

The centenary of glass electrode: from Max Cremer to F. G. K. Baucke

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Abstract More than 100 years passed since 1906 when M. Cremer has measured for the first time the emf which builds up when two aqueous solutions with different acidity or alkalinity are separated by a thin glass membrane and since 1909 when F. Haber and Z. Klemensiewicz have obtained acid–base titration curves with the help of this device, thereby developing the glass electrode (GE) as an analytical tool. Twenty years later pH measurements with GEs became one of the most frequently performed procedures in research and industrial laboratories, in medicine, biology, agriculture, etc. That happened thanks to the progress made in measuring techniques and also in the development of special glasses. The latter, in turn, was a consequence of studying the dependence of electrode properties of glasses on their composition. That also resulted in the development of glasses for GEs having sensitivities toward M^+ ions (Na^+ , K^+ , Ag^+ , etc.) and glasses for measuring redox potentials. The data on the properties of GEs accumulated in the twentieth of last century formed the sound basis of the theory of glass electrodes. B.P. Nikolskii's thermodynamic ion exchange theory has gained general recognition since 1937. Nikolskii's equation is widely used for the description of behavior not only of GEs but also of other ion-selective electrodes. Two approaches are distinguished in the evolution of the theory: one that is based on the assumption on the non-ideality of a glass membrane (Izmailov et al., Lengyel et al., Schwabe et al., Eisenman, and others) and the other approach based on the concept of

various ionogenic groups in glass and their dissociation (Nikolskii, Schultz, and their colleagues, later Buck and Morf). The understanding of the potential of a glass electrode as an interfacial potential was replaced by the idea of a membrane potential, i.e., a potential drop including two interfacial potential drops and two diffusion potentials (Eisenman, Nikolskii's school, Doremus, etc.). The equilibrium at the boundary which determines the interfacial potential specifies the boundary conditions for the diffusion potential. The electrode properties of the glasses (the extension and slope of electrode function, its selectivity, etc.) in many respects depend on the mobilities of ions and the mechanism of their transport in the glass. A deeper insight into the functioning of the glass electrode was achieved by studying concentration profiles of ions in the glass layers which were altered by interaction with a solution, especially in combination with studies of the chemical and electrochemical processes on the glass/solution boundary, the dynamics of the GE potential, and the other properties of the glass surface. Dr. F.G.K. Baucke has made a significant contribution to GE studies. Using high-resolution techniques (IBSCA and NRA) to study the glass surface, he was able to give the most detailed description of the surface layers in case of lithium silicate glass. He described the equilibrium at the glass/solution boundary as a dynamic equilibrium not only in terms of thermodynamics, but also of electrochemical kinetics. For the first time in the literature of GEs, he has pointed to the electrochemical mechanism of formation of the GE potential as a consequence of charge division at the boundary (the dissociation mechanism). His activity in the field crowns the century with dignity.

To Dr. F.G.K. Baucke, my old friend and best opponent.

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Introduction

“Nothing tends to the advancement of knowledge as the application of a new instrument” (Sir Humphrey Davy, 1824). This was said concerning the thermometer, but rightly, this can be said also about the glass electrode (GE), which was developed in the first decade of the twentieth century, and which—by the middle of the century—turned out to be the most frequently used tool for pH measurements. The frequency of pH measurements with GEs in science and industry is only outnumbered by temperature measurements! The number of GE’s produced in the former USSR reached some hundreds of thousands per year.

Since the nineteenth century (and even earlier), glass was known as a solid electrolyte and a semi-permeable membrane in some galvanic cells; see the review of F. Scholz in this issue [1], where that time is divided into three periods. We can consider the third and the fourth periods (according to [1]), linked to the names of M. Cremer [2] and F. Haber [3] (1906–1909), as the end of prehistory and the onset of the history of the GE. Following [1], we will try to set off periods in the history of the development both of the theory and practice of the GE. I realize that the division may seem conventional and subjective.

1. The time from the mentioned onset to the end of 1920s was the period of a primary accumulation of data concerning the properties of GEs. A special glass for GEs was developed by MacInnes and Dole.
2. The 1930s: GEs of the MacInnes and Dole glass were launched for industrial production (Corning 015), and vacuum tube amplifiers were introduced firstly by Beckman and later by other manufacturers. This stimulated the wide application of GEs in labs and plants. The first theories of the GE were formulated; among them Nikolskii’s thermodynamic ion exchange theory and equation were published in 1937, and since that time, they are widely accepted by scientists. This period was reviewed in some books (ref. 3 and 8 in [1]); I add to them the Dole [4] and Pchelin [5] books, which were prominent in the USA and the USSR, respectively.
3. From the 1940s to the middle of the 1960s: The pH-GEs of lithium silicate glasses and pM-GEs of alkali aluminosilicate glasses and also modern pH meters are produced. Further developments of the GE theory by Nikolskii and Schultz, Eisenman, a.o. are the following: *generalized* theory, the GE potential as a membrane one, dependence of the GE properties on glass composition. The book [6] edited by Eisenman (1967) sums up this period.
4. From the middle of the 1960s to the present: The study of surface layers of the GEs combined with studies of

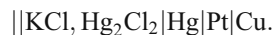
other GE properties, including electrochemical kinetics. Extensive development of non-glass membrane ion-selective electrodes (ISE) applied the GE theory, especially the Nikolskii equation. Special chapters in the books on pH measurements (e.g., [7, 8]) and ISE (e.g., [9, 10]) are devoted to GEs. Baucke’s great activity in the field of study of the surface layers, with his very sensitive depth-resolving analytical methods, and GE electrochemistry; dissociation mechanism [11, 12].

Meanwhile, the following is written in [12] about the thermodynamic theories and hypotheses which have been proposed from 1930s to the mid-1970s: “This work yielded theories and hypotheses, some of which describe the glass electrode function amazingly well, but it could not yield any knowledge about the physical processes at and in the membrane glass. The response mechanism thus remained unknown. This unfortunate state changed only in the mid-seventies when sufficiently sensitive depth-resolving quantitative analytical methods had become available.” I would like to leave the reader an opportunity to judge for himself as to what extent this state was “unfortunate.”

An invention and the primary accumulation of data concerning the properties of glass electrodes

In the twentieth century, physiologist M. Cremer [2] was the first who observed the emf response of a galvanic cell with a glass membrane to the acidification and/or alkalization of a water solution, but he did not propose the GE as a tool. The electrochemists F. Haber and Z. Klemensievicz [3] did this using the cell, which became classical for measurements with GE:

Cu|Pt|HCl solution|glass membrane|solution to titrate



They performed acid–base titration curves with such a cell. Also, they qualitatively compared these curves with those obtained with a Pt|H₂ electrode. The absences of an effect of H₂ or catalytic action of Pt on solution components were underlined in the case of glass. They proposed the analytical tool (“instrument” according to Davy), i.e., the electrode, whose “phase potential changed reversibly with logarithm acidity or alkalinity.” It is remarkable that at the same year 1909 the quantity pH was proposed by Sørensen, as a measure of acidity or alkalinity. Haber was familiar with Cremer’s work [13, 14], but he had much greater experience in electrochemistry, in particular, in studies of different cells, to be able to repeat Cremer’s experiments at a higher level.

Haber was also the first who used the term “glass electrode” as early as in 1907 [15] as antonym to the term

“porcelain electrode.” Though, that was rather an O₂ and a H₂ sensor having a glass membrane covered by Pt or Au and placed between two hot gas mixtures than a glass electrode as we understand it now. To the best of our knowledge, the term glass electrode, as it is understood today, was used for the first time in German by Freundlich and Rona in 1920 [16] (the paper was presented by Haber to the Prussian Academy of Science) and by Brown in English in 1924 [17]. Freundlich and Rona [16] pointed to the difference between the GE potential and electrokinetic (ζ) potential. The first was insensitive to surfactants like crystal violet.

In 1922 W. Hughes [18] directly compared the GE with a hydrogen electrode. He found that the glass surface potential was approximately a linear function of the logarithm of hydrogen ion concentration, if this was greater than 10⁻¹¹ mol/L. M. Dole pointed out [4] that Hughes was the first person to realize the sodium error of the GE. He revealed also other important properties of GE: insensitivity to redox systems and certain adsorbing species, such as Th⁴⁺ and gelatin.

The next big step in the development of GE was made by K. Horovitz and H. Schiller in Vienna [19, 20]. They worked with glasses which differed from those of the previously mentioned authors, and they showed that such GEs exhibit a pH response in acidic solutions, and a linear response to the logarithm of the concentration of metal ions, like Na⁺, K⁺, Ag⁺, in neutral and alkaline solutions. They named such GEs “mixed electrodes.” They believed that the GEs obtained that property as a result of ion exchange sorption of these ions from the respective solutions. Shortly later, Quittner [21] has demonstrated that the mentioned ions (including H⁺) can—field driven—enter the glass and move within the glass.

Further studies and successful application of pH-GEs are connected with the development of special glasses for GEs.

The glasses for GEs and some GE constructions

pH-GEs

The authors mentioned above worked with industrial German (Jena) and experimental English (Sheffield) glasses [22]. The years 1928 and 1929 were marked by the introduction of the glasses specially synthesized for pH-GEs (Table 1). The most successful glass turned out to be that of MacInnes and Dole (Corning 015) [24, 25]. Its industrial production and also the introduction of vacuum tube amplifiers (pH meters) by many instrument-making companies (firstly by Beckman) since the beginning of the 1930s promoted the triumphal procession of GEs in laboratories, plants, etc., within the next 20 years.

The linear range and almost Nernstian H⁺-function of GEs made of the MacInnes and Dole glass was limited to the pH range ~0.3 to 9–10, depending on Na⁺ ion concentration in a solution. In more acid solutions, deviations are observed, negative by sign (“acid errors”), in more alkaline ones—positive deviations (“sodium” or “alkaline errors”). A lot of research on MacInnes and Dole glasses were devoted in the 1930s, firstly, to the elucidation of the causes of these deviations (see later) and, secondly, to the development of glasses for GEs with a more expanded region of linear H⁺-function.

In 1932 Sokolov and Passynskii [26] proposed the lithium silicate glass (Table 1) with an upper pH limit of the H⁺-function of 10.5 in Li⁺-containing solutions and even higher in Na⁺-containing solutions. However, Dole [4] was unable to confirm their results because of the extremely high electrical resistance of GEs. This was then achieved by Avseevich from Leningrad University, USSR [27, 28], measuring the emf of the cell with an electrometer. Moreover, he developed his own lithium silicate glasses [28] (Table 1) with lower resistance and expanded H⁺-function.

Avseevich obtained his results at the end of 1930s, but the war prevented their publications. After Avseevich's death, they were published by B.P. Nikolskii in 1949–1951 [27, 28]. Despite that late publication, Dole mentioned them already in 1941 in his book ([4], p. 134). Dole also described the properties of GEs from Beckman National Technical Laboratories, marked as 1190E and 4990-E ([4], pp. 132–134), with a high upper limit of H⁺-function. These GEs were produced out of a lithium-containing glass [22].

The most successful modification of lithium silicate glasses for GEs was made by Perley [30, 31] (Table 1). He proposed the glass system Li₂O–Cs₂O–La₂O₃–SiO₂. Since the 1950s of the last century till now, the GEs, which are produced by many manufacturers in different countries, are based on this system.

The glasses for GEs with preferentially M⁺-function

The glasses, which Horovitz and Schiller used to obtain their mixed electrodes [19, 20], were characterized by the presence of Al₂O₃ and B₂O₃ in their composition, as opposed to glasses for pH-GEs. On the other hand, Hughes [23] showed that the presence of Al₂O₃ in the glass composition made this glass unsuitable as pH-GEs. Later, Lengyel and Blum [32] studied the properties of glasses of the system Na₂O–CaO–Al₂O₃–B₂O₃–SiO₂, and they selected the glasses of type D, mainly without CaO (see *D_a* in Table 2) with Na⁺-function in neutral and alkaline solutions. Glass *D_a* was used by Lengyel and Vincze [43] for determination of Na⁺, which evolved from electrode glass as a result of exchange of H⁺. Schultz et al. used this

Table 1 The glasses for pH-GEs

Marking	Composition	Author, year [reference]
Sodium silicate glasses (wt.%)		
Low-melting Thuringia soft glass	Na ₂ O–CaO–SiO ₂ + add.	M Cremer, 1906 [2] F Haber et al. 1907, 1909 [3, 15] H Freundlich, P Rona, 1920 [16]
No 793A, Sheffield	Na ₂ O–CaO–SiO ₂ + add.	WS Hughes, 1922 [18]
“Hughes’s glass”	20Na ₂ O–8CaO–72SiO ₂	WS Hughes, 1928 [23]
“MacInnes & Dole glass,” Corning 015	22Na ₂ O–6CaO–72SiO ₂	DA MacInnes, M Dole, 1929, 1930 [24, 25]
Lithium silicate glasses (mol.%)		
LiCa	18Li ₂ O–9CaO–72SiO ₂	SI Sokolov, AG Passinskii, 1932 [26]
LiBa	26Li ₂ O–3.6BaO–70.4SiO ₂	GP Avseevich, 1938–1948 [27, 28]
LiMg	26.5Li ₂ O–12.3MgO–61.2SiO ₂	
LiCa	25Li ₂ O–7CaO–68SiO ₂	HH Cary, WP Baxter, 1949 [29]
	Li ₂ O–Cs ₂ O–La ₂ O ₃ –SiO ₂	GA Perley, 1948, 1949 [30, 31]
Present day glasses for pH-GEs	21–33 Li ₂ O, 2–4 Cs ₂ O, 3–5 La ₂ O ₃ (Nd ₂ O ₃ , Er ₂ O ₃), 2–4% CaO (BaO)–SiO ₂ (till 100%)	All world manufacturers

composition as the basis for developing a set of Na⁺ sensitive GEs and even their K⁺-sensitive analogs (with K₂O instead of Na₂O in their composition) [33, 34] (Table 2).

In 1957 began the feverish activities of the biophysicist George Eisenman in the field of GEs. On the basis of an intensive study of electrode properties of the glass systems Me₂O–Al₂O₃–SiO₂ [37, 38], where Me¹ are alkali metals, he established a link between the Me₂O:Al₂O₃ ratio and M⁺ selectivity for different Me. He recommended some compositions of glasses for GEs. Two of them with Me=Na are given in Table 2. They were extensively used, especially in biological and medical studies. He also noted that with Me=Li, the same extent of Na⁺-selectivity may be obtained with smaller concentrations of Al₂O₃ in the glass, than with Me=Na. Some lithium-containing glasses for Na⁺-GEs are also given in Table 2.

Of great importance was the publication of the book “Glass electrodes for hydrogen and other cations. Principles and practice” [6] by G. Eisenman as editor. In it were summarized his and other authors’ (including Nikolskii’s school) activities in the field of theory and practice of GEs for many years and opened a path for R&D of ion-selective electrodes with non-glass membranes.

GEs for redox potential measurements

“Membrane glasses for redox measurements have not been successful either” [12] On the contrary, we informed [44] and intend to show here that such glasses and GEs made of

¹ Here and later, we will designate the alkali metal of glass as Me, but the same or other one from solution as M⁺.

them were developed in our laboratory and well studied by Pisarevskii et al.; they are produced industrially, and they are widely used.

As part of the systematic studies of the dependence of the electrode properties of glasses Me₂O–R_xO_y–SiO₂ on their composition, described below, some elements R of variable valence were involved. When R=Fe(II,III), Ti(III, IV), the glasses containing R_xO_y in appropriate concentrations obtained electronic conductivity, and GEs made of them possessed an electron sensitivity (i.e., electron (or redox) function; ROM-GEs) [45, 46]. Precautions had to be observed to increase the concentration of the lowest valent metal oxides and suppress the ionic conductivity by using a mixed-alkali effect. To be more exact, this material should be called “glass-like” or “glass-crystalline,” but operational properties of glass are still preserved, which allows production of ROM-GEs using a glassblower torch. Metallic silver or copper is used as inner contact.

The ROM-GEs behave like electrodes of noble metals in solutions of reversible redox systems, such as Fe³⁺, ²⁺, Fe[CN]₆³⁺/Fe[CN]₆⁴⁺, quinone/hydroquinone, etc. At the same time, they are insensitive to redox systems with a gaseous component, such as (1/2)Cl_{2(g)}/Cl[–], H⁺/(1/2)H_{2(g)}, and also O_{2(g)}/H₂O, the latter property allowing to measure redox potential of different systems in aerobic conditions. For the ROM-GEs of the Ti-containing glass, the equilibrium potentials were realized in Eu^{3+,2+} and Ce^{4+,3+} systems; formal potentials at pH=0 are –0.4 and +1.6 V, respectively, i.e., beyond the limits of the water thermodynamic stability.

The ROM-GEs were studied not only by equilibrium (potentiometric) methods, but also by several dynamic electrochemical methods [44, 47–49]. The standard exchange current densities for different redox systems were

Table 2 The glasses for pM-GEs

Marking and properties	The composition (mol.%)	Author, year [reference]
Sodium (potassium) silicate glasses		
Schott, Jena 59; 16; 1447; 397. Na ⁺ , K ⁺ , Ag ⁺ -functions	Na ₂ O–B ₂ O ₃ –Al ₂ O ₃ –SiO ₂ + add.	K Horovitz, H Schiller, 1923–1925 [19, 20]
<i>D_a</i>	11Na ₂ O–11B ₂ O ₃ –3Al ₂ O ₃	B Lengyel, E Blum, 1934 [32]
Na ⁺ -function	75 SiO ₂	
<i>D_a</i> and its variants	(11–25)Na ₂ O–(9–12)B ₂ O ₃ –(3–5)Al ₂ O ₃ –(till 100%)SiO ₂	MM Schultz et al., 1953–1955 [33, 34]
Na ⁺ -function	(15–25) K ₂ O–(9–12) B ₂ O ₃ –(3–5) Al ₂ O ₃ –(till 100%)SiO ₂	MM Schultz et al., 1955–1958 [35, 36]
Potassium analogs;		
K ⁺ -function	11Na ₂ O–18Al ₂ O ₃ –71SiO ₂	G Eisenman, since 1957, [37, 38], Corning
NAS-1118. Na ⁺ -function and high Na ⁺ -selectivity	27Na ₂ O–4Al ₂ O ₃ –69SiO ₂	G Eisenman, since 1957, [37, 38], A lot of manufacturers
“Cation selective” glass NAS-2704 type. K ⁺ (Na ⁺ , NH ₄ ⁺ , Tl ⁺)-function and some K ⁺ -selectivity	24Na ₂ O–5B ₂ O ₃ –9Al ₂ O ₃ –62SiO ₂ and 21Na ₂ O–3B ₂ O ₃ –12Al ₂ O ₃ –64SiO ₂	MM Schultz et al. [39] USSR, since 1965
ESL-51		
Lithium silicate glasses		
39278. Na ⁺ -function and selectivity	26.2Li ₂ O–12.4Al ₂ O ₃ –61.4SiO ₂	Beckman [40]
BH-67A, -68, -69, -104. Na ⁺ -function and selectivity	Li ₂ O–Al ₂ O ₃ –SiO ₂	Electronic Instruments Ltd, UK [41]
ESL-10. Na ⁺ -function and selectivity	16Li ₂ O–8Al ₂ O ₃ –76SiO ₂	AA Belyustin et al., [42] USSR, since 1965

measured, also boundary capacitances, etc. The ROM-GEs were produced on industrial scale in former USSR and were used in chemical industry, biotechnology, analytical laboratories [47]. See also another application in the next section.

pH-GEs and pM-GEs with a solid internal contact

“Solid metallic and other internal contacts [to glass membrane, A.B.] have been tried but were unsuccessful so far, mostly because of principle reasons” [12]. The following principles must be fulfilled [50]:

- 1) The electrode process at the boundary of an ionic conducting membrane and an electronic conducting contact must be reversible.
- 2) The exchange current of the process has to be sufficiently large comparing to the current flowing through the system under the conditions of measurement.
- 3) Absence of side processes at the boundary

With the observance of these conditions, the potential is stable and reproducible. All of these conditions have been observed for the GEs with metal solid contact (MSC), invented by the scientists of the Leningrad (now Saint Petersburg, SPb) State University [44, 51, 52]. The MSC consists of a thin alkali metal alloy layer evenly spread over the inner surface of a glass membrane, a vacuum being inside. The alkali metal is the same Me as in the glass composition; the second metal is tin or indium.

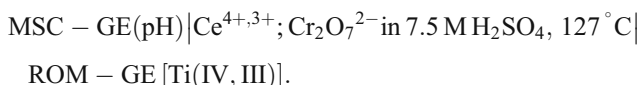
Previously pure alkali metals and their alloys (amalgams) were sometimes used as reversible contacts in GEs, see, e.g., [53, 54], but these constructions were impractical. The decrease of Li or Na activity by 12–13 orders of magnitude in an alloy comparing to pure metal makes the construction of the MSC-GEs completely safe. At the same time, it is possible to relate their standard potentials E^\ominus to the SHE scale, under conditions of thermodynamic equilibrium at all phase boundaries in a cell with a GE of any glass composition. The contact acts as an electrode of the first kind with glass as an ion-conducting medium (instead of water).

The clear advantages and also some surmountable drawbacks of MSC-GEs are listed in [44]. The main advantages are high reproducibility and stability of E^\ominus values, which permits in some instances using the factory calibration, wide temperature range, permitting their sterilization at 150 °C with water steam and using at high temperatures, etc.

Another construction of the contact was realized at SPb State University [50, 55], rather to demonstrate the principles, than for practice: The GE bulb was blown of the two-layer stick composed of two glass compositions:

ionic conducting $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ on the outside and mixed electronic–ionic conducting $\text{Na}_2\text{O}-(\text{Fe}_2\text{O}_3+\text{FeO})-\text{SiO}_2$ with copper as a conductor inside. The construction worked perfectly [50].

Both the MSC- and ROM-GEs were united in a promising device involving a cell for direct chemical oxygen demand (COD) potentiometric determination [44, 47, 56–58], based on using $\text{Ce}^{3+/4+}$ as redox probe (and also oxidant) and dichromate as the main oxidant. The cell without liquid junction is the following:



Here, the MSC-GE plays the role of the reference electrode with a very stable potential even under drastic conditions (boiling 7.5 M H_2SO_4 !); the ROM-GE is selective to the $\text{Ce}^{4+,3+}$ redox system. Both Cr^{6+} and Ce^{4+} take part in the oxidizing (“wet burning”) of an added reductant, organic or/and inorganic, but the ROM-GE reacts only to the changes in an equilibrium system $\text{Ce}^{4+,3+}$, connected with the changes in the non-equilibrium system $\text{Cr}^{6+,3+}$.

Nikolskii thermodynamic ion exchange theory and its development

The main task of the scientists, who began to work with GEs, was to describe quantitatively the known properties of GEs, in the first place the H^+ , and later Na^+ electrode function. Already Haber and Klemensiewicz [3] used for this a Nernst-type equation to describe the voltage drop across a membrane. They explained the appearance of H^+ (and OH^-) in the solid phase (glass) as a result of quelling of the glass in a water solution and regarded their concentration as constant. This point of view was suggested later by Hughes [23], who added a concept on the buffer action of a silicic acid and sodium silicate, existent in the quelled layer of the glass.

Since Hughes (1922) [18] and Brown (1924) [17] realized the sodium error of the GE, the equation describing GE properties had to take into account an effect of Na^+ on its electrode function. The best known equation with such quality is the Nikolskii equation:

$$E = E^\ominus + \frac{RT}{F} \ln(a_{\text{H}^+} + K a_{\text{Na}^+}) \quad (1)$$

where E is the emf of a galvanic cell commonly used for measurements with GE, E^\ominus is its standard value including the potentials of the reference electrodes, liquid junction potential, and characteristics of the inner side of the glass membrane and inner solution; R , T , and F have a common

meaning; a_{H^+} and a_{Na^+} are the ion activities in an external solution; and K is an “influence factor” of Na^+ ion on H^+ -function of GE. This factor has different meaning in different theories.

It is the Nikolskii ion exchange theory which is the most commonly used in this field of knowledge. Even his opponents do not disprove this fact.

Preceding formulae

One of the first conceptions, taking into account the effect both of H^+ and Na^+ ions on the GE potential, was that of L. Michaelis [59], who considered the glass membrane as porous and semi-permeable for cations, and the GE potential as a diffusion potential, ΔE_D , between external (') and inner (") solutions:

$$\Delta E_D = \frac{RT}{F} \ln \frac{u_{\text{H}^+} c'_{\text{H}^+} + u_{\text{Na}^+} c'_{\text{Na}^+}}{u_{\text{H}^+} c''_{\text{H}^+} + u_{\text{Na}^+} c''_{\text{Na}^+}} \quad (2)$$

where c_i is the ion concentration in a solution, u_i is the ion mobility in the pores, filled with solution, $i=\text{H}^+$ or Na^+ . This equation can be easily given the form of Eq. 1 with $K = u_{\text{Na}^+}/u_{\text{H}^+}$, and solution activities instead of concentrations, but already Dole [60] pointed out that for glasses with pH response keeping till pH 10, this coefficient must be about 10^{-11} , which seems improbable. Further studies showed that glass membranes have no pores and that H^+ cannot be transported through the glass membranes.

K. Lark-Horovitz² [61, 62] published a very interesting formula for the potential difference between two sides of a glass membrane dividing two solutions (') and ("), containing cations 1 and 2, taking part in the ion exchange between glass and solution:

$$\Delta E = \frac{RT}{F} \ln \frac{c'_1 + K c'_2}{c''_1 + K c''_2} \quad (3)$$

Here, c_1 and c_2 are the ion concentrations in solutions; $K = k_1 u_2 / k_2 u_1$; u_1 and u_2 are the ion mobilities in glass; k_1 and k_2 are the distribution coefficients (as we consider them today). In [61] k is called a solution tension and in [62] *Lösungdruck* (German term for solute pressure/tension). Note that this quantity depends on the thermodynamic characteristics of both the glass and the solution. Equation 3 can also be easily transformed into the form of Eq. 1 for external solution, if the concentrations in inner solution are kept constant. There was no derivation and experimental proof of Eq. 3 in [61, 62], and other authors made that later (see further down).

² Karl Horovitz (1892–1958) became Lark-Horovitz when he married Betty Lark in 1926. Since 1929 till 1958, he was head of the Physics Department of Purdue University, USA.

M. Dole [4, 63], using quantum statistical method and considering energy states of ions in solution and on surface and considering fractions of unit glass surface covered by hydrogen and sodium ions, derived the following equation for the sodium error ($\Delta E = E - E_H$)

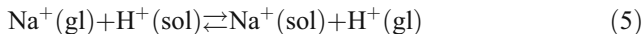
$$\Delta E = \frac{RT}{F} \ln \left(\frac{c_{H^+} + e^{(Q_{Na^+} - Q_{H^+})/RT} c_{Na^+}}{c_{H^+}} \right) \quad (4)$$

where $Q_{H^+} = U_{H^+}^{0S} - U_{H^+}^{0G}$, $Q_{Na^+} = U_{Na^+}^{0S} - U_{Na^+}^{0G}$, and the quantities U^0 are the energies of the lowest quantum level of respective ion in the solution (S) and on the glass surface (G); c_{H^+} and c_{Na^+} are concentrations in the solution.

It is possible to understand this equation as one for potential difference between an external solution, containing H^+ and Na^+ , and inner solution, containing H^+ only ($c_{H^+} = \text{const}$). Then Eq. 4 also can be readily brought to the form of Eq. 1 with $K = e^{(Q_{Na^+} - Q_{H^+})/RT}$.

Nikolskii’s “simple”³ theory [64, 65]⁴ (see also [68])

From the preceding, it may be seen that the stage was set for the appearance of Nikolskii’s ion exchange theory. His intimate knowledge of thermodynamics and his experience in the studies of ion exchange processes in soils were contributory factors. He assumed that the following equilibrium of ion exchange



exists between a surface layer of the glass (gl) and the solution (sol). The state of equilibrium for the (reciprocal) reaction is expressed by the law of mass action: $K_a = a_{H^+} a'_{Na^+} / a_{Na^+} a'_{H^+}$, where a_i and a'_i are the ion activities in the solution and glass, respectively. Then, the condition of an equilibrium for exchanging ions was written as the equality of their electrochemical potentials $\bar{\mu}_i = \mu_i + z_i F \Psi$ in different phases, where μ_i is the chemical potential of the ion, z_i its charge, and Ψ the electrostatic potential of the homogeneous phase in which the ion is immersed. At equilibrium

$$E = E_{H^+}^\ominus + \frac{RT}{F} \ln \frac{a_{H^+}}{a'_{H^+}} = E_{Na^+}^\ominus + \frac{RT}{F} \ln \frac{a_{Na^+}}{a'_{Na^+}}$$

³ The term “simple” theory did not appear before the main theoretical concepts had been developed in the generalized theory (1945–1953) considered later.

⁴ The paper [65] was the most cited Nikolskii’s work outside Russia. So some time, the reference to [65] has been omitted by many authors because of his world-famous equation type (Eq. 1). It is worth noting that the equation was derived, its experimental testing [66, 67] was made at Leningrad University, and respective papers were ready as early as in 1934, but in 1935, Nikolskii and his family, as many other Leningrad intellectuals, was subjected to repression and forwarded to exile in the city of Saratov. The papers [64–67] were represented by Saratov University.

where $E = \Psi^{gl} - \Psi^{sol}$ is the Galvani potential difference on the one side of the GE membrane, $E_{H^+}^\ominus$ and $E_{Na^+}^\ominus$ are equal to $\frac{\mu_i^{\ominus,gl} - \mu_i^{\ominus,sol}}{F}$; μ_i^{\ominus} ’s are the standard values of μ_i ’s.

Two important assumptions were introduced.

1. Activities of H^+ and Na^+ ions in the glass were considered to be equal to their concentrations: $a'_i \equiv c'_i$. This means that activity coefficients γ_i ’s were assumed independent of the degree of substitution of one kind of ion by another; γ_i ’s $\equiv 1$.
2. The total concentration of H^+ and Na^+ ions in the glass layer subjected to ion exchange has a constant value equal to the concentration of fixed “anionic sites” c'_{R^-} : $c'_{H^+} + c'_{Na^+} = c'_{R^-} = c^0 = \text{const}$. (A similar assumption was made by Lark-Horovitz [61, 62]).

After some transformations, we obtain Nikolskii’s equation:

$$E = E^\ominus + \vartheta \log \left(a_{H^+} + K_{H^+,Na^+}^{exch} a_{Na^+} \right) \quad (6)$$

where $\vartheta = 2.303 \frac{RT}{F}$, $E^\ominus = E_{H^+}^\ominus - \vartheta \log c^0$, K_{H^+,Na^+}^{exch} is the exchange constant:

$$K_{H^+,Na^+}^{exch} = \frac{a_{H^+} a'_{Na^+}}{a_{Na^+} a'_{H^+}} = \exp \frac{\left(\mu_{H^+}^{\ominus,gl} - \mu_{Na^+}^{\ominus,gl} \right) - \left(\mu_{H^+}^{\ominus,sol} - \mu_{Na^+}^{\ominus,sol} \right)}{RT} \quad (7)$$

Contrary to widespread fallacies, B.P. Nikolskii and his school never considered the reaction (5) as potential-determining. It explains how the H^+ ions appear in the surface layer of the glass. If the equilibrium is shifted to the right, they fill up the ion exchange capacity at and under the boundary, and the potential-determining equilibrium will be $H^+(sol) \rightleftharpoons H^+(gl)$ in the region of H^+ function; otherwise, it is $Na^+(sol) \rightleftharpoons Na^+(gl)$ in the region of Na^+ function⁵. The total ion exchange membrane capacity is great in comparison with the solution concentration. The filling of several molecular layers by M^+ ions from the solution ($M^+ \neq Me^+$) is enough to provide the buffer action of the membrane-solution system.

The constant K_{H^+,Na^+}^{exch} characterizes the selectivity of the sorption by the membrane of the ions from the solution and the position of the transition region [50]. A similar role plays Baucke’s “selectivity product” ([11], p. 83).

The same form, as Eq. 6, has the equation for emf E of the common galvanic cell with GE and eliminated liquid junction potential. The E^\ominus value in this case includes also

⁵ From the point of view of electrochemical kinetics, in the H^+ -function region exchange current densities $i_{H^+}^0 > i_{Na^+}^0$, in the Na^+ function region $i_{H^+}^0 < i_{Na^+}^0$.

the characteristics of the inner solution and reference electrodes.

Equation 6 was subjected to experimental testing [66, 67]. The experimental emf well coincided with the ones calculated by Eq. 6 in the regions of the pure H^+ - (at $a_{H^+} \gg K_{H^+,Na^+}^{exch} a_{Na^+}$) and Na^+ -function (at $a_{H^+} \ll K_{H^+,Na^+}^{exch} a_{Na^+}$) but did not agree quantitatively with experimental emf in the region intermediate between these functions (the transient region). The transient of the theoretical curves was much more pronounced than the experimental one. This discrepancy (and also some inconstancy of K_{H^+,Na^+}^{exch} value) required reconsideration of some of the concepts of the simple theory and promoted further studies.

The development of ion exchange theory

The development before 1965 was described in detail in our chapter [68] of the book [6]; because of this, some items will be only shortly mentioned here.

The proofs of some concepts

1. The existence of the ion exchange reaction of the type $H^+(sol) \rightleftharpoons Na^+(gl)$, $Na^+(sol) \rightleftharpoons Na^+(gl)$, $K^+(sol) \rightleftharpoons Na^+(gl)$, etc., was shown for different electrode glasses by usual analytical (in the 1930s and 1940s of last century) and radioactive tracer (in the 1950s and 1960s of last century) methods [43, 69–73].
2. Schultz [74, 75] has demonstrated the sodium function of the GEs of different glasses by direct comparison with the sodium amalgam electrode in cells without liquid junction.
3. The equation of the type Eq. 6 was expanded to the case of three cations H^+ and metal ions L^+ , M^+ . If $a_{H^+} \ll K_{H^+,L^+}^{exch} a_{L^+}$ and $a_{H^+} \ll K_{H^+,M^+}^{exch} a_{M^+}$, we have

$$E = E^\ominus + \vartheta \log \left(a_{L^+} + K_{L^+,M^+}^{exch} a_{M^+} \right) \quad (8)$$

It was shown in [76–78] that Eq. 8 describes the pure L^+ - and M^+ -functions nearly exactly, and the discrepancy between theory and experiment in the transient region from L^+ - to M^+ -function is much less than in the case when H^+ participates.

An inconstancy of activity coefficients in a glass

There were two theoretical approaches to explain the discrepancy and find an equation which fully describes the experimental curve. Both of them demanded the revision of some assumptions of the simple theory. The partisans of that first approach were Ismailov and Vasil'ev [79], Lundquist [80], Lengyel et al. [81], Eisenman [37,

73], and Schwabe and Dahms [82]. Either empirically or theoretically, they established some relationship between ion activities and their concentrations in the glass (the rejection of the assumption 1 of the simple theory). The most successful and known equation in the framework of the first approach was derived by Eisenman et al. [37, 73] based on the assumption that $a'_i = c'_i{}^n$.

$$E = E^\ominus + n\vartheta \log \left(a_{L^+}^{1/n} + K_{L^+,M^+}^{1/n} a_{M^+}^{1/n} \right) \quad (9)$$

If $L^+ = H^+$, $n > 1$, and Eq. 9 may be fit to experimental curve. If L^+ and M^+ are metallic ions, as a rule $n = 1$. It is readily seen that at $n = 1$, Eq. 9 transforms to Nikolskii's Eqs. 6 (or 8) and is often named as Nikolskii–Eisenman equation.⁶

The “generalized” theory

The second approach developed by Nikolskii and his school revised the assumptions related, firstly, to homogeneity of ionic bonds and, secondly, to constancy of the sum of ionic sites in the glass. Qualitatively, the idea of energetic inhomogeneity of ionic bonds in the glass was formulated as early as in 1937 [66, 67]. The first version of the quantitative theory, called the “generalized” one, was published in 1953 [84].⁷ It was based on the assumption that in the glass exist different kinds of silicate fixed “anions” having discrete bond strengths with H^+ ion. Formulae were derived which could describe the smooth transition from H^+ - to Na^+ -function. It was concluded from the formulae that at a large difference in the strength, a step may appear on the pH curve. Such steps were observed later [85], firstly, for GEs of glass of the composition $Me_2O-Al_2O_3-SiO_2$ ($Me=Li, Na$; see below). This stimulated the development of the second version of the generalized theory [68, 86, 87].

Some new concepts were taken into consideration in this version; these were the ionogenic groups HR_i and MR_i , where R_i^- are the fixed “anions” in the glass, and the equilibrium of their dissociation. Further, the concept of weak and strong acidity is used for groups of HR_i type, e.g., $[SiO_{3/2}]OH$ group is the weak acid and $[AlO_{4/2}]^- H^+$ is the strong acid (see below). Because of the dissociation, the value $-\vartheta \log c_{R^-}$, which is included in the E^\ominus value of Eqs. 6, 8, and 9, is not constant (that was neglected in assumption 2 of the simple theory). The search of a dependence of $c'_{R^-} = \sum_i^n c'_{R_i^-} = c'_{H^+} + c'_{M^+}$ on $a_{H^+}^{sol}$ and $a_{M^+}^{sol}$ is the essence of the formulae derivation [68, 86, 87]. Here,

⁶ In [83] an empirical equation is quoted under this name, which was derived neither by Nikolskii nor Eisenman.

⁷ The formulae were reported in 1945, but involvement of Nikolskii in the Soviet atom project hindered the publication.

we limit ourselves to two practically important cases: (1) one kind of the R⁻ sites and weak dissociating ionogenic groups (e.g., [SiO_{3/2}]OH and [SiO_{3/2}]OM) and (2) two kinds of the R_i⁻ sites and differently dissociated groups (e.g., both the same+respective Al-containing groups mentioned above). For the case (1), we have

$$E = E^\ominus + (\vartheta/2) \log \left(a_{\text{H}^+} + K_{\text{H}^+, \text{M}^+}^{\text{exch}} a_{\text{M}^+} \right) + (\vartheta/2) \log \left(a_{\text{H}^+} + \alpha K_{\text{H}^+, \text{M}^+}^{\text{exch}} a_{\text{M}^+} \right) \tag{10}$$

where $\alpha = k^{\text{H}}/k^{\text{M}}$ is the ratio of the dissociation constant of the groups in H- and M-forms.

For the case (2), we have

$$E = E^\ominus + (\vartheta/2) \log \left(a_{\text{H}^+} + K_{\text{H}^+, \text{M}^+}^{\text{exch}} a_{\text{M}^+} \right) - (\vartheta/2) \log \left[\left(a_{\text{H}^+} + \alpha_1 K_{\text{H}^+, \text{M}^+}^{\text{exch}} a_{\text{M}^+} \right)^{-1} + \beta \left(a_{\text{H}^+} + \alpha_2 K_{\text{H}^+, \text{M}^+}^{\text{exch}} a_{\text{M}^+} \right)^{-1} \right] \tag{11}$$

Here, $\alpha_i = k_i^{\text{H}}/k_i^{\text{M}}$; $\beta = k_2^{\text{H}} c_{\text{R}_2}^{\text{O}} / k_1^{\text{H}} c_{\text{R}_1}^{\text{O}}$; $c_{\text{R}_i}^{\text{O}} = c_{\text{HR}_i} + c_{\text{MR}_i} + c_{\text{R}_i^-}$.

Equation 10 describes the smooth transient from H⁺- to M⁺-function of GEs of the glasses with predominant effect of one kind of the ionogenic groups. The values E^\ominus and $K_{\text{H}^+, \text{M}^+}^{\text{exch}}$ have to be determined experimentally; α is the fitted parameter. Equation 11 was used to describe the E–pH curves for GEs from a set of glasses of the system (mol. %) 22Na₂O–xAl₂O₃–(100–x)SiO₂ (x = 1, 2, 2.2, 4, and 7) [68, 88]. At x ≤ 4 the step-wise E–pH curves were obtained. Equation 11 described them well (except x = 1) with rather small amount of the fitted parameters. In Eq. 11 index 1 is related to the [AlO_{4/2}]⁻H⁺(M+) groups, index 2 to the [SiO_{3/2}]OH(M) ones. The most varied fitted parameter was the β value. The parameters fitted for c_{Na⁺} = 3 mol/L in solution conserved their value for 0.1 mol/L solution. It is important to emphasize that not a single other theory could describe even qualitatively the stepwise E–pH curves.

The GE potential as a membrane one

Basic notions and equations

The GE potential was considered in the theories described above as a phase boundary potential (or more exactly, as the sum of the phase boundary potentials at two sides of the GE membrane). Since 1962 a new approach appeared, in which the potential came to be regarded as the membrane potential, i.e., as the sum of two phase boundary potentials and two diffusion potentials in surface layers at two sides of the glass membrane. This approach was preceded by works of Marshall [1948], Scatchard [1953], and Helfferich (see in [68]) on galvanic cells with ion exchange membranes. The considering of two diffusion potentials is specific for a

glass membrane and some other membranes with an unchanged bulk, where electrical charge is transferred by one kind of ions inherent to a membrane material, e.g., Na⁺ in a sodium silicate glass.

The diffusion potential in a membrane inevitably occurs in a working galvanic cell, if the membrane divides two solutions containing exchanging ions with different mobilities in the membrane. “Ion exchange is the counter-ion interdiffusion” ([89], Ch. 6). The equilibrium at the phase boundary determines the boundary conditions for calculation of the diffusion potential. This consideration has led to the equations for the total potential at external side of the membrane:

$$E = E^\ominus + \vartheta \log \left(a_{\text{L}^+} + \frac{u_{\text{M}^+}}{u_{\text{L}^+}} K_{\text{L}^+, \text{M}^+}^{\text{exch}} a_{\text{M}^+} \right) \tag{12}$$

⁸ [90, 91] instead of Eq. 8, and

$$E = E^\ominus + n\vartheta \log \left(a_{\text{L}^+}^{1/n} + \frac{u_{\text{M}^+}}{u_{\text{L}^+}} \left(K_{\text{L}^+, \text{M}^+}^{\text{exch}} a_{\text{M}^+} \right)^{1/n} \right) \tag{13}$$

[92] instead of Eq. 9. In the equations u_{M^+} and u_{L^+} are the ion mobilities in the surface layers of the glass; the assumptions about glass as an ideal (for Eq. 12) and nonideal *n*-type (for Eq. 13) ion exchanger remained valid at the derivation; *n* acquired an additional meaning as the thermodynamic factor $n = d \ln a / d \ln c$ in equations for interdiffusion, remaining an empirical parameter. The ratio $u_{\text{M}^+} / u_{\text{L}^+}$ was taken as constant at the derivation. Considering the products $\frac{u_{\text{M}^+}}{u_{\text{L}^+}} K_{\text{L}^+, \text{M}^+}^{\text{exch}}$ and $\left(\frac{u_{\text{M}^+}}{u_{\text{L}^+}} \right)^n K^{\text{exch}}$, we can see that they represent new constants, determined from potentiometric measurement and named K^{pot} (or K^{sel} —selectivity coefficient). It is easy to see that the replacement of the value K^{exch} by K^{pot} changed neither the shape of Eqs. 8 and 9 nor their ability (Eq. 9) or failure (Eq. 8) to describe adequately the smooth transient from L⁺=H⁺- to M⁺-function. No doubt, the splitting of the constant K^{pot} in two factors, one of which can be named the *energetic factor* (K^{exch} , see Eq. 7) and the other the *dynamic factor* ($u_{\text{M}^+} / u_{\text{L}^+}$), is of theoretical and practical importance.

Comparing the behavior and characteristics of the ROM-GEs with those of other redox-sensitive electrode materials, such as Pt, glassy carbon, SnO₂, etc., Pisarevskii [44, 47] has formulated a conception of the electrode selectivity to a certain redox system (*i*). The term “selectivity” implies that an electrode is able to realize a partial equilibrium with system *i*, in spite of the presence of a competitive system *j*. By analogy with $K_{\text{L}^+, \text{M}^+}^{\text{pot}}$ in ionometry, the quantity $K_{i,j}$ is introduced as a measure of the redox selectivity. The physical meaning and numerical value of $K_{i,j}$ depend on the nature of stages limiting the competitive electrode reactions. In some instances, $K_{i,j}$ (as $K_{\text{L}^+, \text{M}^+}^{\text{pot}}$) is the product of two factors: an energetic one $\left\{ \exp \frac{a_i (E_i^\ominus - E_i^\ominus)}{\vartheta} \right\}$ and a

⁸ The Lark-Horovitz Eq. 3 could be recast to this form.

kinetic one $\left(\frac{i_{0e}^{0j}}{i_{0e}^{0i}}\right)$ or $\left(\frac{i_{0,e}^{0j}}{i_{0,d}^i}\right)$, where E^\ominus 's are the standard potentials of the systems, α_j is the imaginary transfer coefficient, $i_{0,e}^0$ is the standard exchange current density for a given system, when the electrode process of the system is limited by electrochemical reaction (e); $i_{0,d}^i$ is the limiting diffusion (d) current density.

The smaller is K_{ij} , the less is an effect of j -system on the equilibrium electrode potential for i -system.

The role of the mechanism of charge transport

The question was raised first in [90] as to how a mechanism of charge (ion) transport in the ion exchanger membrane can affect the diffusion potential and the electrode selectivity. The problem was solved quantitatively in [93–97]. The ions L^+ and M^+ which participated in Eqs. 12 and 13 are the “free” (dissociated, interstitial) ones (this mechanism was named as “solvation” (s) as the ions were considered as solvated with glass phase). If so, it is difficult to explain the dependence of the factors belonging to the K^{pot} , determining the GE selectivity, on the glass (or ion exchanger) composition. The participating of the ions bonded in ionogenic groups, in the transport and their activities in the K^{exch} , is a necessary condition for the existence of this dependence. Some of such mechanisms were proposed in the mentioned papers, besides (s): vacancy (v), mixed ($s+v$), croquet (cr), and directed dissociation (dd).

The algorithm of derivation in [93–96] was as follows. An initial relation for emf E of a galvanic cell with a membrane dividing solutions 1 and 2 containing ions L^+ and M^+ is

$$E = \frac{RT}{F} \ln \frac{a_{L^+}^{(2)}}{a_{L^+}^{(1)}} + \frac{1}{F} \int_{x=0}^{x=d} t_{M^+}^* d(\mu_{M^+}^* - \mu_{L^+}^*)$$

$$= \vartheta \log \frac{a_{L^+}^{(2)}}{a_{L^+}^{(1)}} + \vartheta \int_{x=0}^{x=d} t_{M^+}^* \log \frac{a_{M^+}^{(2)}}{a_{L^+}^{(1)}} \quad (14)$$

where t_{M^+} is the transference number of M^+ ion in the ion exchanger (or in surface layer of the glass); d is the thickness of the membrane. Quantities corresponding to the selected mechanism are marked with asterisks. t_{M^+} can be expressed in the terms of respective mobilities u_i and volume concentrations c_i of the free ($i=L^+, M^+$) or bonded ($i=LR, MR$) ions. Then the relations between the concentrations and also activities L^+ and M^+ (or/and LR and MR) in the solid phase, on the one hand, and ion activities in the solutions, on the other hand, have to be found and inserted into Eq. 14. The conception of the dissociation of the ionogenic groups [86, 87] is widely used in the derivations.

The most general conclusions from this and other papers are as follows: The GE is selective to an ion if both types of

the ion, free and bonded ones, are involved in the charge transfer. The ion has to be firmly bonded in an ionogenic group and at the same time be mobile.

The integral expressions in [93–96] were derived for the cases, when the electrode behavior of the glass was determined by only one prevailing sort of groups based on sites R^- . Attempts to expand this approach to the glasses with commensurable effect of two sites R_1^- and R_2^- (stepwise E -pH curves) met with some difficulties at integration of expressions for t_i . These difficulties were overcome with a method proposed in [96], where the following equations were derived by differentiation of Eq. 14:

$$\frac{dE}{d \log a_{L^+}} = \vartheta \left[t_{L^+} + t_{M^+} \left(\frac{d \log a_{M^+}}{d \log a_{L^+}} \right) \right], \text{ and at} \quad (15)$$

$$a_{M^+} = \text{const.} \left(\frac{dE}{d \log a_{L^+}} \right) = \vartheta t_{L^+}$$

(A similar equation was derived by Isard [22]). Equation 15 is of fundamental importance; it characterizes the extent to which the slope of an electrode function will be more or less close to the theoretical Nernstian. If $t_{L^+} < 1$, the slope will be sub-Nernstian, what is widely met in glass and other ion-selective electrodes.

In [98] the t_{H^+} -pH curves are analyzed with the help of Eq. 15, as applied to the glass with vacation transfer mechanism and two sorts of ionogenic groups (a heterogeneous-site membrane [99]), instead of stepwise E -pH curves.⁹

The dependence of the electrode properties of glasses on their composition

The first approximation: an effect of the energetic factor

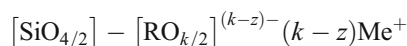
Considerable efforts of scientists over many years have led to the selection of such compositions of glasses for GEs which are optimal for each field of application. This came about as a result of systematic studies of the dependence of electrode properties of glasses on their composition. Examples are Perley's [30, 31] and Eisenman's [38] studies of the systems $Li_2O-R'_xO_y-R''_yO_z-SiO_2$ and $Me_2O-Al_2O_3-SiO_2$ respectively. Our studies of the glasses $Me_2O-R_xO_y-SiO_2$, where $Me=Na, Li$; R 's are the elements of I–V groups of the periodic system, were summarized in [68]. Many chapters of [6] sum up the first step of these studies. Two main results can be distinguished, one of which falls in the electrochemistry of glass H^+ - and ion-

⁹ The integration was made in [99], and stepwise curves were described, when the vacations and defects were taken in account for the phase boundary potential, but for diffusion potential, free ions moving over interstitials were assumed (see also [9, 10]).

selective electrodes, the other of which belongs to the science of the chemical structure of glass.

Binary alkali-silicate glasses $\text{Me}_2\text{O}-\text{SiO}_2$ (15–36 mol% Me_2O ; $\text{Me}=\text{Li}, \text{Na}$) are the original glasses for the following comparison. GEs of these glasses are characterized by the $K_{\text{H}^+, \text{M}^+}^{\text{pot}}$ values of 10^{-8} – 10^{-12} . It is permissible to consider their potential up to pH 7–10 to be determined only by H^+ ions (H^+ -response) and that M^+ ions begin to influence the potential at higher pH values. The reason is that a binary glass has weak acidic ionogenic groups $[\text{SiO}_{3/2}]\text{OH}$. The bond strength of H^+ in these groups is mainly covalent and very strong. If R_xO_y is added as a third oxide to the glass composition, then the ion R^{z+} being placed in the $[\text{SiO}_{3/2}]\text{OH}$ group's environment results in a polarizing effect on the O–H bond. This effect may be stronger or weaker than the effect of the ion Me^+ which had been situated previously at this site. If the effect is weaker, the O–H bond becomes stronger, the H^+ -response of the GE expands into the higher pH region, and the $K_{\text{H}^+, \text{M}^+}^{\text{pot}}$ value decreases. $\text{R}=\text{Cs}, \text{Ca}, \text{and Ba}$ function in such a way. If the effect is stronger, the O–H bond weakens, the H^+ -response region narrows, and the $K_{\text{H}^+, \text{M}^+}^{\text{pot}}$ value increases slightly ($\text{R}=\text{Mg}, \text{Be}, \text{La}$). We have named these phenomena “the electrode effect of a second network-modifying ion” (the first is Me^+ ion).

The network-forming ions R^{z+} act dramatically: their incorporation into the silicate network at the synthesis is followed by the change of a coordination number k or the inter-atomic distances R–O inherent to R_xO_y oxide. The polarizing effect of these R^{z+} is so powerful that they form their own element-silicate ionogenic groups:



while glasses are synthesized (hereinafter reference to $[\text{SiO}_{4/2}]$ in such groups is omitted for simplicity). Such behavior is inherent to $\text{R}=\text{Al}, \text{B}, \text{Ga}, \text{Fe(III)}$ (partly) ($z=3, k=4$); Sn, Zr ($z=4, k=6$). The subsequent exchange of Me^+ for H^+ or M^+ from the solution results in the formation of the $[\text{RO}_{k/2}]^{(k-z)-}$. $(k-z)\text{H}^+$ (or M^+) groups, which are strongly acidic in H^+ form. The O–H and O–M bonds in these groups do not differ significantly either in their character (they are mostly ionic) or in their energy. This results in an early disruption of the H^+ response (at pH=1 to 3) and in a sharp increase (as compared to binary glass) of the $K_{\text{H}^+, \text{M}^+}^{\text{pot}}$ values up to 10^{-1} to 10^{-3} . If a fairly small quantity (1–4 mol.%) of the network-forming oxide R_xO_y is added, then the appearance of the $[\text{RO}_{k/2}]^{(k-z)-}$. $(k-z)\text{H}^+$ groups manifests itself as a “step” in the E -pH curve at a pH value of (1 to 3) to (5 to 6) followed by the E value decreasing because of the predominance of silicate groups. At greater concentration of the network-formers, the GE responds to pH changes only in the region of the strong acidic solutions, and it shows M^+ -function at $\text{pH}>3$ to 4.

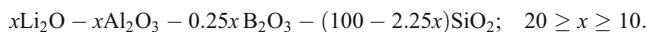
While studying the E -pH curves of the glasses of the system $\text{Me}_2\text{O}-\text{R}_x\text{O}_y-\text{SiO}_2$, we succeed in finding the structural role of the modifying ions, the intermediately modifying ions, and the network-forming or intermediate network-forming ions for about 30 elements of the periodic system [68]. On frequent occasions, we found such structural role with this method earlier than it was found through other direct structural-sensitive methods.

The explanation of these phenomena is based on the energetic factor. However, this factor is inadequate to explain the peculiarities of the GE behavior when the more complicated glasses are studied, e.g., glasses of four-component systems such as $\text{Me}'_2\text{O}-\text{Me}''_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$, $\text{Me}_2\text{O}-\text{R}_x\text{O}_y-\text{R}_u\text{O}_z-\text{SiO}_2$, as well as in some other cases. We have to search for some other factors, the first among them being the dynamic factor.

The second approximation: the inclusion of the dynamic factor [100]

We give some examples.

- 1) A set of the glasses $x\text{Li}_2\text{O}-y\text{Al}_2\text{O}_3-(100-x-y)\text{SiO}_2$; $36 \geq x \geq 12, 28 \geq y \geq 3$ mol.% ($x:y=1:1, 2:1, \text{ and } 4:1$);



(The method and the results of the studies for the last set are published in detail in [101, 102].)

The E -pH curves for GEs of these glasses are typical for the glasses with a predominant influence of the $[\text{AlO}_{4/2}]^-$ sites. By comparing the shape of the curves, one can see the decreasing H^+ - and the increasing M^+ -selectivity of GEs with the Li_2O diminishing concentration as well as the larger selectivity to Na^+ compared with Li^+ . Therewith, the distinction between the $K_{\text{H}^+, \text{Li}^+}^{\text{pot}}$ and $K_{\text{H}^+, \text{Na}^+}^{\text{pot}}$ values run up to two to three orders of magnitude for the same glass, and $K_{\text{Li}^+, \text{Na}^+}^{\text{pot}}$ values increase by three to four orders of magnitude. This can be hardly explained taking into consideration only the energetic factor because the behavior of all of these glasses is determined by the same $[\text{AlO}_{4/2}]^- \text{Li}^+$ ionogenic groups and because it is believed that the $K_{\text{Li}^+, \text{M}^+}^{\text{exch}}$ values alter little or not with the Li_2O concentration.

Consider in this connection the change of the dynamic factor $u_{\text{Na}^+}/u_{\text{Li}^+}$. For explanation we have calculated the value $[\text{Si}]/[\text{Al}]$ in all glasses, i.e., the ratio of the indicated component concentrations in the glass. The variation of these values which run up to three to four with the Li_2O concentration decrease, reflecting the increase in the degree of screening of $[\text{AlO}_{4/2}]^-$ tetrahedra by $[\text{SiO}_{4/2}]$ tetrahedra. If the ions move by vacancy mechanism through the $[\text{AlO}_{4/2}]^-$ sites, they have to penetrate the barrier of $[\text{SiO}_{4/2}]$ tetrahedra

surrounding them in the glasses with the minimal Li_2O concentration. Na^+ ions move in the $\text{SiO}_{4/2}$ medium easier than Li^+ ions. At the increase of the Li_2O (and Al_2O_3) concentrations, the degree of screening decreases, and Li^+ ions can jump directly from one $[\text{AlO}_{4/2}]^-$ tetrahedron to another.

On the data [103] for fused silica, extrapolated from 350 °C to room temperature, the mobilities ratio $u_{\text{Na}^+}/u_{\text{Li}^+}$ is of the same order as $K_{\text{Li}^+, \text{Na}^+}^{\text{pot}}$ for our glasses, i.e., 10^3 – 10^4 . An additional fact is that the electrical conductance of the glass 5% Li_2O –95% SiO_2 at 20 °C is three- to four-order larger than for similar sodium silicate glass [104].

2) The glasses of the series (mol.%) $x\text{Me}'_2\text{O}$ – $(24-x)\text{Me}''_2\text{O}$ – $y\text{Al}_2\text{O}_3$ – $(76-y)\text{SiO}_2$

(where Me' – Me'' are Li–Na, Na–K, and Li–K; x and $(24-x)$ varied from 0 to 6; $y=0, 2, \text{ or } 12$) [100].

The curves $K_{\text{H}^+, \text{M}^+}^{\text{pot}} - x$ for GEs of these mixed-alkali glasses are very much like the curves describing the known mixed-alkali effect in conductance and other properties of glasses linked with ion motion, i.e., these are the curves with extremes at some intermediate x value. To be more exact, we can study only the initial sections of the curves, because further the electrical resistance of the GEs becomes so high that it is impossible to measure their potential. This is a direct manifestation of the mixed-alkali conductance effect.

While Me' changes for Me'' in the glass composition, it is possible to observe the $K_{\text{H}^+, \text{M}^+}^{\text{pot}}$ values alterations, which only to some extent could be explained in terms of the first approximation. This is possible to use for the sections of the curves which correspond to the substitution of the smaller ion by a larger ion, i.e., for the ion with a weaker polarizing effect on O–H bond in $[\text{SiO}_{3/2}]\text{OH}$ and $[\text{AlO}_{4/2}]\text{H}^+$ groups. The opposite cases cannot be explained in terms of our first approximation.

So far, the mixed-alkali effect has no unique explanation in spite of a considerable number of hypotheses. We restrict here our comments to noting the similarity of these phenomena and to underscoring the applicability of the “second approximation” to the explanation of the course of the curves (see also [100]).

3) The explanation of the electrode properties of some other complex glasses is impossible without taking into account the dynamic factor. We mean the alkali glasses containing three network-forming oxides ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{B}_2\text{O}_3$ or $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{ZrO}_2$) and glasses with two network-forming oxides (e.g., $\text{SiO}_2 + \text{Al}_2\text{O}_3$ or $+\text{B}_2\text{O}_3$) and two network-modifying oxide with one movable (Li or Na) and the second hardly movable cation (e.g., MeO and even Cs_2O) [105, 106]. The latter takes up the position in the $[\text{AlO}_{4/2}]\text{Me}^{2+}$ - or $[\text{BO}_{4/2}]\text{Me}^{2+}$ -groups and weakens

or even entirely excludes the manifestation of these groups in the electrode behavior. This fact is of a practical importance: small amounts of Al_2O_3 or ZrO_2 in a pH-sensitive glass with CaO or BaO can expand the field of its usage because improving its chemical durability.

Sometimes the “dynamic factor” has to be invoked for explanation of electrode properties also of ternary glasses. So in [44], it is shown that after a special treatment, the GEs of Li_2O – La_2O_3 – SiO_2 glasses La^{3+} ion remaining in the leached layer hinders for a long time Na^+ to enter the glass, i.e., decreases the Na^+ mobility and thereby expands the H^+ -function region.

The surface layers

Ion concentration profiles and methods of their study

We could see from the preceding that the electrode properties of glasses are among the structure-sensitive physicochemical properties of glasses along with conductance, diffusion, internal friction, etc., in which both the bond strength of ions in the glass and the ion mobilities are reflected. The peculiarity of the electrode properties is that they reflect not only the properties of the glass itself but the features of a layer developing on the glass surface as a result of its interaction with solutions. The systematic study of the dependence of the glass electrode properties on their composition contributes to the knowledge of glass structure and its surface layers as well as of the mechanism of glass–solution interaction.

The first concentration profile of Na^+ in the surface layer of the sodium silicate glass containing 4% SrO, treated with water, was shown [107] by the research group, engaged in the GE problems (B. v. Lengyel school). This was achieved by the method of HF etching. A lot of other glasses were studied with this method. Later various spectroscopic methods were applied to this (for review, see [11, 108, 109]). Among them, especially IBSCA (ion bombardment for spectrochemical analysis) and NRA (nuclear reaction analysis) have to be noted. F. Baucke used both of them very effectively [11].

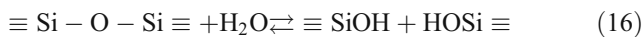
There are two main types of the surface layers: (1) of a “simple” smooth profile with a steep gradient of Me^+ , beginning from the very glass/solution boundary, and (2) containing a more or less lengthy leached layer followed by thin layer with a steep Me^+ gradient transient to the bulk Me^+ concentration. The gradient curve is S-shaped in this case. Some level of the “residual” Me^+ nearly without gradient may be seen sometimes in the leached layer.

The gradient layers are called also ion exchange ones, which shows the place where this process occurs. The mentioned “simple” profile reflects a “simple” ion interdiffusion, the S-shaped—the ion interdiffusion accompanied with some other process, e.g., enhanced with glass network hydrolysis [108, 110, 111].

The processes going on in the surface layers

This problem is widely studied in connection with glass chemical resistance (for review, see [108–111]). We dwell here on the processes which are important for the GE action mechanism. The interaction of a silicate glass with aqueous solution may, as a first step, be traced back to two basic reactions, i.e., *dissolution* and *leaching* [109]. The first affects mainly the Si–O network, the second—the movable components of the glass (Me^+ ions). The non-alkali glass components, such as Ca, Al, etc., are not leached but are subjected to dissolution together with the network. It is the leaching process, which gives rise to both types of the surface layers, described above. The essence of this process is ion interdiffusion, which results in the formation of the concentration profiles.

Besides this, the main reaction which proceeds both at the glass/solution boundary and in the depth of the surface layer is hydrolysis (\rightarrow) and condensation (\leftarrow):



The reaction is reversible; the direction depends on many factors. The hydrolysis enhances the interdiffusion [108, 110, 111]; the condensation leads to an accumulation of molecular water in the leached layer [109]. Alternating sequences of both processes initiate the rearrangement of the network up to a microphase separation with water-filled channels. This does not occur with the more resistant glasses, e.g., with lithium silicate or aluminosilicate ones. The foregoing is indicative of heterogeneity of the glass surface layers.

The methods of surface layer studies were applied in combination with other methods, among them measuring of electrical conductance and IR spectroscopy. The methods were used both for solving the problems of the GE mechanism and for general problems of glass/solution interaction.

The surface layers and electrical measurements¹⁰

Dynamic electrochemical studies of GEs are complicated by the high ohmic resistance of the glass and the two-sided nature of the GE membrane. These difficulties may be obviated by application of special methods of measuring followed by an appropriate data analysis.

Impedance studies of GEs involving network analysis have been conducted both theoretically and experimentally by Buck [112–114] and Brand and Rechnitz [115, 116]. They distinguished between the intact (“ideal”) glass membrane and the membrane with hydrated film, describ-

ing them as different components of equivalent circuits. Respective components are reflected in impedance diagrams. After analysis of these diagrams, the values of the time constants τ (order of few milliseconds to 10^2 ms), resistances R_g , and capacitances C_g (average order 0.5×10^2 pF/cm²) have been calculated for some commercial pH- and pM-sensitive GEs ($\tau = R_g C_g$; index g means here “geometric”).

The film or decomposed silica gel layer on real GEs was treated as a separate medium with low density of fixed site through which ions move by diffusion–migration to the intact bulk. Such a film is peculiar to pH-GEs and not present to an appreciable extent on pM-GEs, but conductivity of the latter may be much less, than in the case of pH-GEs [115, 116].

The properties of the surface layer of some commercial lithium silicate GEs have been intensively investigated by Wikby with the HF-etching method in combination with a DC pulse technique [117–124]. The resolution of the voltage–time curves gave four time constants (τ_i) and four resistances (R_i) corresponding to two kinetic processes, fast ($\tau_1, \tau_2 \sim$ ms; $\Delta H_{\tau_1, \tau_2, R_1, R_2} \sim 15.4 \pm 0.6$) and slower ($\tau_3, \tau_4 \sim$ s; $\Delta H_{\tau_3, \tau_4, R_3, R_4} \sim 24.4 \pm 3.5$; [averaged by this author (A.B.)]). Here, ΔH is the activation energy of the conduction process, kilocalories per mole, of the mentioned quantities, derived for the temperature range 10–35°C. The characteristics of the fast process are ascribed to the bulk ($\tau_b, \Delta H$, and these for slower one to the gel (leached) surface layer ($\tau_s, \Delta H$). It was found that ΔH_s for conduction is of the same order as ΔH for outflux of Li^+ ions from the glass (leaching experiments). A surface resistance maximum that localizes in the ion exchange (transient, gradient) layer of pH-GEs, in its initial part. It was shown also [125] that in the part of this layer, closer to the bulk, may appear also some resistance minimum.

It was even suggested to consider the place with the resistance maximum as “the most critical interface in the GE membrane” [126], where the equilibrium between the glass and the solution is established and reestablished fastest. The outer section of the surface layer (leached, gel layer) with low Me^+ concentration gradient does not impede the process.

The preceding related to pH-GEs of the MacInnes and Dole glass type with developed leached layer [125]. Such a layer is not characteristic of pM-GEs. The surface resistance (R_s) maximum for such GEs is located near the very glass/solution boundary, and the R_s smoothly decreases to the bulk along the ion exchange layer.

Kiprianov in our laboratory studied the behavior of two types sodium aluminosilicate (NAS) glasses for pM-GEs: (I) preferentially K^+ -selective one of NAS-2704 type (Table 1) and (II) preferentially Na^+ -selective NAS-2010 and NAZrS-3013₅01₅ [127–129]. The HF-etching, potenti-

¹⁰ For review of this topics till 1974, see also [9].

ometry, steady state polarization curves, and potential step techniques were used. It was found that in NaCl solutions, there were no impediments for the heterogeneous reaction $\text{Na}^+(\text{gl}) \rightleftharpoons \text{Na}^+(\text{sol})$. The standard exchange current density is estimated at $1 \times 10^{-4} > i_{0,\text{Na}}^0 > 2 \times 10^{-6} \text{ A/cm}^2$, and capacitances C_g were of the same order of magnitude as in [112, 113]. This value does not contradict to i_0 values for NAS-2704 $(7.5 \pm 2.5) \times 10^{-4} \text{ A/cm}^2$ and for NAS-1906 $1 \times 10^{-5} \text{ A/cm}^2$, estimated in [127] according to the data on sorption Na^+ obtained by Eisenman [73] and Moiseev [130].

Baucke [11, 131] has estimated exchange current densities for heterogeneous reaction $\text{H}^+(\text{gl}) \rightleftharpoons \text{H}^+(\text{sol})$ for pH-GE of the order of magnitude 10^{-3} A/cm^2 .

The treatment of the NAS-2010 and NAZrS-3013₅01₅ glasses with neutral KCl solutions led to the appearance of the additional resistance R_s . The resistivity of the surface layer ρ_s in this case was estimated to be three orders of magnitude greater than the bulk resistivity ρ_b . This did not relate to the K^+ -selective glass NAS-2704 in the case of neutral KCl solutions but took place when KCl + KOH solutions were used. The activation energy, kilocalories per mole, computed in the temperature range from 4 to 50 °C, was 15 ± 1 for ρ_b and 23 ± 1 for ρ_s , which agrees with values estimated by Wikby for pH-GEs [117].

Similar measurements with a potential step technique [129] applied to the vacuum-processed cells Na(metallic)/glass NAS-2704/Me(metallic), where Me were Na, K, or Cd, gave in the case Me=Na the same results as in NaCl solutions; when Me=K, the results were the same as in KCl + KOH solutions. The contact with Cd was blocking and irreversible.

Later Kiprianov [132] has changed the experimental procedure. He treated the inner surface of the tubes of the glass type NAS 2704 with solutions, therewith obtained the leached layer. Then he etched step by step this layer by HF solution and measured the resistance between two mercury contacts after every etching. In such a way he obtained the profile of the conductivity. The conductivity of the leached layer resulted from the treatment of the glass by 0.1 M HCl or KCl solutions was by three to four orders of magnitude higher than the bulk conductivity. The conductivity profile had a complex shape: a minimum near the very surface, a maximum in the beginning of the ion exchange layer, and another minimum in the middle of the layer. The first minimum is due to the enrichment of the outer layer by the silica as a result of a condensation process and the formation of a poor conductive sublayer of the glass of the approximate composition KAlSi-100486. The second minimum is due to the mixed-alkali effect ($\text{K}^+ - \text{Na}^+$).

The surface layers and GE response time

The studies of the GE response time are important both for practice and theory (for review, see [9, 10, 133, 134]). Here,

the theoretical aspect only will be discussed. The transient processes during the concentration jump may be classified (1) as existent in the region of one cation function and (2) with partial or complete transition to another cation function [134]. In the first case the response time depends mainly on the quickness of the solution replacement. If it takes tens to hundreds of milliseconds, then the response time registered in some papers was of the same order for pH-GEs in the region of their H^+ -function and for pNa-GEs of a sodium aluminosilicate glass in the region of their Na^+ -function.

The potential dynamics in the region of one ion function

The potential temporal course in the case (1) is described with exponential equations, from which the most general is the semi-empirical equation

$$\Delta E_t = \sum_i^n \Delta E_i^\ominus [1 - \exp(t/\tau_i)] \quad (17)$$

where ΔE_t is the total emf jump within the time t ; ΔE_i^\ominus is the contribution of an i th component to the final jump ΔE^\ominus ; $|\Delta E_i^\ominus| = |E_{i,t \rightarrow \infty} - E_{i,t \rightarrow 0}|$; τ_i is a time constant.

For the time order of tens to hundreds of milliseconds, Eq. 21 was derived [135, 136] based on the theory of electrode kinetics of charge transfer processes and the theory of rate processes (see also [9]). In this case $n=1$, $\tau = 1/k$; k is the rate constant.

For the more realistic case of the solution replacement in the time of the order of seconds and greater, another approach was proposed [10, 137]. The diffusion processes are considered as determining the response time. The main step of such processes for the concentration jump in the region of one cation (J^+) function is the diffusion through the unstirred solution layer adjacent to the liquid/solid boundary (the Nernst diffusion layer) with a thickness δ and diffusion coefficient D_j . Then Eq. 17 approximately holds with $n=1$, $\tau = 4\delta^2/\pi^2 D_j \sim \delta^2/2D_j$, in the form:

$$\Delta E_t = \Delta E^\ominus \left[1 - \frac{4}{\pi} \exp(t/\tau) \right] \quad (17a)$$

exactly in a linear range at $\Delta E^\ominus \ll RT/F \sim 25 \text{ mV}$; then $\Delta E^\ominus \sim RT/F (a_j - a_j^0)/a_j$.

We used Eq. 17 for describing the potential dynamics of some experimental and commercial GEs [134] (for details see also [138–140]). The experimental data were obtained in a cell of volume 10 mL in which threefold solution change occurred per 1 s. Data evaluation by Eq. 17 has given the following results: The number n never exceeded 3. The slowest process was characterized with τ_1 value of the order of 100 s, the fastest with $\tau_3 \sim 1$ s, and τ_2 till 10 s. The contribution of ΔE_3^\ominus in ΔE^\ominus was mostly 100% (never less than 75%) in the cases of the “good” commercial

pH-GEs (H^+ -function) and experimental pNa-GEs of sodium aluminosilicate glasses (Na^+ -function). The contribution of ΔE_1^\ominus was 0–10%. The process characterized by τ_3 was regarded as a diffusion through Nernst layer; with τ_2 as a diffusion in the solution detained in the pores of glass surface; with τ_1 as an ion interdiffusion in the leached (in the walls of the pores) or even ion exchange layer of the glass. Such conclusions are based on the following facts: τ_2 values were greater for rugged (etched with HF solution) GEs than for GEs with flame-polished surface; the “activation energies” ΔH , computed in the temperature region 20–40 °C for τ_2 and τ_1 , were 7 ± 1 and 15 ± 3 kcal/mole, respectively. The first value is somewhat greater than for diffusion in a “free” solution (≤ 4 kcal/mole), the second is characteristic for diffusion in a solid.

The potential dynamics in the transition region from one cation function to another, including the establishing of a new ion function [134]

This case is characterized often (but not always!) by non-monotonic course of the $E-t$ curves, and the appearance of potential overshoots after sudden changes in cation composition of bathing solutions. Such phenomena were observed sometimes also in the region of one ion function in the presence of other cations, lasting for a few seconds and resulting from the ion interdiffusion in the stagnant Nernst layer.

When we deal with two or more potential-determining ions, the slowest processes, responsible for establishing of a final potential value, occur mostly in the glass surface layers and are characterized by longer response times—minutes, hours, days, even months. The most significant of these processes is the ion interdiffusion, which may be complicated by such processes as hydrolysis↔condensation, microphase separation, etc., resulting in structural transformations of the layer.

There is a known thermodynamic statement originally formulated by M. Plank and used by Helfferich, Doremus, Eisenman, Schultz, and Stephanova [141] in a discussion of the problems of membrane electrodes: “if a membrane is structurally uniform and only two mobile ions take part in an ion exchange process, the diffusion potential does not depend on concentration profiles and is determined uniquely by the boundary conditions.”

The other side of this phenomenon is the question, whether E depends or not on t (more exactly, E_D as a component of the total E). For only two exchanging ions, L^+ and M^+ , and at the assumptions which were made in the derivation of Eqs. 14 and 15, such as $\gamma_i^{gl} = \text{const.} = 1$, $u_{M^+}/u_{L^+} = \text{const.}$, $(c_{L^+} + c_{M^+})^{gl} = c^0 = \text{const.}$, there is no dependence of E on t . Moreover, this holds also if γ_i^{gl} and u_{M^+}/u_{L^+} vary with the boundary concentrations, being

their univocal functions. “The diffusion potential should change with time only if there is some change in structure of the glass itself with time or position, giving changes of mobility ratio or thermodynamic factor with time or position.” [91]

In the same chapter [91], Doremus has proposed an equation for the potential of a glass membrane consisting of two parts I and II, differing in their composition and/or structurally, and respectively, by their u_{M^+}/u_{L^+} and $K_{L^+,M^+}^{\text{exch}}$ values, i.e., K_{L^+,M^+}^{pot} . The situation at the interface between the parts may become a source of a change of E with t .

“An example of this situation occurs in the hydrated layer on GEs. As long as the ions diffusing into the glass are confined to a hydrated layer that has uniform properties, the potential is constant. However, if the foreign ions<...>reach the boundary between hydrated and dry glass in appreciable concentrations, the potential will change with time if appropriate properties of the two part are different” [91]

Let us write down the Doremus equation for one (external) side of the GE membrane, designating I=s (surface), II=b (bulk):

$$E = E^\ominus + \vartheta \log \left(a_{L^+} + K_{L^+,M^+}^{\text{pot},s} a_{M^+} \right) + \vartheta \log \left(c_{L^+}^{s,b} + \left[K_{L^+,M^+}^{\text{pot},b} / K_{L^+,M^+}^{\text{exch},s} \right] c_{M^+}^{s,b} \right) - \vartheta \log \left(c_{L^+}^{s,b} + [u_{M^+}/u_{L^+}]^s c_{M^+}^{s,b} \right) \quad (18a)$$

Here, $c_i^{s,b}$ is the ion concentration (mole fraction) at the leached layer/bulk boundary or, more exactly, somewhere in the ion exchange layer.

Take up an additional assumption $[u_{M^+}/u_{L^+}]^s = 1$ [10]. It means that there is no diffusion potential in the leached layer. Then the last term of Eq. 18a is zero and $K_{L^+,M^+}^{\text{exch},s} = K_{L^+,M^+}^{\text{pot},s}$; Eq. 18a transforms in

$$E = E^\ominus + \vartheta \log \left(a_{L^+} + K_{L^+,M^+}^{\text{pot},s} a_{M^+} \right) + \vartheta \log \left(c_{L^+}^{s,b} + \left[K_{L^+,M^+}^{\text{pot},b} / K_{L^+,M^+}^{\text{pot},s} \right] c_{M^+}^{s,b} \right) \quad (18b)$$

Basing on Doremus equation (for both sides of the GE) and the assumption $[u_{M^+}/u_{L^+}]^s = 1$, Morf [10] has described the potential kinetics including the overshoots of different kind. It was shown in [134] that under certain condition, the equation of this type may be used also for description of an asymmetry potential E_{as} of GE in the H^+ - and Na^+ -function regions and of a specific effect of non-aqueous solvent on the GE behavior [142, 143]. Structural changes in the surface layers, such as hydrolysis↔condensation processes, give rise to difference in their ion selectivity. So, the condensation causes a selectivity increasing in favor of H^+ ion and a potential shift in the direction of more positive values; an effect of the hydrolysis is opposite.

A lot of experiments quoted in [134] support the validity of the two-part layer approach, but some experiments suggest that there are more than two layers with different properties which determine different potential levels. Firstly in [134] and later in [144], the model of an inhomogeneous altered surface layer with n ($1 \dots k \dots n$) sublayers was proposed. The model is based on the same assumptions as the two-layer one described above. An ion interdiffusion over the sublayers involves the appearance of some quasi-steady state potential levels of the GEs which correspond to a local equilibrium (steady state) at intermediate boundaries between sublayers (e.g., between k th and $(k+1)$ th sublayer). A term of the type $E^{\ominus,k} - E^{\ominus,k+1} = \vartheta \log K_{L^+,M^+}^{\text{pot},k}$ contributes to E^{\ominus} of GE. When the interdiffusion reaches the n th sublayer being transient to the glass bulk, the steady state potential is established.

Experiments involving Ag^+ ions

In the intervening period between [134] and [144], we studied the GE potential dynamics and the composition of surface layers of some alkali aluminosilicate glasses after transfer of the GEs and glass specimens from HNO_3 or MNO_3 solution into AgNO_3 solution and vice versa [145–147].

The silver ion differs in nature from alkali ions M^+ . The bond $\text{Ag}-\text{O}$ is more covalent than $M-\text{O}$, and the polarizability of Ag^+ ion is far beyond that of M^+ .

The Ag^+ ion from aqueous solutions does not penetrate into alkali-silicate glasses without alumina, and GEs of such glasses do not possess a Ag^+ function. On the contrary, the glasses with alumina manifest this. A great selectivity of these GEs to the Ag^+ ion was found in a steady state: The difference between the E^{\ominus} for H^+ and M^+ ions, on the one hand, and Ag^+ , on the other, reaches 300–350 mV, respectively. This corresponds to selectivity coefficient as great as $\sim 10^6$ in favor of Ag^+ . When the direction of the exchange was $M^+(\text{H}^+) \rightarrow \text{Ag}^+$, the steady state was reached in a few hours; at the inverse direction, this took days for M^+ ions and even months for H^+ ion.

The selectivity coefficients $K_{M^+,\text{Ag}^+}^{\text{pot},n}$ which corresponded to steady state were called as “formal” ones, whereas $K_{M^+,\text{Ag}^+}^{\text{pot},s}$ related to quasi-steady state of the very surface were called “real.” They are of the order of magnitude $1-10^2$ for $M^+=\text{H}^+$ or $M=\text{Li}^+, \text{Na}^+, \text{K}^+$, respectively. The electrode functions of these ions are also obtained at rapid measurements.

At an intermediate time the potential changes or quasi-steady state potential levels were observed. The dynamics of GEs potentials correlated with the temporal changes in the ionic composition of the glass surface layers. So, the potential values that we calculated with the modified Doremus Eq. 18b agreed well with our experimental values. For the calculation, we substituted in the Eq. 18b ($L^+=\text{H}^+$,

$M^+=\text{Ag}^+$) the values of residual concentration of the ions in a surface sublayer near ion exchange one at intervals.

It turned out that the best linearizing function of the time t is $\log t$. Diagrams $E-\log t$, where t covered the period from hours to months, constituted of two to three linear parts, whose intersection points, by our opinion, corresponded to the time of the passing the pseudo-phase boundaries by the interdiffusion front.

Conclusion

The development of the GE theory and practice within 100 years of its existence is in sufficient detail presented above. However, the picture remains incomplete without the description of the large contributions which Dr. F.G.K. Bauke has made for a proper understanding of glass electrodes. His activity during the last quarter of the twentieth century is documented in many papers and presentations at representative conferences both on electrochemistry, analytical chemistry, metrology, and on properties of glass. The book [11], of which he is the main author, is among the most important books about GE, and it crowns the century with dignity.

Using a technique with the highest resolution in the study of the glass surface (IBSCA and NRA), he presented the most complete and detailed description of the surface layers and their development for the case of lithium silicate glass. He describes the equilibrium at the glass/solution boundary as a dynamic equilibrium not only in terms of thermodynamics, but also of electrochemical kinetics. For the first time in the literature about GE, he concentrated our attention on the electrochemical mechanism of formation of the GE potential as the consequences of a charge division at the boundary (the dissociation mechanism). Previous authors implied this, but this statement has not been expressed with such clearness and completeness, as in Bauke’s papers. All other sides of GE functioning (ionic mobility, diffusion potential, Na^+ -function, etc.) are also discussed in detail in his papers and in [11].

Undoubtedly, the research of Bauke and his concepts mark a considerable progress in the understanding of the mechanism of glass electrodes, but it seems to us that they do not disprove everything done before him. Such questions, as dependence of electrode properties on glass composition and structure (especially the properties determined by the mobility of ions), an expanded course of the GE potential in the transition region, dynamics of potential at transition from one GE function to another, and so on, represent a challenge to the apologists of Bauke’s concepts.

The reader can see from this review that the works of B. P. Nikolskii and his school found numerous supporters and followers all over the world during the 70 years of the

100-year-old history of the glass electrode. Bauke characterized the state of the glass electrode science in the period before the emergence of his own works as “unfortunate.” He writes, “Obviously, the great success of Nikol'skii's thermodynamic equation handicapped the development of new ideas on the glass electrode mechanism for at least five decades, a period which could therefore be termed the Nikol'skii hiatus in analogy to the Nernstian hiatus [Bockris] in electrode kinetics some decades earlier” ([11], p. 52). (*We can consider this comparison as a rather complimentary! A.B.*)

In Russian, the word “hiatus” sounds as “ziyanie” and has rather negative character (gap, lacuna), but change only one letter: “s” instead of “z,” and the word transforms. “Siyanie” means “shine, light, glow, radiance.” I would like to show that the discussed period enriched the science with useful ideas and experimental data, on the base of which a lot of practical advancements were made.

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