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Dynamics of the Potential and the Mechanism of Action of Ion-selective Glass Electrodes

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Studies on the dynamics of the potential of glass electrodes with hydrogen and metal ion functions are considered. The transient processes occurring in the concentration jump in the region of response to one cation and with partial or complete transition to response to another cation are classified. The transition phenomena are described on the basis of the thermodynamics of ion exchange and diffusion kinetics in the liquid and solid phases. The influence of ion-exchange processes in the surface layers of glasses and at the interface with the solution on the dynamics of the glass electrode potential is considered. The bibliography includes 90 references.

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I. INTRODUCTION

Ionometry—potentiometry using ion-selective membrane electrodes (ISE) of different types and designed for different purposes—has been developing vigorously during the last decade. Numerous monographs, collections of papers, and reviews dealing with the development, principles of operation, and applications of ISE have been published; a specialist journal began publication in 1979.[1] However, in this stream of information there has been a surprisingly small proportion of studies devoted to the dynamic properties of ion-selective electrodes. This was already noted in the first theoretical review of the dynamics of the ISE potential[2]. Since then the position has altered somewhat; at any rate, among the characteristics of ISE mention is now always made of the time when they attain a stationary potential.

The study of the dynamics of the potential of ISE is important primarily for their practical applications as devices whereby processes can be monitored potentiometrically and regulated. In industrial apparatus and in research carried out using ISE it is necessary that the response time of the ISE to a change in the concentration of the relevant substance is shorter than the time taken to complete the given process with participation of this substance. The response time of ISE is influenced by a multiplicity of factors: the nature of the membrane of the ISE, their design, the hydrodynamic and temperature conditions of the experiment, the concentration and qualitative composition of the solution, etc. The knowledge of the quantitative relation between these factors and the ISE response time determines the correct employment of such electrodes.

The present review deals mainly with theoretical aspects of the problem. A thermodynamic theory of the membrane potential of ISE with membranes of glass or other ion-exchange materials has now been established. According to this theory, the stationary membrane potential consists of interfacial (Donnan) potential jumps on either side of the membrane and the diffusion potential within the membrane phase, determined by the opposed streams of ions involved in the exchange and by the difference between their mobilities ($\bar{u}$). The equilibrium mobilities, more precisely their functions such as the transport numbers $\bar{t}_i$ and their ratios, enter into important characteristics of the electrode function such as the slope[3] of the relation between E and the logarithm of the ionic activity:

$$dE/d\ln a_i = \bar{t}_i RT/F, \quad (1)$$

the potential coefficient of the selectivity of the function in the system of ions I^+ and J^+:

$$K_{ij}^{pot} = K_{ij}\bar{u}_j/\bar{u}_i, \quad (2)$$

and Nikol'skii's fundamental equation of the thermodynamic ion-exchange theory of ISE[4]:

$$\varphi = \varphi^0 + \frac{RT}{F}\ln(a_i + K_{ij}^{pot}a_j). \quad (3)$$

Here ϕ is the electrode potential, ϕ^0 the standard potential, E the e.m.f. of the galvanic cell, a_i and a_j are the activities of the ions I^+ and J^+ in solution, $\bar{u}_i$ and $\bar{u}_j$ their mobilities in the glass, K_{ij} is the ion exchange constant (the energy factor), $\bar{u}_j/\bar{u}_i$ the migration factor, R the gas constant, T the absolute temperature, and F the Faraday.

Information about the migration factor cannot be obtained from the potentiometric experiments alone. For this purpose, additional experiments are required, particularly the study of the fluxes of ions entering and leaving, the kinetics of the attainment of a steady potential, etc. It is not clear *a priori* whether the ionic mobilities in the surface layers of the glass, altered by the interaction with solutions, are the same as for the unchanged glass. In kinetic experiments components of the potential which disappear in the stationary state may be manifested.

For various reasons, the present review will be confined to glass electrodes (GE) of different kinds and designed for different purposes. Firstly, GE, particularly those for potentiometric pH titrations, are the most widely used ISE in both laboratory practice and for industrial monitoring and regulation. Secondly, the equilibrium (stationary) properties of GE have been most thoroughly investigated. Thirdly, the theory of the stationary electrode behaviour of Ge has been most thoroughly developed and in this respect GE can serve as a kind of model for other ISE, at least those with an ion-exchange membrane. It has been suggested that the kinetic concepts developed for GE can also be partly extended to other ISE and conversely.

The results of the study of the dynamic properties of GE will be considered mainly from the standpoint of the mechanism of their action under particular experimental conditions. Attention has been concentrated on the electrochemical method of concentration jumps[5] as one which is most consistent with, on the one hand, the high-resistance system investigated and, on the other hand, with the usual conditions under which GE

are employed. If necessary, results (hitherto few but nevertheless significant) obtained by other electrochemical methods, involving the passage of a current through a GE from an external source, are invoked for the purpose of explanation.

The term transient processes will be given to the variation with time of the potential on passing from one stationary potential level to another. In the literature the term transient phenomena is sometimes understood as the non-monotonic variation of the potential during this period, but we shall employ it in its wider significance. As regards the classification of transient processes, the following can be distinguished for GE: (1) when the concentration of the solution is altered in the region of a stationary electrode function with respect to the given cation; (2) in the region of transition from the response with respect to one cation to the response with respect to another; (3) in the region of "acid deviations" associated with the influence of the anion on the cationic function; (4) when the solvent is altered and in non-aqueous solvents.

With few exceptions, the last two cases will not be considered in the present review. The consideration of the third case would require too much space; the available data are very contradictory, although there is no doubt that the potential varies rapidly with time in the region of the acid error (see, for example, Bates[6]). In the fourth case there is also a possibility of the observation of transient phenomena (see, for example, Ivanovskaya[7]), but, so far as the present author is aware, specific kinetic studies on the influence of the change of the solvent have not been carried out.

The principal aim of the present review is to survey the available data on the dynamics of the attainment of a steady potential of GE under various conditions and the results of attempts at a quantitative description of the transient phenomena and their theoretical treatment.

II. DYNAMICS OF THE POTENTIAL IN THE REGION OF RESPONSE TO ONE CATION

1. Experimental Results

Table 1 presents the results referring to the H^+ function of GE for potentiometric pH titrations and Table 2 deals with the dynamics of GE in the region of response to different metal ions. By virtue of specific features, the causes of which will become clear subsequently, the initial columns in Tables 1 and 2 differ somewhat. In Table 1 only H^+ is the potential-determining ion and it is not indicated. The preparation of GE, i.e. preliminary soaking in any one solution whose composition is in the region of the H^+ function, is important only for experimental, but not industrial, pH titration glasses and, if necessary, this will be mentioned in the text. The metal ion function of GE made of any glass and their dynamic properties are influenced significantly by the preliminary treatment and a separate column is provided for its characteristics in Table 2.

All the results for the H^+ function have been obtained under the conditions of special dynamic experiments with the fastest possible concentration jump. The authors of earlier

Table 1. Dynamics of the potentials of glass electrodes in the region of their H^+ function.

No.	Glass*	Solutions	Duration of concn jump, s	Response time or τ, s (20-25 °C)	Remarks	Refs.
1	NaCa-21$_4$06$_2$	buffer solution at pH > 1	$3\cdot10^{-3}$	$(3\div120)\cdot10^{-3}$; $\tau=3\cdot10^{-3}$	thickness of membrane 5-10 μm	8
2	lithium glass Electrofact 6C28		<1	$\tau_1=1.3$; $\tau_2=15$	flow rate 6 cm s^{-1}	9
3	NaCa-21$_4$06$_2$; general purpose lithium glass	acids in aqueous or aqueous organic solutions	—	—	classification of types of kinetic curves; extrapolation to $t=0$	10, 11
4	general purpose lithium glass	standard buffer solutions at pH 1-14, aqueous and non-aqueous	≪1	$t_{0.5}=0.25$ (aq.) $t_{0.5}=50$—200 (non-aq.)	response time in aqueous solutions shorter than the time of replacement of solutions	12
5	LiCsLa (HHT) type ESL-41-04	buffer solutions pH 1 ⇌ (3-10)	not indicated	$\tau=23$; τ from 13 to 38; $\tau=62$ (pH 9→1); $\tau=144$ (pH 1→9)	in a flow cell in a non-flow cell with stirring in a non-flow cell without stirring—extrema; see text	14
6	lithium glass; Corning pH 476022; 476051. Thomas pH 4855-B15	buffer solutions	~1	$\tau=2.8$ **; $\tau=2.3$ **; $\tau=6.9$ **	in a stream; no information about solutions, flow rate, etc.	15
7	not indicated	strong acids, pH 3; alkalies, pH 11; CH_3COOH; HCl (10^{-3} N)+NaCl (0.1 N) ⇌ HCl (10^{-3} N); HCl (10^{-3} N)+$MgCl_2$ (0.1 N) ⇌ HCl (10^{-3} N)		$t_{0.8}=4$	flow rate 27-42 cm s^{-1}	16
			~1		extrema, see text	
8	HHT, Na-20	pH 2.1 ⇌ 3.05	~1	$\tau_3=0.3$ (87%); $\tau_2=6$ (13%); $\tau_3<0.3$ (>70%); $\tau_2\cong7$ (≅20%); $\tau_1\cong100$ (~10%)	exact compositions of solutions at pH 2.1 and 3.05 respectively: 0.009 N HCl + 0.001 N NaCl and 0.001 N HCl + 0.009 N NaCl	17—20
	NaAl-2010; NaAl-2704	HCl 0.1 ⇌ 0.01 N		$\tau_3=1.3$ (~50%); $\tau_2=7.1$ (~30%); $\tau_1=33$ (~20%); $\tau_3\sim1.4$ (~75%); $\tau_2\sim8$ (~15%); $\tau_1\sim45$ (~15%)	treatment of data in terms of Eqn. (13), see below. The average values of τ_i are presented for direct and reverse experiments together with approximate values of $\Delta E_i^0/\Delta E$(%)	

* The designations of the compositions of the glasses, when they are known, are based on a system which can be understood from the following examples: NaCa-21$_4$06$_2$ is a glass containing (mole %) 21.4 Na_2O, 6.2 CaO, and the rest, i.e. 72.4, SiO_2; NaAl-2704—27 Na_2O 4 Al_2O_3 and 69 SiO_2. If the quantitative composition is unknown, the known qualitative characteristics of the composition are indicated, the symbols of the elements indicating the oxides; SiO_2 is not indicated: LiAl(Li_2O–Al_2O_3–SiO_2); LiCsLa (Li_2O–Cs_2O–La_2O_3–SiO_2), etc. Sometimes commercial designations of the electrodes and glasses are given: HHT, Beckman 39 046, etc. The same designations are used in Table 2 and in the text.

** The values of τ at 300 K; the corresponding activation energies are 7, 4.3 and 2.2 kcal mol^{-1}.

studies, where metal ion functions were investigated, were interested in the GE dynamics only incidentally and attention was concentrated on the stationary potentials. Nevertheless useful kinetic observations, summarised in Table 2, were made in such studies.

The principal factor for subsequent analysis is the relation between the time of the concentration jump and the time of the electrode response. The latter is expressed either by the degree of completion of the transient process between one stationary potential level and another ($t_{0.5}$, $t_{0.8}$, $t_{0.95}$) or simply by the time t when the process is believed to have been completed.

The majority of the potential–time curves in the region of variable concentrations under consideration are characterised by a monotonic exponential relation for which the following empirical expression will be adopted[2]:

$$E_t = E_1 + (E_2 - E_1)[1 - \exp(-Kt)], \quad (4)$$

where E_t is the e.m.f. at time t, E_1 and E_2 are the stationary e.m.f.'s in solutions *1* and *2*, and K is a constant. Henceforth, we shall use also the abbreviated formulation

$$\Delta E_t = \Delta E^0[1 - \exp(-t/\tau)], \quad (5)$$

where $\Delta E_t = E_t - E_1$, $\Delta E^0 = E_2 - E_1$, and $\tau = 1/K$.

The quantity τ is a convenient characteristic of an exponential transient process: $\tau \cong t_{0.63}$; $2\tau \cong t_{0.83}$; $3\tau \cong t_{0.95}$; $5\tau \cong t_{0.99}$. In certain cases the exponential approximation is satisfactory, while in others it is too inexact. Sometimes the process is described by the sum of several exponential relations[2,17-20] or other functions of time[2]. If the response times in Tables 1 and 2 are characterised by the quantity τ without further comment, the implication is that the exponential approximation is regarded as satisfactory.

Consideration of the "time of jump" and "response time" columns in Tables 1 and 2 leads to the conclusion that, in response to the concentration jump occurring over a period of

Table 2. Dynamics of the potentials of glass electrodes in the region of metal cation functions.

No.	Ion	Glass	Preparation of electrodes	Concn. range (–) or jump (⇌), equiv. litre^{-1}	Method and time of replacement of solution	Response time, s	Remarks	Refs.
1	Na^+	NaAl-1118, NaAl-2704	0.1 *N* NaCl, several days	$1.0—10^{-4}$	transposition accompanied by washing with water	$\leqslant 60$	properties stabilised after soaking for several hours	21
2	K^+	NaAl-2704, NaAlZn-270303, KAl-2005	0.1 *N* KCl, several months	$10^{-1}—10^{-4}$	ditto	10—20	properties stabilised after soaking for a week	21–23
3	Li^+	LiAl-2310 (BH-68), NaAl-1118	0.1 *N* LiCl, several days	$10^{-1}—10^{-2}$ $10^{-1}—10^{-2}$ 1—20	» » »	$>15 \cdot 60$ $\sim 15 \cdot 60$ $<15 \cdot 60$	$S_{exp} = S_{theor} = 2.3\,RT/F$ $S_{exp} < S_{theor}$ $S_{exp} \approx S_{theor}$, flow type electrode	21–23
4	Ag^+	NaAl-1118, NaAl-2704	0.1 *N* $AgNO_3$, not less than 24 h	$10^{-1}—10^{-6}$	»	~ 60	—	21, not transl. ditto 24
5	Tl^+	KAl-2005	0.1 *N* $TlNO_3$, not less than 12 h	$10^{-1}—10^{-4}$	»	$2 \cdot 60$	—	21
6	NH_4^+	NaAlZn-270303	0.1 *N* NH_4Cl, several months	$10^{-1}—10^{-4}$	»	10—20	see remark concerning item 2	21
7	Na^+	LiAl-2310 (BH-68), LiAl (BH-104)	0.1 *N* NaCl, storage	$10^{-1} \rightleftharpoons 10^{-2}$, $10^{-3} \rightleftharpoons 10^{-4}$	transpostion	$(2—7) \cdot 60$	wiping better than washing; response time is longer in dilute solutions	25
8	Na^+, K^+, Li^+, Rb^+, Cs^+	NaAl, NaB, NaTi, NaAlP, LiAl	soaking in solution of triethanolamine hydrochloride; pH 7.8	$0 \rightarrow 10^{-4} \rightarrow$ $\rightarrow 10^{-3} \rightarrow$ $\rightarrow 10^{-2} \rightarrow$ $\rightarrow 10^{-1} \rightarrow 1.0$	transposition	$(5—60) \cdot 60$	"unprepared" electrodes, see text	26
9	Na^+, K^+	NaAl-2704 (Beckman 39137)	not indicated	$0 \rightleftharpoons 0.05 \rightleftharpoons$ $\rightleftharpoons 0.5 \rightleftharpoons 1.0$	immersion or dilution; 1.5 s	1.5—3.1		27
10	Na^+	NaAl-2704 (Beckman 39047) LiAl (Beckman 39046)	0.1 *N* NaCl, at least 24 h	$0.05 \rightarrow 0.01$	turbulent stream, 4.5×10^{-3} s	$\tau = 12.2 \cdot 10^{-3}$; $\tau = 27 \cdot 10^{-3}$	our calculation: pure RC-effect	28
11	Na^+, Li^+, Ag^+, NH_4^+, K^+	NaAl-2704 (Beckman 39047)	0.1 *N* M^+, at least 24 h	$0.05 \rightarrow 0.01$	ditto	$t_{0.8} = 10 \cdot 10^{-3}$; $t_{0.9} = 0.2$	—	28
12	Na^+, Li^+, Ag^+	LiAl (Beckman, 39046)	ditto	ditto	»	—	pure RC-effect	28
13	K^+, NH_4^+	ditto	ditto	$0.05 \rightarrow 0.01$; $0.05 \rightarrow 0.1$	turbulent stream, 4.5×10^{-3} s	$\lg[(E_{eq} - E_t)/E_{eq}]$ varies linearly with $t^{1/2}$ during a period up to 2 min	—	28
14	Na^+	NaAl-2704, NaAl-2010 LiAl-1608	0.1 *N* NaCl, six days	$0.1 \rightleftarrows 0.01$	1 s	$\overrightarrow{\tau_3} = 0.6$ (100%); $\overleftarrow{\tau_3} = 0.4$ (100%); $t_{0.95} = 6$	calculation by Eqn.(13)	19, 20
15	K^+	NaAl-2704 NaAl-2010	0.1 *N* KCl, six days	ditto	1 s	$\overrightarrow{\tau_3} = 0.6$; $\overrightarrow{\tau_2} = 5.7$; $\overleftarrow{\tau_3} = 0.6$; $\overleftarrow{\tau_2} = 2.7$; $\overrightarrow{\tau_3} = 0.5$ (100%); $\overleftarrow{\tau_3} = 0.7$; $\overleftarrow{\tau_2} = 11$	calculation by Eqn.(13)	19, 20

approximately 1 s, the transient process in the region of the H^+ and M^+ functions is completed during a period less than 10 s; when the solution is changed (over a period of the order of milliseconds with the aid of special devices) the response time is also of the order of milliseconds. The latter result is of fundamental importance both for the characterisation of the electrode and for the understanding of the essential features of the processes controlling the dynamics of the attainment of a steady potential. We shall consider this in greater detail.

It is highly likely that the arrest of the establishment of a steady potential after the concentration jump achieved[8,28] over a period of several milliseconds is caused by the charging of a capacitance C through an ohmic resistance R: $\tau = RC$. It has been shown in at least one study[28] that, after an "instantaneous" change in the Na^+ concentration from 0.05 to 0.01 M, the $\Delta E_t - t$ curves for Beckman 39 047 and 39 046 glass electrodes (NaAl-2704 and LiAl respectively) resemble the curves after the "instantaneous" application of an $(RT/F) \ln (0.05/0.01) = 38$ mV potential pulse. The $\Delta E_t - t$ curves are different for each electrode (in conformity with the difference between the ohmic resistances).

For the same types of glasses (but for larger GE), $\tau = 1.8$ and 4.3 ms at 25 °C have been measured[29] (see also Lakshminarayanaiah[13]); hence the capacitances for the corresponding R were found to be 40 and 32 nF cm^{-2} respectively. For a tenfold difference between the values of R the values of τ were found to differ[28,29] approximately by a factor of two (12.2 and 27 ms—see Table 2). It may be that the values of τ include a contribution from an electrochemical transient process.

It has been found[30] that after a stepwise (after a period of approximately 10 μs) change in the potential of a GE of NaAl–2704 glass in NaCl solutions the relaxation process is completed in approximately 10 ms, which led to the conclusion that the standard exchange current density for the transient process $Na^+(glass) \rightleftharpoons Na^+(soln)$ is greater than 2×10^{-6} A cm^{-2}. All these facts permit the conclusion that the relaxation time for the transient processes $H^+(glass) \rightleftharpoons H^+(soln)$ and $Na^+(glass) \rightleftharpoons Na^+(soln)$ for GE subjected to an appropriate preliminary treatment is of the order of milliseconds or less.

It is seen from the data in Tables 1 and 2 that, for a slower change of solution, over a period of approximately 1 s, the GE response time is also approximately 1 s or (frequently) longer. One should note that in those cases where it was possible to observe processes completed in milliseconds after the change of solution, investigators did not follow the subsequent variation of the potential. Conversely, in observations on processes lasting seconds and minutes, we find that the millisecond process has already been completed and one can only conclude that the two groups of processes may have different mechanisms. Two groups of theories, devoted to the kinetics of glass and in general ion-selective electrodes, correspond to the two groups of processes and their characteristics.

2. Theoretical Treatment

The theories of the first group are based on the hypothesis of an energy barrier which must be overcome by ions in order to pass from solution to the glass and conversely[12,31] (for a description of the results of Johansson and Norberg[12], see Lakshminarayanaiah[13]). The theories of the transient overvoltage are analogous to this approach in electrochemical kinetics[32]. In theories of the second group the diffusion processes in the solution and in the glass (diffusion kinetics) are considered to be the cause of the slow attainment of the GE potential. Both groups of theories have been considered by Shatkay[2] and we shall confine ourselves to a brief description of the conclusions of earlier studies and a more detailed consideration of later investigations, which have not been included in the earlier review[2].

It may be expected, in confirmity with experimental data (Tables 1 and 2), that the efforts of theoreticians should be directed to the explanation of the exponential $\Delta E_t - t$ relation. Indeed, when a number of more or less well-founded assumptions are made, both groups of theories lead to equations of type (4) or (5). Judging from Shatkay's review[2], a particularly large number of assumptions, simplifications, and simple errors have been made by Rechnitz and Hameka[31]; fewer were made in Johansson and Norberg's study[12]. The physical significance of the parameter K in Eqn.(4) is difficult to interpret in this approach and its numerical value is difficult to predict.

As a result, in order to confirm the relation of type (4) which they obtained, Rechnitz and Hameka[31], for example, used the results of a study[26] of the dynamics of the attainment of the K^+ function of GE made from glasses based on the $Na_2O-Al_2O_3-SiO_2$ systems not subjected to an adequate preliminary treatment, as a result of which the attainment of a steady potential took tens of minutes. The same data have been used[2] for the correlation analysis of the applicability of Eqn.(4) and others. Johansson and Norberg[12] used their own data, obtained in aqueous and non-aqueous solutions (Table 1), to test this equation. They used $t_{0.5}$ as a characteristic of the time; this quantity proved to be three times greater for non-aqueous solutions than for aqueous solutions. The time $t_{0.5}$ which they found[12] for the GE response in aqueous solutions is closer to that found by Disteche and Dubuisson[8] and Rechnitz and Kugler[28] and also by Buck and Krull[29] and Kiprianov et al.[30] for the relaxation of electrical impulses. According to Buck's classification[33-35], this is the relaxation time of the space charge in the conducting system.

The second group of theories is based on the ideas of diffusion kinetics. It is assumed that the diffusion of ions to the exchange site in the glass takes place slowly with a coefficient D, via a diffusion layer of the solution with a thickness δ, which retards the attainment of a steady potential, while the attainment of ion-exchange equilibrium at the glass-solution interface (including the exchange of identical ions) is much faster. The Nernst equation holds at any instant t in the following form:

$$\varphi_t = \varphi^0 + \frac{RT}{F} \ln \frac{c_{k,t}}{\bar{c}_k}, \qquad (6)$$

where ϕ_t is the potential at the interface, ϕ^0 its standard value, $c_{k,t}$ the concentration of the potential-determining k^{th} ion in solution in the immediate vicinity of the exchange site, and $\bar{c}_k$ its concentration in the solid phase, which is constant under the conditions of the k^{th} function of the GE. Thus the determination of the $\phi_{k,t} - t$ or the $\Delta E_t - t$ relation reduces to determining the $c_{k,t} - t$ relation.

The latter is obtained as a solution of the differential equation of Fick's Second Law in the following form, for example [15]:

$$c_t = c_1 + (c_2 - c_1) \left\{ 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp \left[-\frac{\pi^2}{4} \frac{D}{\delta^2} (2n+1)^2 t \right] \right., \qquad (7)$$

where c_1 and c_2 are the concentrations in solutions *1* and *2* and the subscript k has been omitted.

The expansion is usually restricted to the first term of the series ($n = 0$), whereupon we obtain for the potential:

$$\varphi_t \approx \varphi_1 + \frac{RT}{F} \ln \left\{ 1 + \frac{c_2 - c_1}{c_1} \left| 1 - \frac{4}{\pi} \exp(-t/\tau) \right| \right\}, \qquad (8)$$

where

$$\tau = \frac{4}{\pi^2}\frac{\delta^2}{D} \approx \frac{\delta^2}{2.5D} \quad (8a)$$

Morf et al.[36] obtained the equation for ϕ_t in a somewhat different form:

$$\varphi_t = \varphi_2 + \frac{RT}{F}\ln\left[1 - \frac{c_2 - c_1}{c_2}\exp(-t/\tau)\right], \quad (9)$$

where

$$\tau = \delta^2/2D. \quad (9a)$$

Buck[35] formulated both equations [(8) and (9)] in the form usually employed in electrochemical literature:

$$\varphi_t = \varphi_1 + \frac{1}{f}\ln\left\{\exp(f\Delta\varphi) - \frac{4}{\pi}[\exp(f\Delta\varphi) - 1]\exp(-t/\tau)\right\} = \varphi_2 + \frac{1}{f}\ln\left\{1 - \frac{4}{\pi}[1 - \exp(-f\Delta\varphi)]\exp(-t/\tau)\right\}, \quad (10)$$

where $f = F/RT$, τ is defined by Eqn.(8a), and $\Delta\phi = \phi_2 - \phi_1$. In further simplifications of Eqns.(8) and (9) it is assumed that the concentration jump $\Delta c = c_2 - c_1$ and the corresponding potential jump $\Delta\phi$ are small, whereupon exponential equations are obtained, for example:

$$\varphi_t = \varphi_1 + \frac{RT}{F}\frac{\Delta c}{c_1}\left[1 - \frac{4}{\pi}\exp\left(-\frac{t}{\tau}\right)\right], \quad (11)$$

which can be reduced to equations of type (4) and (5) describing the $\Delta E_t - t$ relation for very short t.

The present author's calculation[20] by Eqns.(8) and (11) for specified $\tau = 1$ s and $\Delta c/c_1$ varying in the range $1 \leq |\Delta c/c_1| \leq 9$ demonstrated the following features. Firstly, the curves corresponding to an increase ($c_2 > c_1$) or decrease ($c_2 < c_1$) of concentration are markedly asymmetric, particularly for large Δc. With increase of the concentration of the ion, the curves are steeper than with its decrease. Secondly, the converse representation of Eqns.(8) and (11) on a semilogarithmic scale ($\lg \Delta E - t$) leads to linear plots passing through calculated points in the region where $t > 0.5$ s. For $t < 0.5$ s, the points deviate from the straight line; this is always the case for Eqn.(8) and for Eqn.(11) only when $|\Delta c/c_1| > 2$. Consequently extrapolation of the straight line from $t > 0.5$ s to $t = 0$ leads to a value of ϕ_1 which deviates more or less significantly from a specified value. However, it is important to note that the values of τ calculated on this basis are 1 ± 0.1 s, i.e. the "specified" value of τ is approximately maintained. From this it follows that in Eqn.(5), which we adopted previously as entirely empirical, the quantity τ can now be regarded as theoretically justified and can be calculated from Eqns.(8a) and (9a) for diffusion kinetics in the layers near the electrode.

The concept of diffusion through the electrode layer of solution (unstirred, Nernst, adhering, stagnant) as the stage which determines the retardation of the attainment of the steady potential of the GE has been used in many studies, including those quoted in Table 1.[9,15,16] The order of magnitude of the quantity τ corresponding to this process can be readily estimated using the known (for electrolyte solutions) thickness of the diffusion layer δ and the diffusion coefficient D of the binary electrolyte or the diffusion coefficient of the ion in the supporting electrolyte with the aid of the criteria defined by Eqns.(8a) or (9a). For $\delta \leq 10^{-2}$ cm and $D \cong 10^{-5}$ cm^2 s^{-1}, it is found that $\tau = 0.5$–5 s. The values of τ or τ_3 in Tables 1 and 2, for experiments where the change of solution was achieved over a period of approximately 1 s, are of the same order of magnitude, as already mentioned.

The study of Hershkovitch et al.[16], not included in Shatkay's review[2], constitutes a significant development of the above concepts. The authors regard the process as the reciprocal diffusion of ions and not as the diffusion of the electrolyte as a whole, as in the majority of previous instances. Account was also taken of the possibility of the generation or disappearance of active ions as a consequence of the reaction in the layer near the electrode. The fundamental differential equation has the following form:

$$\frac{\partial c_j}{\partial t} = D_j\frac{\partial^2 c_j}{\partial x^2} + R_j - \sum_k \frac{z_k}{z_j}(D_k - D_n)\frac{\partial}{\partial x}\left(t_j\frac{\partial c_k}{dx}\right), \quad (12)$$

where subscripts j, k, and n correspond to ions (cations and anions), z are the charges, x is the distance in the range $0 \leq x \leq \delta$, D are the diffusion coefficients, tj is the transport number of the ion, and R_j is the rate of generation of the ion Jz_j.

For a solution of a strong binary electrolyte (acid or base), the first term is significant and the case discussed above obtains [equations of type (7) and (8)]. For solution flow rates of 27–42 cm s^{-1} in acid solutions at pH 3, the values of δ are in the range 0.014–0.016 cm and $t_{0.8}$ is up to 4 s. A satisfactory agreement has been achieved between the calculated and experimental curves. For a solution of a weak electrolyte (CH_3COOH), account is taken of R_j—in the present instance, the rate of dissociation. The experimental process is completed faster than predicted by the calculation, possibly owing to the obstacle-free penetration of electrolyte molecules through the charged component of the double layer. This can explain, in particular, the faster attainment of a steady potential in buffer solutions compared with unbuffered solutions. Finally, yet another special case was examined by Hershkovitch et al.[16]—mixed solutions of the type HCl + NaCl and HCl + $MgCl_2$. Experimental $\Delta E_t - t$ curves with extrema, due to the different mobilities of the two cations and the common anion in solution, were predicted and obtained for this case. Such extrema in the region of the H^+ function of the GE have been observed[14] in buffer solutions under unfavourable hydrodynamic conditions and in the region of metal ion functions by Friedman[22,37], Rechnitz[28,38], and Eisenman[21]. The above extrema, except that described by Mokhov and Leikvishvili[14], were usually attributed to the time-dependent sensitivity of the GE surface to one of the cations and will be considered in the next section. However, mention should be made of their possible "purely solution" origin.

Both in the study of Hershkovitch et al.[16] and in the studies quoted previously[9,15], as well as many others, the diffusion through the liquid "stagnant" layer is believed to be the main if not the only cause of the retardation of the attainment of a steady potential; for example, Hershkovitch et al.[16] did not even indicate the kind of glass used in the experiments. However, it has been noted[9] that, when an attempt is made to describe the attainment of a steady potential in later stages (for $t > 6$ s), it is found that this cannot be achieved with the aid of the exponential function (characterised by $\tau \cong 1$ s) used in the early stages and another exponential function (with $\tau \cong 15$ s) must be introduced. Markovic and Osburn[15] did not arrive at such conclusions, but in the case of one of the glasses they obtained an activation energy $E_a \cong 7$ kcal mole^{-1} for τ, which is greater than for "purely solution" diffusion. These facts necessitate the hypothesis of yet another process in the glass or at its interface with the solution. As already mentioned, the electrochemical exchange reaction is very rapid (over a period of milliseconds). It is natural to suppose that, for $\tau \cong 10$ s, we are dealing with diffusion in the solid phase.

Tables 1 and 2 present the results of a number of studies[17-20] in terms of the values of τ_i corresponding to the equation

$$\Delta E_t = \sum_{i=1}^{3} \Delta E_i^0 [1 - \exp(-t/\tau_i)], \quad (13)$$

where

$$\Delta E_i^0 = |E_{i\,t\to\infty} - E_{i,t=0}| \quad (13a)$$

is the jump in e.m.f. corresponding to the completion of the ith process;

$$\Delta E^0 = \sum_{i=1}^{3} \Delta E_i^0 \quad (13b)$$

is the overall jump in e.m.f. after the completion of all the processes. Thus $\Delta E_i^0/\Delta E^0$ is the contribution of the given process to the overall jump.

In the above studies not more than three exponential components were required to describe the dynamic GE curves with an average error of ±20% for identical GE subject to an error in the measurement of e.m.f. of 1 mV. The numbering of the exponential functions, starting from the "slowest", corresponds to the order in which the experimental curves are represented on the semilogarithmic scale. The "fastest" exponential function, characterised by $\tau_3 \leqslant 1$ s and $\Delta E_3^0/\Delta E > 50\%$ (frequently >75%) has been attributed[20] to processes involving the slow replacement of the stagnant layer of liquid near the electrode. The next exponential function ($2\text{ s} < \tau_2 < 20$ s; $10\% \leqslant \Delta E_2^0/\Delta E^0 \leqslant 30\%$) was attributed to the diffusion of acid within the pores of a thin (approximately 10^{-5} cm) surface layer of glass (see also Buck[39]). For glass Na-20, the activation energy for this process is approximately 7 kcal mole^{-1}. The quantities τ_3 and τ_2 "sense" the difference in the roughness and porosity of the GE surfaces, for example a flame-polished surface and a surface subjected to etching with an HF solution, the difference in the acid anion (HCl and H_2SO_4), and the direction of the change in the concentration of the solution.

The last exponential function ($\tau_1 \cong 100$ s with $\Delta E_1^0/\Delta E^0 \leqslant 10\%$) can be attributed, if it is manifested at all, to the mutual diffusion of the cations in the glass pores, i.e. in the solid phase; $D \leqslant 10^{-12}$ cm^{-2} s^{-1}. In many cases there are two exponential functions. For the Na^+ ion and GE made from sodium–aluminosilicate glasses, there is a single exponential function with the $\tau_3 \cong 1$ s and $\Delta E_3^0/\Delta E^0 = 100\%$. When the comments on the results of Rechnitz and Kugler[28] are considered (see Table 2), the only cause of the retardation of the GE response in this case is the diffusional change in the composition of the layer of liquid near the electrode.

As already stated in connection with Eqn.(5), the approach resulting in Eqn.(13) can be used as a purely empirical procedure[2,17-20]. The present author now believes that at least τ_3 has a theoretical justification [criteria defined by Eqns. (8a) and (9a)]; τ_2 and τ_1 can be treated by analogy. The quantities ΔE_i^0 are still empirical, although it is evident that $(RT/F)\ln(\Delta c/c_1)$ makes a large contribution to ΔE_3^0.

Attempts to derive Eqn.(13) theoretically have been described in the literature. For example, in relation to the F^--selective electrode with an LaF_3 membrane (which is sometimes regarded as an anionic analogue of GE), an equation has been derived[40] with two exponential components; however, one of these was attributed to diffusion and the other to a surface reaction. The corresponding experiment was carried out over the range 1–44 min.

Among empirical and semiempirical equations describing experimental data with a high degree of accuracy, there is a hyperbolic expression for the time variation[2,40]; in some time intervals it is more convenient to employ the dependence on $t^{1/2}$. These equations have been compiled by Buck[35].

III. TRANSITION FROM RESPONSE TO ONE CATION TO THE RESPONSE TO ANOTHER

1. Classification of Phenomena and Experimental Results

In the given case it is necessary to take into account the involvement of at least two and frequently three potential-determining cations in the electrode reaction and one of the cations can have a multiple charge.

In the previous section the response to only one cation I^+ was as a rule considered. The presence of an "interfering" ion for a specified ratio of the concentration of I^+ and J^+ did not affect the equilibrium potential of the GE in the region of its I^+ function. This section deals with the dynamics of the GE potential and with the form of the kinetic curves in cases where the presence of the cation J^+ (or J^{2+}) has the following effects: (1) does not affect the equilibrium potential in the region of the I^+ function but does affect the dynamics of its attainment[14,16,22,28,37,38,41-43]; (2) causes a deviation from the I^+ function and a transition to the "mixed" $I^+ + J^+$ function[28,38,41,43-48]; (3) causes a transition to the full J^+ function[19,21,47,49-61].

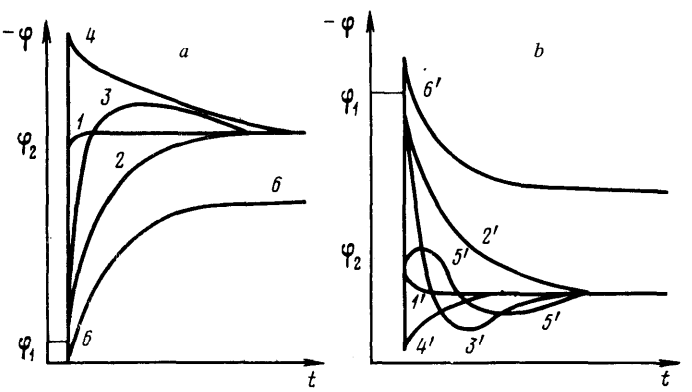


Figure 1. Schematic representation of dynamic curves for two cases: for transient processes in the region of I^+ function in the presence of J^+ or on transition to (from) the mixed $I^+ + J^+$ function: *a*) dilution with respect to I^+; *b*) concentration with respect to I^+; for transient processes with almost complete replacement of I^+ by J^+ in solution: *a*) when the stationary selectivity of the GE with respect to I^+ is higher than with respect to J^+; *b*) when the selectivity is lower. Curves 5′, 6, and 6′ refer solely to the second case—see Bobrov and Rudenko[54] and Belyustin et al,[19] respectively.

The first two cases are frequently encountered in practical applications of GE and the last is of great theoretical interest. The phenomena associated with the first two cases have been studied using pH titration GE made from lithium and sodium glasses for the pairs of ions H^+–Na^+,[14,16,41,44-48] H^+–Mg^{2+},[16] and H^+–Li^+;[45,47] series based on the increasing influence of M^+ and M^{2+}, determined from the height of the extremum on the ϕ–t curve (see Fig.1 above) have been published for GE

with metal ion functions made from NaAl-1118 [23,37,42,43,49] and NaAl-2704 [28,38] glasses for the pairs of ions Na^+–K^+, [22,37,42,49] Na^+–M^+ ($NH_4^+ < Cs^+ < Rb^+$, K^+), and Na^+–M^{2+} ($Mg^{2+} \leq Co^{2+}$, Ni^{2+}, $Zn^{2+} < Ca^{2+} < Mn^{2+} < Sr^{2+} < Cd^{2+} < Cu^{2+} < Ba^{2+} < Pb^{2+}$).

The third case—transition from the full H^+ function to the postulated M^+ function in an alkaline solution ($M^+ = Li^+$, Na^+, or K^+)—obtains in the study of GE made from glasses based on the Na_2O–CaO–SiO_2 system[47], pH titration lithium glasses[47], and the model lithium and sodium silicate glasses Li-27, LiB,[50] Na-16, Na-25,[51] and Na-20 [52–54] (the numerous studies by Bobrov and coworkers on the dynamics of the potential of GE made from non-silicate glasses are not considered here; they have been surveyed elsewhere[57,58]). For GE with a predominant response to metal ions, the transiton

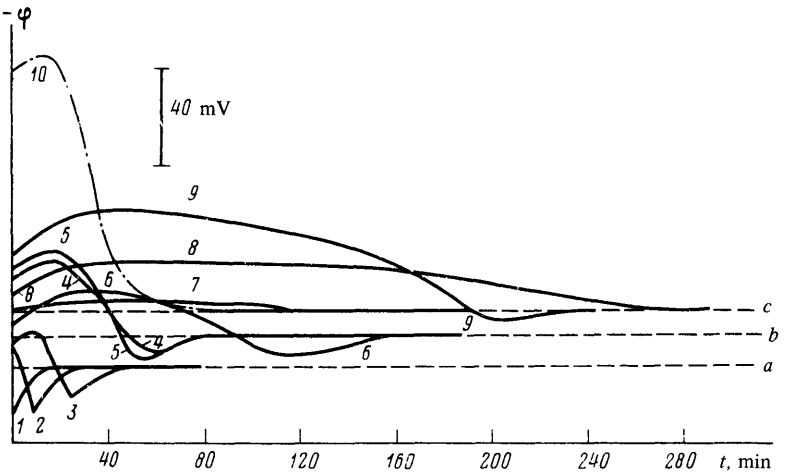


Figure 2. Dynamics of the potential of a GE of Na-20 glass in a buffer solution at pH 6,86 after treatment in a solution of the same pH and then in 1 *N* NaOH; GE subjected to a preliminary treatment for 3–4 min in a 1 : 1 HF + HCl solution at pH −0,6 *a*)–*c*) stationary potential levels corresponding to soaking for 1,2–3, and 7 days in a solution at pH 6.86 at 17–20 °C; duration of treatment (in days) in solution at pH 6,86: *1*) 0; *2*) 2/24; *3*) 5/24; *4*) and *5*) 2; *6*) 3; *7*) 10–7; duration of treatment (in days) in 1 *N* NaOH solution: *1*)–*4*), *6*), and *8*) 1; *5*) 9; *7*) 3/24; *9*) 7; *10*) 1/24 (90 °C) and 1 (17 °C). The figure has been constructed on the basis of the data of Bobrov and Rudenko[54] with the authors' permission.

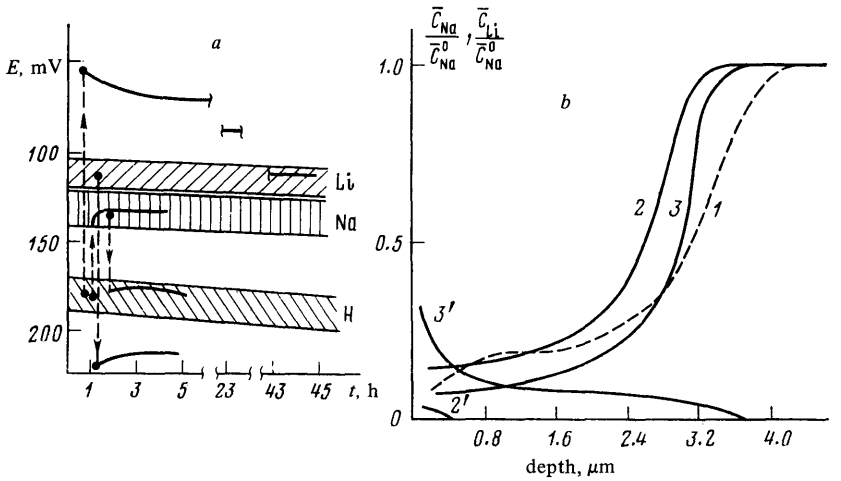


Figure 3. Dynamics of the potential of a GE of NaAl-2704 glass soaked for eight days in 0,1 *N* HCl, NaCl, or LiCl with replacement of one solution by another (a) and the corresponding distribution of the concentrations of Na (curves *1*–*3*) and Li (curves *2'* and *3'*) in the surface layers of the glass (*b*) after soaking the latter for 8 days in 0.1 *N* HCl and subsequent treatment in 0.1 *N* LiCl for different periods (days): *1*) 0; *2*) and *2'*) 1; *3*) and *3'*) 3. The shaded bands (representing the experimental scatter of data for a series of electrodes) correspond to stationary levels of potential obtained after prolonged soaking in 0,1 *N* HCl (H), NaCl (Na), or LiCl (Li).[59]

from the region of the H^+ function to that of the M^+ function has been studied using LiAl,[19,55] LiAlGe,[56] NaBAl, NaAl–2704, and NaAl-1118 [29] glasses. For GE of this type in neutral and alkaline solutions containing Na^+ or K^+, the transient phenomena, in which the involvement of the H^+ ion is not postulated, were studied using glasses with low (NaBAl) and high (NaAl–1118, LiAl) Na^+-specificities[19,21,59–61], and also NaAl-2704 [19,21] glass. Transitions of the type $(tris)^+ \rightleftharpoons M^+$ ($M^+ = Na^+$, Li^+, Ag^+, NH_4^+, Rb^+, Cs^+, or K^+) and $(tris)^+ \rightleftharpoons M^{2+}$, where $(tris)^+$ is the cation of the base tris(hydroxymethyl)-aminomethane and M^{2+} has the significance indicated above, have been studied using the NaAl-1118 glass.

The most characteristic observed feature of the kinetic curves considered in this section is their non-monotonic variation: there are extrema on the $\phi-t$ curves (although this is not obligatory). Fig.1 illustrates schematically the types of curves obtained experimentally in the studies mentioned above. Examples of real curves are presented in Figs.2 and 3 (see opposite).

The absolute height of the extrema reaches 60 mV in individual cases[43], although it is usually smaller. The duration of the transient processes in mixed solutions is between several seconds (in this case they can have a "solution" origin as in studies[16,28,38,43] dealing with M^{2+}, except Ba^{2+} and Pb^{2+} in Ref.43) and 30–60 s.[41–49] In the complete transition from one function to another the duration of the processes is between several minutes and tens of minutes and hours[19,21,50–56,61]. A drift continuing for days is frequently noted[31,50–58].

The principal components of the above processes are the exchange reactions

$$Li^+(glass) + I^+(soln) \rightleftharpoons I^+(glass) + L^+(soln) \qquad (14a)$$

or

$$I^+(glass) + J^+(soln) \rightleftharpoons J^+(glass) + I^+(soln) \qquad (14b)$$

(where L^+ is the "intrinsic" mobile cation of the glass), which lead to the breakdown of the constancy of the activity of the L^+ or I^+ cations in the glass ($\bar{a}_l$ or $\bar{a}_i$) which is a necessary condition for the Nernst equation to hold for the L^+ or I^+ function.

The ion-exchange process can be complicated by non-ion-exchange processes involving the hydration of the glass, its corrosion, etc., which lead to the formation of layers with a structure different from that of the bulk of the glass. Diffusion through such layers or their very formation are believed[41,43–48,50–58] to be a factor which determines the dynamics of the potential both for a response to a single ion and in the cases considered here.

2. Theoretical Treatment

The kinetic relations described for the potential can be explained in terms of the modern theory of the membrane GE potential, mentioned in the introduction[4,21] and modified by the hypothesis of surface layers differing in their structure from the bulk of the glass membrane[62].

The unmodified theory dealt with an ion-exchange membrane separating solutions, designated by single and double primes, containing cations I^+ and J^+ having the activities a_i', a_j', a_i'', and a_j'', the concentrations $\bar{c}_i$ and $\bar{c}_j$ within the membrane, and the mobilities $\bar{u}_j$ and $\bar{u}_i$. If the ratio of the ionic activity coefficients within the membrane $\bar{\gamma}_j/\bar{\gamma}_i$, the ratio of the mobilities $\bar{u}_j/\bar{u}_i$, and the activities of the ions in the solution of one side of the membrane (for example, that designated by a double prime) are assumed to be constant, then the overall membrane potential is described by an equation of type (3) [taking into account Eqn.(2)].

The possible dependence of ϕ on t subject to these limitations has been discussed[63,66] and it has been concluded that, for two ions involved in exchange and reciprocal diffusion, the relation will cease to hold after the attainment of equilibrium at the interfaces between the membrane and the solutions designated by single and double primes even when the variation of the concentration profiles within the membrane is a continuous process. The point is that for two ions, the values of $\bar{u}_j/\bar{u}_i$ and the transport numbers $\bar{t}_i$ and $\bar{t}_j$ are single-valued functions of the limiting concentrations and the independence of ϕ of t after the attainment of equilibrium is observed even for $\bar{u}_j/\bar{u}_i \neq$ const.[62,64], while the membrane phase can be non-ideal under these conditions ($\gamma_j/\gamma_i \neq$ const.). For more than two exchanging ions bearing charges of the same sign, the independence of ϕ of t can be observed only for an ideal membrane ($\bar{\gamma}_i, \bar{\gamma}_j = 1$) and subject to the conditions $\bar{u}_k/\bar{u}_1 =$ const.[64,65] (here k denotes any ion and 1 denotes the first cation).

The theory, derived for any ion-exchange membrane, has been extended to a glass membrane with modified surface layers and a fixed thickness in which current is transported by a single cation L^+. All the changes in the surface layers were reduced to ion exchange despite the fact that the occurrence of stresses[64] and hydration (solvation), hydrolytic, silanol group condensation, etc. reactions in such membranes have been known for a long time. Furthermore, all these reactions can lead to the breakdown of the above conditions ensuring the independence of ϕ from t as a result of a change in the structure of the membrane as a function of time and space.

Savage and Isard[26] pointed to hydration as a possible cause of the time variation of the GE potential. Shul'ts and Ivanovskaya[7,67] considered the influence of non-aqueous solvents on the GE potential and its dynamics. Isard[62] took into account the available experimental data for the structure and properties of the surface layers of glasses[68–72] (the present author could add to these the data in Refs.18, 46 to 48, 73–83, etc.), and linked them to the observations made on the dynamics of the GE potential (a number of studies of are quoted[21,26,41]). He arrived at an important conclusion: if the surface hydrated (leached) layer of glass is homogeneous and there are no concentration gradients (there is no diffusion potential), then equilibrium is established between the surface layer, the solution, and the bulk of the glass and the final potential has the value that it would have if there were no surface layer. The same conclusion was arrived at by Shul'ts[84] as early as 1960, which served as a basis for a number of studies in which a relation was found between the chemical composition of the initial glass and its electrode properties[85–87].

When the solution is changed rapidly, concentration gradients may arise in the outer part of the surface layer of the glass and an "external diffusion" potential can be established (the same diffusion potential for the outer layer has also been reported by Baucke[83]). These gradients are gradually "dissipated" and new concentration levels are established throughout the leached layer up to the inner gradient layer, where the "internal" potential acquires a new value. A similar explanation has been given by Hozumi and Akimoto[43].

The above considerations are largely qualitative. A quantitative treatment of the dynamics of the GE potential on transiton from one function to another has been given by Morf[66] on the basis of the Doremus[64] two-layer model of the glass membrane. Doremus considered a glass membrane consisting of two homogeneous components I and II with different ratios $(\bar{u}_j/\bar{u}_i)^I$ and $(\bar{u}_j/\bar{u}_i)^{II}$ and exchange constants K_{ij}^I and K_{ij}^{II} at the interfaces with the solutions designated by

single and double primes respectively in equilibrium with this membrane. He obtained the following expression for the overall membrane potential:

$$\varphi = \frac{RT}{F}\left[\ln\frac{a_i' + K_{ij}^{I}(\bar{u}_j/\bar{u}_i)^{I}a_j'}{a_i'' + K_{ij}^{II}(\bar{u}_j/\bar{u}_i)^{II}a_j''} + \ln\frac{\bar{c}_i^{I,II} + \frac{K_{ij}^{II}}{K_{ij}^{I}}\left(\frac{\bar{u}_j}{\bar{u}_i}\right)^{II}\bar{c}_j^{I,II}}{\bar{c}_i^{I,II} + \left(\frac{\bar{u}_j}{\bar{u}_i}\right)^{I}\bar{c}_j^{I,II}}\right], \quad (15)$$

where $\bar{c}_i^{I,II}$ and $\bar{c}_j^{I,II}$ are the concentrations of ions in the immediate vicinity of the inner interface between components I and II on the side of I. The ratio K_{ij}^{II}/K_{ij}^{I} reflects the difference between the standard chemical potentials of the ions in I and II. At this interface there is an interfacial potential jump. In the derivation of Eqn.(15) the same assumptions were made as in the derivation of Eqn.(3) but separately for each component I and II.

If $(\bar{u}_j/\bar{u}_i)^{I}K_{ij}^{I} = (\bar{u}_j/\bar{u}_i)^{II}K_{ij}^{II}$ and phases I and II are ideal, then, for an initially homogeneous membrane, we obtain $\phi \neq \phi(t)$ following the attainment of equilibrium at the interfaces. If the phases are non-ideal, then the maintenance of such independence requires that the activity coefficients in different phases should be identical functions of concentration [identical values of the "thermodynamic factor" n in the equality $(\bar{u}_j/\bar{u}_i)^{I}(K_{ij}^{I})^{1/n} = (\bar{u}_j/\bar{u}_i)^{II}(K_{ij}^{II})^{1/n}$]. If this is not so, then $\phi = \phi(t)$ when the concentration changes at the inner interface.

Suppose that component I is a hydrated surface layer of the glass in the I^+-form and component II is the bulk of the glass. When the membrane is immersed in a solution designated by a single prime, containing J^+, the J^+ ions will begin to diffuse through I to II, but $\phi = \text{const.}$ as long as the diffusion occurs within I. When J^+ reaches the inner interface between I and II at a sufficient concentration, the potential will begin to change and will vary with time until the attainment of equilibrium at this interface.

Morf[66] adopted Eqn.(15) as the initial expression. The inner solution (designated by a double prime) is constant; then, omitting the single prime, we obtain from Eqn.(15):

$$\varphi = \varphi^0 + \frac{RT}{F}\ln\left[a_i + K_{ij}^{I}\left(\frac{\bar{u}_j}{\bar{u}_i}\right)^{I}a_j\right] + \frac{RT}{F}\ln\left\{\left[\bar{c}_i^{I,II} + \frac{K_{ij}^{II}}{K_{ij}^{I}}\left(\frac{\bar{u}_j}{\bar{u}_i}\right)^{II}\bar{c}_j^{I,II}\right]\Big/\left[\bar{c}_i^{I,II} + \left(\frac{\bar{u}_j}{\bar{u}_i}\right)^{I}\bar{c}_j^{I,II}\right]\right\}. \quad (16)$$

Morf retained the assumptions adopted by Doremus and added the following ones: (a) the diffusion of ions through I is slower than the attainment of equilibrium on the outer interface but faster than the diffusion in II; (b) the overall concentration of cations in the surface layer I is constant: $\bar{c}_i^{I} + \bar{c}_j^{I} = c^{OI} = \text{const.}$; (c) $\bar{u}_i^{I} = \bar{u}_j^{I} = \bar{u}^{I}$. The latter assumption greatly reduces the generality of the derivation, but cannot be avoided. It implies in fact that the diffusion potential in the surface layer is assumed to be zero and all the changes in the potential as a function of time are attributed to the change of the interfacial potential at the inner interface—a procedure used in a number of studies[2,15,39].

The solution of the diffusional equation for the concentration at this interface $\bar{c}_i^{I}$ at any instant is found in the form

$$\bar{c}_i^{I} = \bar{c}_{1,i}^{I} + (\bar{c}_{2,i}^{I} - \bar{c}_{1,i}^{I})\,f(t), \quad (17)$$

where $f(t) = 0$ when $t = 0$ and $f(t) = 1$ when $t \to \infty$. Here $\bar{c}_{1,i}$ and $\bar{c}_{2,i}$ are the initial and final concentratons corresponding to equilibrium with solutions 1 and 2, where the ionic activities are $a_{1,i}$, $a_{1,j}$ and $a_{2,i}$, $a_{2,j}$. The form of $f(t)$ is determined by an equation of type (7) containing a parameter τ defined by an equation of type (8a).

For the case under consideration, the general equation of the ϕ–t relation is as follows [we now go over to Morf's notation for I and II: I = s (surface) and II = m (membrane)]:

$$\varphi = \varphi^0 + \frac{RT}{F}\ln[a_{1,i} + K_{ij}^{pot}(m)\,a_{1,i}] + \frac{RT}{F}\ln\left[\frac{a_{2,i} + K_{ij}^{pot}(m)\,a_{2,i}}{a_{1,i} + K_{ij}^{pot}(m)\,a_{1,i}}f(t) + \frac{a_{2,i} + K_{ij}(s)\,a_{2,i}}{a_{1,i} + K_{ij}(s)\,a_{1,i}}[1 - f(t)]\right]. \quad (18)$$

Here K_{ij}^{pot} and K_{ij} have the same signficance as in Eqn.(2). Analysis of Eqn.(18) shows that, for $t < 0$, the equilibrium potential is specified by the initial solution ($a_{1,i}$, $a_{1,j}$) and by the properties of the bulk of the membrane; for $t = 0$ (the instant of the completion of the change of solution), the response of the surface itself to the change in activities is added to this; when $t \to \infty$, a potential determined by the properties of the final solution and the bulk of the membrane is established.

For intermediate values of t, Eqn.(18) predict curves of the following type when $a_j = a_{1,j} = \text{const.}$ and a_i is variable (Fig.1):

(a) Curves *1* and *1'* when the surface and the bulk of the glass are selective with respect to I:

$$K_{ij}^{pot}(m) \ll 1,\ K_{ij}(s) \ll 1;$$

(b) Curves *2* and *2'* when the surface is selective with respect to J^+ and the bulk of the glass is selective with respect to I^+:

$$K_{ij}^{pot}(m) \ll 1,\ K_{ij}(s) \gg 1;$$

(c) Curves *3* and *3'* or *4* and *4'* when the surface is selective with respect to I^+ and the bulk of the glass is selective with respect to J^+:

$$K_{ij}^{pot}(m) \gg 1,\ K_{ij}(s) \ll 1^{66}.$$

Eqn.(15) also has a number of corollaries which are important for the understanding of properties of GE such as the asymmetric potential, the specific solvent effect, and other phenomena associated with the variation of the standard potential ϕ^0 and its drift (without affecting the Nernst function). To make the system concrete, we shall put $I^+ = H^+$ and $J^+ = Na^+$ in Eqn.(15); suppose that the existence of regions I and II reflects the asymmetry of the properties of the glass membrane arising either in the preparation of the GE or as a result of the action of solutions designated by single and double primes on each side. The asymmetry is manifested in the potential, as long as one of the components (I and II) has not been "worked through" and as long as equilibrium is not established at the inner interface between I and II. We shall assume that phase I consists of the entire modified surface layer of glass in contact with the solution designated by a single prime and phase II is the bulk of the membrane and the modified surface layer on the other side. Then $\bar{c}_H^{I,II} = 0$ and we have from Eqn.(15)

$$\varphi = \frac{RT}{F}\ln\frac{a_H' + K_{HNa}^{I}(\bar{u}_{Na}/\bar{u}_H)^{I}a_{Na}'}{a_H'' + K_{HNa}^{II}(\bar{u}_{Na}/\bar{u}_H)^{II}a_{Na}''} + \frac{RT}{F}\ln\frac{K_{HNa}^{II}(\bar{u}_{Na}/\bar{u}_H)^{II}}{K_{HNa}^{I}(\bar{u}_{Na}/\bar{u}_H)^{I}}. \quad (19)$$

This equation was first derived[7,67] to account for the specific influence of the non-aqueous solvent on the GE potential and has been used[88,89] to describe the asymmetric GE potential (ϕ_{as}). Indeed, in the region of the H^+ function, when $a'_H \gg K_{HNa}^{I}(\bar{u}_{Na}/\bar{u}_H)^{I}a'_{Na}$, $a''_H \gg K_{HNa}^{II}(\bar{u}_{Na}/\bar{u}_H)^{II}a''_{Na}$, and $a'_H = a''_H$, we have

$$\varphi_{as,H} = \frac{RT}{F}\ln\frac{K_{HNa}^{II}(\bar{u}_{Na}/\bar{u}_H)^{II}}{K_{HNa}^{I}(\bar{u}_{Na}/\bar{u}_H)^{I}}. \quad (19a)$$

In the region of the Na^+ function, the opposite inequalities hold, and when $a'_{Na} = a''_{Na}$, we have

$$\varphi_{as,\,Na} = 0. \qquad (19b)$$

We shall extend the approach developed in relation to a one-sided leached layer in a number of studies[62,64,66] and others, to a real leached layer having for a number of reasons an inhomogeneous structure (we assume, as before, that $I^+ = H^+$ and $J^+ = Na^+$). This inhomogeneity is modelled by a sequence of n layers differing in the values of $(\bar{u}_{Na}/\bar{u}_H)^{(k)}$ and in the standard chemical potentials of the ions (and hence in the values of $K^{(k)}_{HNa}$ and the interfacial potential jumps; here k is the number of the layer).

If all the surface layers have been equilibrated with one another and with the solution with respect to the H^+ and Na^+ ions, then, according to Eqns.(15) and (18), the potential is determined by the equilibrium between the solution and the nth layer adjoining the bulk of the membrane and tentatively retaining its structure and properties. When the situation in solution is altered, a new equilibrium is established slowly as the reciprocal diffusion front passes the interfaces between the layers and equilibria are established at the latter. Suppose that equilibrium has been established at $k-1$ interfaces and that the concentration profile changes in the kth layer without reaching its interface with the $(k+1)$th layer. We then have an expression for the overall potential of the type of Eqns.(15) and (16):

$$\varphi^{(k)} = \varphi^0 + \frac{RT}{F}\ln\left[a_H + K^{(k)}_{HNa}(\bar{u}_{Na}/\bar{u}_H)^{(k)}a_{Na} + \right.$$
$$\left. + \frac{RT}{F}\ln\frac{\bar{c}^{(k)}_H + \dfrac{K^{(k+1)}_{HNa}}{K^{(k)}_{HNa}}\left(\dfrac{\bar{u}_{Na}}{\bar{u}_H}\right)^{(k+1)}\bar{c}^{(k)}_{Na}}{\bar{c}^{(k)}_H + (\bar{u}_{Na}/\bar{u}_H)^{(k)}\,\bar{c}^{(k)}_{Na}}. \right. \qquad (20)$$

Suppose that for some reason [the condensation of ≡SiOH (see below) groups, the interaction with OH^-, etc.] we have $c^{(k)}_H \to 0$. We then obtain in the region of the H^+ function

$$\varphi^{(k)}_H = \varphi^0 + \frac{RT}{F}\ln\frac{K^{(k+1)}_{HNa}(\bar{u}_{Na}/\bar{u}_H)^{(k+1)}}{K^{(k)}_{HNa}(\bar{u}_{Na}/\bar{u}_H)^{(k)}} + \frac{RT}{F}\ln a_H. \qquad (20a)$$

In the region of the Na^+ function subject to the same condition, we have

$$\varphi^{(k)}_{Na} = \varphi^0 + \frac{RT}{F}\ln\left[K^{(k+1)}_{HNa}(\bar{u}_{Na}/\bar{u}_H)^{(k+1)}\right] + \frac{RT}{F}\ln a_{Na}. \qquad (20b)$$

We may note that, when there is a rapid alteration of the H^+ or Na^+ concentration in solution, the extent of the corresponding response is determined by the closeness to unity of the H^+ or Na^+ transport number in the first layer of the glass in equilibrium with the solution [see Eqn.(1)].

In Eqns.(20a) and (20b) terms which are constant under the conditions where the reciprocal diffusion front passes the kth layer are added to the potential ϕ^0. The time during which constant values of the potential are retained at the intermediate "quasi-stationary" level depends on the thickness of the layer $\delta^{(k)}$ and the reciprocal diffusion coefficient $D^{(k)}_{HNa}$. The $(k+1)$th layer is then in equilibrium with the subsequent layers and the parameters K_{HNa} and $(\bar{u}_{Na}/\bar{u}_H)$ characterising it can be replaced by the parameters of the nth layer and can be introduced into the expression for ϕ^0. We then obtain from Eqn.(20a)

$$\varphi^{(k)}_H = (\varphi^0)' - \frac{RT}{F}\ln\left[K^{(k)}_{HNa}(\bar{u}_{Na}/\bar{u}_H)^{(k)}\right] + \frac{RT}{F}\ln a_H. \qquad (21)$$

When the reciprocal diffusion front reaches the nth layer, the potential reaches a stationary level and no longer changes, provided that no structural changes take place within this layer.

Differences between the structure and properties of the layers can arise when the GE is soaked in solution, as a result of ion-exchange processes such as hydration, corrosion, hydrolysis ⇌ condensation (hydroxylation ⇌ dehydroxylation) by the reaction

$$\equiv Si{-}O{-}Si\equiv + H_2O \rightleftarrows 2 \equiv Si{-}OH, \qquad (22)$$

the sorption of acid by the outer layer from a concentrated solution, etc.

Presumably the low-temperature condensation of the ≡Si–OH groups, observed by infrared spectroscopy[74,75,77] for the surface layers of many silicate glasses after leaching with acid and leading to an increase of their chemical stability towards a number of reagents, including HF solutions[78], results simultaneously in an increase of the selectivity of the H^+ function of the GE, i.e. in a decrease of $K^{pot}_{HNa} = K_{HNa}\cdot(\bar{u}_{Na}/\bar{u}_H)$. Hydrolysis has the opposite effect. It then follows from Eqn.(22) that, on condensation in the kth layer, a $\phi^{(k)}$ potential in the region of the H^+ function should shift towards positive values and on hydrolysis the shift should be towards negative values. We shall now quote several examples.

In Wikby's study[46] glass electrodes made from $NaCa\text{-}21_4O6_2$ glass were hydrated for a long time in a 10^{-4} M NH_4HCO_3 solution at pH 7. The electrodes were then transferred to an etching solution (0.1 M HCl + 0.3% HF). A potential of approximately 340 mV was established initially and was then maintained for several tens of minutes, whereupon it changed abruptly to approximately 250 mV and then remained constant. The first, quasi-stationary level corresponds to equilibrium with the leached layer, in which considerable condensation was observed for this glass[74,75,77], and the second, stationary level corresponds to equilibrium with the internal ion-exchange layer adjoining the bulk phase.

Bobrov and coworkers[52,54] noted a shift of the stationary potential of GE made from Na-20 glass in a negative direction when the electrodes were soaked in an acid or neutral solution, which was regarded as the result of an internal increase of the alkalinity of the liquid within the pores. Consequently, under these experimental conditions, it was possible to postulate the maintenance of equilibrium with respect to H^+ ions between the solution and the internal ion-exchange layer adjoining the bulk phase. In this layer there is a possibility of the hydrolysis of the ≡Si–O–Si≡ bonds, leading to an increase of K^{pot}_{HNa}.

Even more striking negative shifts of ϕ were observed after treating the glasses in alkaline solutions (Fig.2), which leads not only to a partial dissolution of the outer layer but also to its loosening and an increase of the overall concentration of ionogenic groups in the residual layer. Then $\phi_{quasi\text{-}st} < \phi_{st}$ when the GE is transferred from alkali to an acid solution. As H^+ diffuses into the bulk phase, the change of potential is described by curve 5′ (Fig.1). The entire multiplicity of curves with extrema can be accounted for similarly (Figs.1 and 2).

We shall note separately the initial sharp extrema on curves of type 4 and 4′ (Fig.1) and also curves of type 6 and 6′. The latter were observed experimentally[19] after a rapid replacement of dilute (10^{-2}–10^{-3} M) $Na^+ \rightleftarrows K^+$ solutions for GE made of NaAl-1118, NaBAl, and LiAl-1608 glasses. Judging from the time required for their manifestation (several seconds for curves 6 and 6′ and several minutes for curves

4 and *4'*), these phenomena are associated with non-stationary processes involving the reciprocal diffusion of ions of different mobilities in the stagnant liquid layer and the adjoining porous surface layer of glass as well as the kinetics of the attainment of the interfacial concentration.

In order to describe such phenomena, it is convenient to solve beforehand Eqn.(12) for mixed solutions. It is also possible that the general causes of the type described above in relation to a porous layer of glass, differing markedly in structure and properties from deeper layers, can also operate in this instance.

For GE made of glasses with a predominately metal ion function, which do not tend to form deep leached layers[79,81], the duration of the transient processes is also small, particularly when two ions are involved, one of which is the "intrinsic" ion of the glass. Thus in GE made of NaBAl glass, soaked in NaCl solutions, the transient process after the replacement of NaCl by HCl in 1 s is completed in approximately 30 s (curves of type *2'* and *3'* in Fig.1), while in the opposite replacement the transient process lasts 2–3 min (curves of type *3* and *4*).[19] For GE made of NaAl-2704 glass, soaked in 0.1M HCl for 1,3, and 8 days, there is a transition to the Na^+ function in 0.1M NaCl in less than 1 h (curves of type *2* in Fig.1; see also Fig.3*a*). The opposite transition is faster (curves of type *2'* in Fig.1 after 1 and 3 days and of type *3'* after 8 days) and is sharper (Fig.3*a*).

Specific features have been noted in the transiton from the H^+ function to the response to an alkali metal ion which is not the intrinsic (L^+) ion of the glass: $H^+ \to Na^+$ for the LiAl glass[19]; $H^+ \to K^+$ [59] and $H^+ \to Li^+$ for the NaAl-2704 glass (Fig.3*a*). As a rule, curves of type *4* are obtained with a rapid attainment of a certain level of potential. However, in subsequent observations (after hours and days)[59] it was found that this level is quasi-stationary. After 24 h in the case of $H^+ \to K^+$ there is a transition to another layer which no longer changes; for $H^+ \to Li^+$, another quasi-stationary layer is established after 24 h and after a further 24 h a final (stationary) level is reached, which is also attained when the GE is soaked in the LiCl solution alone. At each level the K^+ or Li^+ function of the GE is manifested approximately. In both cases the potential at the stationary level is more positive than at the quasi-stationary level.

The attainment of the stationary level of potential coincides in time (approximately 40 h) with the attainment by the Li^+ ions of the internal interface between the leached layer and the bulk phase at a depth of 3 μm (Fig.3*b*). The use of these parameters for the calculation of D_{LiNa} by Eqn.(8a) leads to reasonable values $D_{LiNa} = 2.5 \times 10^{-13}$ cm^2 s^{-1}, which agree well with the values calculated from concentration profiles after treating the NaAl-2704 glass with LiCl solutions[90]. The reverse transition from the K^+ or Li^+ function to the H^+ function is also accompanied by the attainment by the potential of a more positive quasi-stationary level than the stationary level (curves of type *4'* for $Li^+ \to H^+$ in Fig.1 and of type *3'* for $K^+ \to H^+$).[59]

The relative positions of the stationary levels correspond to the series of equilibrium specifities[21] after prolonged soaking of the GE in solutions of the corresponding ions. The distribution of the quasi-stationary levels depends on the time of the observation and, for the same time, on the solution concentration[19].

When an attempt is made to explain theoretically the phenomena described, complications arise due to the involvement of three ions in the process. In this case there is no unambiguous relation between the mobility ratio or the ionic transport numbers in the glass, on the one hand, and the ionic concentrations at the interface, on the other. However, we suggest that this case can be reduced in most instances to the previous one, i.e. it is possible to neglect the contribution of the third potential-determining ion to the sum of the transport numbers at the given interface between the layers. Thus, when the mutual diffusion of metal cations in a glass with an increased Al_2O_3 content, in equilibrium with neutral or alkaline salt solutions, is considered, it is possible to neglect the contribution of H^+.[79]

On being soaked in HCl, a glass with a low Al_2O_3 content, for example, NaAl-2704, tends to form a leached layer. When the GE soaked in HCl is transferred to an LiCl solution, at the beginning of the process one can neglect the contribution of Na^+ and the quasi-stationary potential levels may be assumed to correspond to the reciprocal diffusion $H^+ \leftrightharpoons L^+$. As already mentioned, the establishment of a stationary level of potential at the end of the process corresponds to the attainment by Li^+ ions of the ion-exchange layer adjoining the bulk of the glass, where the reciprocal diffusion $Li^+ \leftrightharpoons Na^+$ is of decisive importance (Fig.3*b*).[59]

IV. CONCLUSION

On the basis of the experimental data examined and the theoretical studies, it is possible to formulate the following picture of the dynamics of the attainment of the potentials of glass electrodes after a stepwise alteration of the concentration of the potential-determining cation in aqueous solution.

1. In the region of the response by the electrode to the "intrinsic" cation of the glass or the exchange function with respect to a given cation I^+ of a "prepared" GE, it is possible to assume that the activity of this cation in the surface layer of the glass is constant and the response time is limited not by the transfer of the charge through the glass/solution interface but by both the diffusion of the electrolyte through the liquid diffusion layer arising near the GE surface and by the mutual diffusion of the ions within the pores and the walls in the outer loosened (hydrated) layer of glass (or by one of the processes indicated). The potential–time curves for the case under consideration have a complex exponential form and consist (when the accuracy of the measurements is to within 1 mV) of not more than three components with characteristic relaxation times $\tau_3 \leq 1$, $\tau_2 \cong 10$, and $\tau_1 \cong 100$ s when the duration of the concentration jump is ≤ 1 s. The contribution of the fastest process, corresponding to diffusion in the liquid layer near the electrode, to the overall change in the potential is usually greater than 50% and frequently 85–100%.

The values of τ_i are resonably predicted by the formula $\tau_i = m\delta_i^2/D_i$, where δ_i is the thickness of the diffusion layer, D_i the reciprocal diffusion coefficient, and m a multiplier ($m = 1$, 0.5, or $4/\pi^2$ in different models of the diffusion layer).

2. In the concentration jump in a mixed solution containing, apart from I^+, an "interfering" cation J^+ in the range of the ratios of the I^+ and J^+ concentrations where the constancy of the activity of I^+ ($\bar{a}_i$) in the surface layer of the glass is virtually unaffected in the stationary state, i.e. the I^+ function is retained, there is a possibility of the retardation of the attainment of a steady potential or of the presence of an extremum on the potential–time curve caused either by the reciprocal diffusion of the electrolyte ions in the diffusion layer of the liquid or by the time-dependent breakdown of the condition $\bar{a}_i = \text{const}$. in the outer surface layer of the glass (the time-dependent sensitivity of this layer to the cation J^{z+}).

3. In the concentration jump in the region of the transition from the I^+ function to the J^+ function of the GE in a mixed solution of I^+ and J^+ or in a pure solution of J^+ the dynamics of the attainment of a steady potential is determined by the low rate of the attainment of the boundary conditions in the ion-exchange reciprocal diffusion of cations in the surface layers of the glass differing in their structure from the bulk of the glass membrane. This structure is established during the preliminary preparation of the GE in a I^+ solution and is the result of non-ion-exchange corrosion, hydration, the hydrolysis of $\equiv Si-O-Si\equiv$ linkages, the condensation of $\equiv SiOH$ groups, the sorption of acid molecules in acid solutions, etc.

Against this background, the main result of the process is a decrease of $\bar{a}_i$ due to the substitution of I^+ ions by J^+ ions and an increase of $\bar{a}_j$ to a constant value. This is accompanied by a change in the phase and diffusion potentials in the glass.

When the boundary conditions are established, the overall GE potential reaches a definite level—in minutes if the native surface interacts with the new solution and a layer with the structure of the bulk phase is formed and in tens of minutes if an altered surface layer exists beforehand. In the latter case this layer can persist for a long time—hours and days (quasi-stationary potential) until the migration of the reciprocal diffusion front into the bulk of the glass results in the attainment of a layer with a different structure and properties, such as K_{ij} and $\bar{u}_j/\bar{u}_i$, i.e. until the boundary conditions change again. The potential can then change more until the attainment of another quasi-stationary level. This continues until the I^+ ions reach the internal ion-exchange diffusion layer having the structure of the bulk phase. A stationary potential level is then established. This level can vary over a very long time (days and weeks) owing to secondary corrosion, condensation, hydration, etc. processes.

At each quasi-stationary level and at the stationary level a I^+ function of the GE, close to the theoretical Nernst function, can obtain, provided that the transport number t_i in the layer in equilibrium with the solution is close to unity.

At the beginning of the process, immediately after the concentration jump, a non-monotonic variation of the potential—time (seconds, minutes) curve is frequently observed owing to the difference between the mobilities and the exchange current of the mutually diffusing ions in the boundary layer of the electrode and in the glass pores, and also as a consequence of the possible large difference between the properties of the surface layer of the glass itself, established by the preliminary treatment, and the properties of the deeper layers.

The semiquantitative theoretical description of the transient curves for the transition from one electrode function to another has been based on the hypothesis of interfaces between the glass layers mentioned above, differing in structure, the exchange constants, and ionic mobilities, and hence of potential jumps at such interfaces and of diffusion-dependent limitations within the layers. The explanation given in the literature for two homogeneous layers has been extended in this review to a large number of layers.

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