even by the concentration variation of  $H_3O^+$  ions. The answer is that the assumption is not at all justified. It may be assumed that also the number of silicate anions changes, if the hydrogen ion concentration decreases in the glass, for instance, due to its being in a chemical equilibrium. The glass, for instance, can be considered as a weak acid of the  $SiO^-$  ions which are in dissociation equilibrium with the cations present and the undissociated  $-SiOH$  resp.  $-SiOK$  groups. The diversity of the equilibrium constant of both dissociations can result in shifting towards the dissociation direction of the equilibrium due to the increase of the alkali ion activity and the decrease of the hydrogen activity. On this basis the variation of the ion concentration can be derived in the function of the relation of the alkali hydrogen activity.

According to the thus completed physical picture, the following processes can be simultaneously in equilibrium with each other.



Besides that the electron neutrality must be valid and the silicate total concentration must be constant in the glass.

Therefore five equations can be written:

$$K = \frac{a_H \cdot a'_K}{a_K \cdot a'_H} \quad (16)$$

$$K_H = \frac{a'_s \cdot a'_H}{a'_{sH}} \quad (17)$$

$$K_K = \frac{a'_s \cdot a'_K}{a'_{sK}} \quad (18)$$

$$x'_H + x'_K = x'_s \quad (19)$$

$$x'_s + x'_{sH} + x'_{sK} = -S \quad (20)$$

$x'_s$  can be computed from the five equations: from (16) (17) (and 18):

$$\frac{a'_H}{a'_K} = \frac{K_H}{K_K} \cdot \frac{a'_{sH}}{a'_{sK}} = \frac{1}{K} \frac{a_H}{a_K} \quad (21)$$

$$x'_{sK} = L \cdot x'_{sH} \quad (22)$$

from (17) (18) and (19):

$$\begin{aligned} (x'_s)^2 &= x'_H \cdot x'_s + x'_K \cdot x'_s \\ (x'_s)^2 &= M \cdot x'_{sH} + N \cdot x'_{sK} \end{aligned} \quad (23)$$

furthermore:

$$x'_{sH} + x'_{sK} = S - x'_s$$

The meaning of the introduced abbreviations:

$$M = K_H \frac{1}{\Gamma'_H} \quad \Gamma'_H = \frac{\gamma'_s \cdot \gamma'_H}{\gamma'_{sH}} \quad (24)$$

$$N = K_K \frac{1}{\Gamma'_K} \quad \Gamma'_K = \frac{\gamma'_s \cdot \gamma'_K}{\gamma'_{sK}} \quad (25)$$

$$L = K \cdot \frac{K_H}{K_K} \cdot \frac{a_K}{a_H} \cdot \frac{\gamma'_{sH}}{\gamma'_{sK}} \quad (26)$$

$$L \frac{N}{M} = K \frac{a_K}{a_H} \cdot \frac{\gamma'_H}{\gamma'_K} \quad (27)$$

from the obtained equations  $x'_{sH}$  can be eliminated:

$$x'_{sH} = \frac{S - x'_s}{1 + L} = \frac{(x'_s)^2}{M + N \cdot L}$$

$$(x'_s)^2 \frac{1 + L}{M + N \cdot L} + x'_s - S = 0$$

$$x'_s = \frac{-1 + \sqrt{1 + 4S \frac{1 + L}{M + N \cdot L}}}{2 \frac{1 + L}{M + N \cdot L}}$$

$$x'_s = \frac{1}{2} \frac{K_H}{\Gamma'_H} \cdot \frac{B}{D} \left( -1 + \sqrt{1 + \frac{4S}{K_H} \frac{D}{B} \Gamma'_H} \right) \quad (28)$$

where

$$D = 1 + L = 1 + K \frac{K_H}{K_K} \cdot \frac{a_K}{a_H} \cdot \frac{\gamma'_{sH}}{\gamma'_{sK}} \quad (29)$$

$$B = 1 + L \frac{N}{M} = 1 + K \frac{a_K}{a_H} \cdot \frac{\gamma'_H}{\gamma'_K} \quad (30)$$

Since the symbols occurring in the equation are all showing positive values, only the + sign has a physical meaning before the root. Also the value of the  $x_s^*$  can be easily expressed:

$$x_{sH}^* = \frac{x_s^* \cdot x_H^*}{K_H} \cdot \Gamma^* = \frac{(x_s^*)^2}{K_H} \cdot \Gamma^*; \quad \Gamma^* = \frac{\gamma_s^* \cdot \gamma_H^*}{\gamma_{sH}^*} \quad (31)$$

$$x_{sH}^* = S - x_s^*$$

$$(x_s^*)^2 \frac{\Gamma^*}{K_H} + x_s^* - S = 0$$

$$x_s^* = \frac{1}{2} \frac{K_H}{\Gamma^*} \left( \sqrt{1 + \frac{4S\Gamma^*}{K_H}} - 1 \right) = \frac{1}{2} \frac{K_H}{\Gamma^*} (\sqrt{1 + A^*} - 1) \quad (32)$$

The quotient of the two ion concentrations are:

$$\frac{x_s^*}{x'_s} = \frac{D}{B} \cdot \frac{\Gamma'}{\Gamma^*} \frac{\sqrt{1 + A^*} - 1}{\sqrt{1 + A'} - 1}; \quad A' = \frac{4S\Gamma'}{K_H} \quad (33)$$

Or in a more practical form:

$$\frac{x_s^*}{x'_s} = \left( \sqrt{1 + A' \frac{D}{B}} + 1 \right) \frac{\sqrt{1 + A^*} - 1}{A^*} \quad (34)$$

The alkaline error is:

$$\Delta \varepsilon = \frac{RT}{F} \ln \left\{ \frac{\gamma_H^*}{\gamma'_H} \left( 1 + K \frac{a_K}{a_H} \frac{\gamma'_H}{\gamma'_K} \right) \left( 1 + \sqrt{1 + A' \frac{D}{B}} \right) \left( \frac{\sqrt{1 + A^*} - 1}{A^*} \right) \right\} \quad (35)$$

Leaving the variation of the activity coefficients again out of consideration:

$$\Gamma' \approx \Gamma^* = \Gamma; \quad A' \approx A^* = A \quad (36)$$

$$e^{\left( \frac{\Delta \varepsilon \cdot F}{RT} \right)} = \exp = B \left( \sqrt{1 + A \frac{D}{B}} + 1 \right) \left( \frac{\sqrt{1 + A} - 1}{A} \right) \quad (37)$$

This expression is to be more difficultly treated and contains three constants, namely the ion exchange constant ( $K$ ) the relation of the dissociation constants ( $K_H/K_K$ ) and the  $A$  constant, which is proportional to the total silicate concentration and the quotient of the acid dissociation constant.

It is very likely that  $A$  is a very high number.

If  $A \gg 1$  and  $\sqrt{A} \gg 1$  (for instance  $A > 10^8$ )

$$\frac{\sqrt{1+A}-1}{A} \approx \frac{1}{\sqrt{A}} \quad (38)$$

In the case of high  $A$  values and a small alkaline error:

$$\exp = e^{\frac{\Delta \varepsilon \cdot F}{RT}} = \sqrt{B \cdot D} = \sqrt{\left(1 + K \frac{a_K}{a_H}\right) \left(1 + K \frac{K_H}{K_K} \frac{a_K}{a_H}\right)} \quad (39)$$

Apart from that, also assuming that  $K_H/K_K$  is a very small number ( $\ll 10^{-4}$ )  $D \approx 1$  and

$$\exp = \sqrt{B} = \sqrt{1 + K \frac{a_K}{a_H}}$$

i. e.

$$\Delta \varepsilon = \frac{1}{2} \frac{RT}{F} \ln \left(1 + K \frac{a_K}{a_H}\right) \quad (40)$$

transforming in analogy with (15)

$$\log (\exp^2 - 1) = \log (K \cdot a_k) + \text{pH} \quad (41)$$

In this log therefore  $(\exp^2-1)$  has to supply in the function of pH a straight line of a slope  $\text{tg } \delta = 1$ . Calculating by the derived relation and ascribing different values to the constants the values of  $\log (\exp-1)$  (Fig. 3) resp.  $\log (\exp^2-1)$  (Fig. 4) and plotting them in the function of

$$\log \left( K \cdot \frac{a_K}{a_H} \right)$$

linear curves are obtained through many unities the tangent of which is, in general, smaller than unity and increases with the values of  $K_H/K_K$ .

The relations thus derived are not in contradiction with experience. They give an explanation for a behaviour for which no one could have so far given by using the old theory. A good agreement is found with the Li-error, which from the point of view of the other theory had an irregular behaviour

(Fig. 4). The constants of the curves in good agreement with the Li-curve is the ion exchange constant between the  $H_3O^+$  and the Li-ions :  $K = 10^{-11}$   $K_H/K_K = 10^{-4}$  the quotient of the dissociation constants in the glass. As a matter of course owing to the small number of reliable measurements available, the validity of this relation and the justification of the physical assumptions is difficult to control. This is particularly difficult because there is no known method for the determination of the dissociation constants, the ion capacity and the activity coefficients in glass. It may be, however, that there will be a possibility when the investigation of the electrochemical behaviour

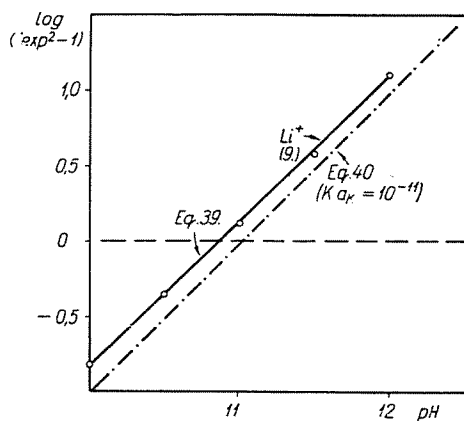


Fig. 4

of the ion exchanging resins also analogous in this respect with the glass electrode.

The second neglect in equation (10), the variation of the activity coefficients owing to the change of the alkali concentration in the glass phase. Hence the problem is whether the following assumption was justified:

$$\frac{\gamma_H^*}{\gamma_H'} = 1 \quad (1)$$

As there is question of ions, it is probable that the activity coefficient varies and that it is first of all and mainly due to the change of the electrostatical interaction. Assuming this it can be said that the part containing the activity coefficient of the chemical potential is equal to the "lattice energy" of the ion-network in the glass phase. If the ions are regularly placed (for instance similarly to the NaCl lattice) the lattice energy would be proportional to the cube root of the ion concentration. Hence

$$-RT \ln \gamma = \text{konst.} \sqrt[3]{x_2'} \quad (42)$$

Therefore

$$\frac{RT}{F} \ln \frac{\gamma_H^*}{\gamma_H'} = \text{konst}' \cdot (\sqrt{x_s'} - \sqrt{x_s^*}) \quad (43)$$

For quantitative calculations the ion concentration in the glass ought to be known (ion capacity), the dissociation constants and before all the structure of the whole system. Qualitative conclusions could be drawn in any case.

If  $K_H/K_K < 1$ , then also the ion concentration increases with the alkaline error, therefore the value of the activity coefficient decreases. Hence

$$x_s^* < x_s' \quad \gamma_H^* > \gamma_H' \quad (44)$$

thus the value of the alkaline error is smaller than the value computed by the neglect.

A divergency of a similar kind is caused by the neglect according to which

$$\frac{4S}{K_H} \cdot \frac{\gamma_s' \cdot \gamma_H'}{\gamma_{sH}'} = \frac{4S}{K_H} \cdot \frac{\gamma_s^* \cdot \gamma_H^*}{\gamma_{sH}^*} = A \quad (45)$$

We have therefore the intention to take into consideration the expression  $A \frac{D}{B}$  had to be multiplied by a number smaller than unity, and the value of this factor decreases with an increasing alkaline error.

Briefly summarizing the results the following can be stated: the glass electrode in an acid medium can be considered as a simple hydrogen electrode, whereas in an alkaline medium as a hydrogen alkali mixture electrode. Its behaviour can be characterized by the equilibrium constant of the hydrogen alkali ion interchange change.

It follows from this theory that the superficial layer of the glass in equilibrium with the aqueous solution is completely alkali-free. For very high alkali concentration an alkali ion is taken up by the glass and the alkaline error is due just to this fact. The anions of the silicate lattice space may be in dissociation equilibrium with the hydrogen resp. alkali ions of the glass. In an alkaline medium also this equilibrium is displaced by the ion exchange and the value of the alkaline error is affected by this potential.

The whole derivation refers to a monovalent ion only. A general explicite solution extended for polyvalent ions encounter insurmountable difficulties.

### Summary

The glass electrode in an acid medium was considered as a simple hydrogen electrode, and in an alkali medium as a hydrogen—alkali mixture electrode. Its behaviour can be characterized by the equilibrium constant of the hydrogen-alkali ion exchange ( $K$ ).

$$\Delta \varepsilon = \frac{RT}{F} \ln \left( 1 + K \frac{a_K}{a_H} \right)$$

Considering the possibility that the anions of the silicate lattice may be in dissociation equilibrium with the hydrogen resp. alkali ions of the glass, signifies a further development of the theory. Considering this effect a more general equation for the alkaline error has been derived, by which an explanation might be given for different phenomena, in a more general way, as by the simple formula of the mixture electrodes.

The alkaline error is :

$$\Delta \varepsilon = \frac{1}{2} \frac{RT}{F} \ln \left[ \left( 1 + K \frac{a_K}{a_H} \right) \left( 1 + K \frac{K_H}{K_K} \cdot \frac{a_K}{a_H} \right) \right]$$

Where  $K_H$  and  $K_K$  the dissociation constants of the silicate anions of the glass,  $a_H$  and  $a_K$ : the activities of the hydrogen and alkali ions, respectively.

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K. OLÁH, Budapest XI. Sztoczek u. 2. Hungary