

From the pH scale to the pO scale. The problem of the determination of the oxygen ion O^{2-} activity in oxide melts

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Abstract This paper considers the problem of the pO = $-\log a_{O^{2-}}$ scale development and standardization in comparison to the pH standard scale. The approaches describing acid–base equilibrium in oxide melts are analyzed with respect to their applicability to determine the basicity of oxide melts. Procedures for pO measurement and standardization in glass-forming melts are suggested.

Keywords pH scale · pO scale · Oxygen ion activity · Acid–base relationships in oxide melts

Introduction

The pH scale for aqueous solutions Measurements of acid–base properties of aqueous solutions, usually yielding pH values, are very common both in complicated chemical and technological processes and in everyday life: pH data are given on the labels of mineral water bottles, soaps, toothpastes characteristics, etc. Because of the importance of pH data, various instruments have been developed for its measurement: glass and ceramic electrodes, electrodes with organic film membranes, and also different pH meters. The general importance of pH data made it necessary to develop the fundamental ideas of acid–base theory for aqueous solutions, as well as to specify the procedures of pH measurement and standardization.

The protolytic acid–base theory was suggested by Brønsted in 1923 and independently in the same year by Lowry; the follow-up development of this theory was mainly the result of Brønsted's work [1]. According to that theory,

acids are substances able to donate a proton (H^+), while bases accept a proton. Acids and bases can be neutral molecules or ions. Applying this theory, a uniform quantitative description of the processes in aqueous solutions can be given using the function $pH = -\log a_{H^+}$, where a_{H^+} is the proton activity. In order to achieve this, a system of approaches of a_{H^+} measurement has been developed, especially the principles of galvanic element constructions. The accurate determination of single ion activities is a well-known problem. The essential points were the standardization of the measurements on the base of some arrangements and the methods of preparation of standards.

The rapid progress in chemical technologies using aqueous solutions, the progress in biology, medicine, agriculture, food and pharmaceutical industries, criminalistics, etc. which took place since the introduction of the Brønsted–Lowry theory made it necessary to develop international pH scales (NBS and BSI) in the middle of twentieth century and to develop devices for pH measurements in aqueous solutions with respect to the requirements of international scales.

The pO scale for oxide melts On the other hand, most modern high temperature technologies deal with a class of liquid-phase objects—oxide melts; obviously, some quantity needs to be defined which expresses the acid–base properties in such melts. High temperature technologies involving operations with oxide melts are an important field of modern industry. The following processes (with their intermediate stages) should be mentioned here:

- glass production—batch baking, glass melting, melt molding; interactions of glass-forming melts with the furnace cladding and the mold
- ferrous and nonferrous metallurgy—the wide range of interactions between the metal, slag, and the reactive

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atmosphere (decarboxylation, desulfurization, dephosphorization, and other processes); interaction of slag with refractory materials of production equipment

- cement production—control of gas atmosphere and basicity measurements in the sample probes

The fact that oxygen ions (O^{2-}) participate in all the above-mentioned processes can be considered as a common feature of them. The determination of the acid–base properties of the oxide melts in high temperature technologies is quite important for the theoretical understanding of the nature of some physicochemical processes in glass-forming melts and slags, as well as for applied tasks, e.g., the prediction of these process tendencies and design of the materials with necessary characteristics. However, in contrast to aqueous solutions, until now there is no common experimental approach to the determination of acid–base properties of oxide melts. Moreover, there is no theoretical concept describing the chemical interactions in oxide melts in the framework of an acid–base theory. The direct use of well-known theoretical and experimental approaches of aqueous solution chemistry for oxide melts is impossible due to the principle differences between water solutions and oxide melts. These differences are: the absence of solvent in oxide melts; low values of dielectric constant; rather high ionization levels of most alkali-containing melts, and as a result, high ionic forces; the presence of structural–chemical associates and polymers of different chemical nature, giving rise to high viscosities of the melts; and wide temperature range of melt phase existence, etc.

Obviously, the above statements are valid for the case of the direct measurements in the melt, i.e., in situ measurements. However, there exist a number of approaches also providing the possibility of obtaining experimental information on the acid–base properties of melts and glasses. For melts, it is the so-called “gas solution method,” in which a gaseous agent like H_2O , SO_2 , CO_2 , or Hg interacts with a melt by forming species like OH^- , CO_3^{2-} , and SO_3^{2-} . The concentrations of the latter are determined after quenching the melt [2–8]. The “indicator method” suggested in [9–11] needs also mentioning: in this approach, the acid–base properties of the glass are considered using the information on the changes of the ion–indicator coordination state (an element with varying valence, e.g., Cr or V is usually used as such an ion–indicator). The data on the state of the ion–indicator in the glass is compared with those of salts of chromium or vanadium acid in aqueous solution. Among the discussed approaches, the scale of “optical basicity” [12–19], which is well known among the specialists in glass science and metallurgy, should be especially mentioned.

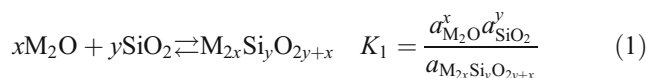
In addition to the experimental methods, there are several empirical approaches based on the consideration

of thermodynamic properties: oxydotropy [20]; Schwartzman criterion [21]; heat effects of the reactions of oxide, salt, and glass formation [22–24]; chemical properties of the melts and their phase diagrams [25, 26]; and “electro negativity” [27]. In fact, the comparison and critical analysis of the above approaches would make a separate special review

It should be mentioned that the development of the high temperature oxygen-conductive material based on stabilized zirconium oxide (YSZ) was a great support for the practical investigations in the field of pO measurements. As a result, a number of papers published in 1970–1990, suggested some interesting approaches for the electrochemical study of glass-forming melts; these approaches were based on the use of electrodes with a kind of solid ZrO_2 -based electrolyte, stabilized by Y_2O_3 , CaO , and Sc_2O_3 .

The contribution of F.K.G. Bauke must be considered as very important: investigations of various galvanic elements of different design and the peculiarities of their use in glass industry, thermal electromotive forces (EMF), appearing in these elements, and corrosive resistance of solid electrolytes have been thoroughly studied by F.K.G. Bauke with high accuracy and consistency [28–30].

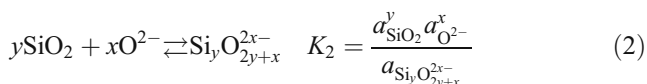
At present, existing concepts of acid–base interactions in oxide melts can be subdivided into three main groups. The first one considers the electroneutral melt components—oxides and salts. At that, acid–base interaction in oxide (e.g., alkali silicate melt, Na_2O-SiO_2 system is taken as an example here and after) can be described as:



This approach is quite convenient since it uses experimentally determined parameters for basicity (acidity) activities of the components or concentrations of electroneutral compounds; its basic drawback is the impossibility to compare the basicity of oxide melts having no common component (Li_2O-SiO_2 and $PbO-B_2O_3$ or $B_2O_3-SiO_2$ and Na_2O-GeO_2). The absence of common component means that it is not possible to use the activity or concentrations of such component to estimate the acid–base properties of the melt.

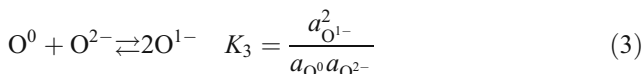
The next approach describes acid–base interactions in oxide melts analyzing the system of ion–molecular equilibria in the melt; the set of components here includes ionic and electroneutral particles; their structure and chemical properties are determined by the melt composition. Within this concept, the quantitative determination of the acid–base properties of the melt can be achieved using the activity of a common melt component. Usually, the O^{2-} ion, considered as a base in the theories of Lewis [31] and Usanovich [32], is taken as that common component. It

should be noted that this concept of acid–base equilibria in oxide melts was first suggested by H. Lux [33]. He also suggested that O^{2-} ion can be considered as a carrier of the base properties of the melt. In the discussed approach, the activity or concentration of O^{2-} ions can be used as a measure for the acid–base properties of a melt and the acid–base interaction in alkali silicate (Na_2O-SiO_2) melt can be interpreted as follows:



This concept gives the opportunity to compare all oxygen-containing melts since there is no necessity for a common oxide in them. For this reason, most models describing acid–base interactions in oxide melts are based on these ionic–molecular interactions in the melt. However, we should mention that the first concept (electroneutral components approach) can be easily converted into the second one (ionic–molecular interactions) by adding the dissociation of the modifying oxides to the metal and oxygen ions and neutral salt components to metal cations and anions [34].

The third approach to describe acid–base interactions in oxide melts is the model suggested by Toop and Samis [35]. It considers three forms of oxygen ions: O^0 —the bridging oxygens forming the structural network of the glass (e.g., $\equiv Si-O-Si \equiv$), O^- —the nonbridging oxygens (e.g., $\equiv Si-O-Na$), and free oxygen ions O^{2-} . For melts, the following equilibrium can be given describing the relation between these forms:



This reaction implicitly considers that the states of O^0 in SiO_2 and the formed silicates, as well as O^- in these silicates, are indiscernible. For this reason, the model by Toop and Samis was rather limited and could not be used for an adequate description of the acid–base interactions in real oxide melts. However, the discussed approach was partly used in all nowadays known models by Masson, Shultz, Dron, and Paul (see [9, 36–39]).

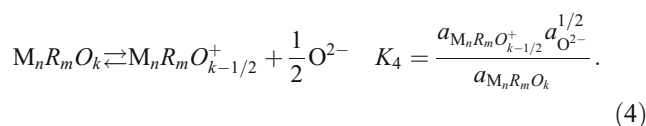
Thus, common chemical approaches considering acid–base interactions giving rise to the formation of neutral salt groups, polymerization–depolymerization processes and complex formation, and acid–base transformations were further developed, particularly in part of quantitative structural and energetic description. All these processes could be interpreted as proceeding with oxygen ion participation. Therefore, in the 1980th, academician M.M. Shultz suggested to the members of his research group, to which the author of this review had the privilege to belong, to undertake a theoretical and experimental research project in order to

develop a common acidity scale $pO = -\log a_{O^{2-}}$ for oxide melts. The extensive theoretical and practical experience obtained during the development of the pH scale for aqueous solutions was the basis for allowing formulation of the main ideas and requirements for an acid scale for oxide melts and also for the elaboration of the working program of its development. The main corner stones are:

- 1) theoretical description of acid–base processes in oxide melts and the determination of a set of chemical transformations responsible for “acid–base” properties of the melt
- 2) the choice of the principle of pO scale implementation (with one defined point or with a set of such points)
- 3) determination of the type of galvanic element; measuring regimes and the frames of their application
- 4) development of laboratory and industrial procedures for pO measurements

General theory of the acid–base interactions in oxide melts

The critical review of the existing approaches (see the brief description above) gave the opportunity to suggest a general theory of acid–base interactions in oxide melts which does not have the drawbacks of the before-mentioned models. This theory is based on Arrhenius dissociation principle, which considers that each substance in a liquid form can dissociate, i.e., detach ions with positive or negative charge. With respect to this principle, oxide melts are considered as a superposition of structural–chemical groups able to attach or detach oxygen ions O^{2-} during acid–base processes; alkali and alkali earth oxides and their salts as well as glass-forming oxides can be considered as such chemical–structural groups. Formulating the dissociation reaction here, one needs to specify the single act of acid–base process. It is known that such single act for protolytic process in water solutions chemistry is donating or accepting of 1 mole of protons H^+ (or H_3O^+). For oxide melts, such single act will be donating or accepting of one half of a mole of oxygen ions O^{2-} , resulting in the change of the charge of structural–chemical group by 1 unit. Generally, this process can be written as

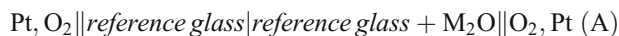


In the frameworks of this approach, the activity of oxygen ions considered as a measure of melt acidity is determined by the dissociation constants of these structural–chemical groups. Here, in reaction (4) the O^{2-} ion behaves as a base,

and the positively charged structural–chemical complex behaves as an acid conjugated to that base. Such an approach has a number of significant advantages. The first advantage is the fact that the determination of O^{2-} ion as a base eliminates the problem of exact acid (counterion) determination. All structural–chemical groups formed due to the dissociation of salts, oxides, and other element–oxygen complexes are acting as acids in a real melt. Since there is no necessity to determine the exact counterion for O^{2-} , the suggested approach can describe the acid–base properties of all oxide melts. The terms “acidity” and “basicity” here become indiscernible because both are determined via O^{2-} activity; therefore, the boundary dividing “acid” and “base” melts is a problem of standardization and quantitative pO measurement.

Practical approaches to pO (EMF) measurements in galvanic elements including oxide melts

As already mentioned, the concept of a pO scale was suggested by H. Lux in 1939. Since that time and till nowadays, a lot of attempts have been undertaken to develop some pO scales based on EMF measurements. First attempts can be found in [40–42]: galvanic elements of the following type were considered as acceptable for the task of pO scale development:



However, this approach is not suitable for the determination of the basicity of oxide melts in terms of pO since the EMF in the considered galvanic follows as:

$$\Delta E = \frac{RT}{2F} \log \frac{a_{\text{M}_2\text{O}}^2}{a_{\text{M}_2\text{O}}^1} \quad (5)$$

where $a^{(1)}$ and $a^{(2)}$ are the activities of an alkaline oxide in the studied and the reference melt, respectively. Equation 5 is correct when the transition number of alkaline metal ions is equal to 1; its accuracy decreases with the increase in the deviation of this number from unity. This fact was decisively supported by experimental studies reported in [28, 43–45]. The impossibility of an exact pO determination in the galvanic elements of (A) and (B) type is due to the fact that determination and standardization of the diffusion potential on the melts interface is impossible here.

The following attempts to measure the basicity of oxide melts intend, in general, the development of galvanic elements with auxiliary electrodes from stabilized zirconium

oxide, porous carbon, alundum, quartz, and beryllium ceramics [29, 46–49]. Let us discuss the problem of ion reversible electrodes for oxide melt measurements in detail. The first (most common one) is the Pt metal electrode, the electrode reaction of which is [50–62]:



Thus, the equilibrium is:

$$K_{\text{O}_2/\text{O}^{2-}} = \frac{P_{\text{O}_2} a_{e^-}^2}{a_{\text{O}^{2-}}^2} \quad (7)$$

Here, it is assumed that a layer of adsorbed oxygen exists on the surface of the platinum electrode. This fact guarantees a high exchange current (up to 40 A/cm²) [51] for reaction (6). On the other hand, it is known that a Pt electrode in a melt is reversible not only for oxygen ions, but it is a redox sensitive electrode, i.e., its potential is determined by exchange currents of all acid–base pairs of the melt, including redox pairs.

In addition, it is known that a Pt electrode corrodes in phosphate melts and in alkaline melts with high alkaline content [53–55] according to the reaction



Hence, an additional acid–base pair (redox pair) is formed here. In this case, the overall reaction on the platinum electrode can be written as:

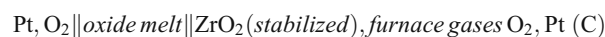


Another electrode, reversible for oxygen ions is an electrode manufactured from ceramics based on zirconium dioxide, stabilized by the 5 mol.% addition of Y₂O₃ or CaO. That electrode is a membrane-type one, the ion transfer reaction for it is



The papers [30, 56–59] describe various versions of the design of electrodes manufactured from stabilized zirconium dioxide and the results of the attempts to measure the EMF of oxygen-containing melts. Summarizing these works, we can subdivide them as

- (a) Electrochemical elements for the determination of the oxygen partial pressure over the oxide melt. Galvanic elements of the following type are used for this task



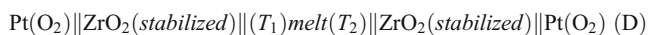
Here, the zirconium electrode works in an atmosphere of pure oxygen, while the platinum electrode is exposed to the ambient furnace gases. The EMF of such element is a

function of the ratio of oxygen partial pressures and can be written as

$$\Delta E = \frac{RT}{2F} \ln \frac{P_{O_2}}{P_{O_2}^{furn}} \approx -\frac{RT}{2F} \ln \left(P_{O_2}^{furn} \right) \quad (11)$$

where $P_{O_2}^{furn}$ is the oxygen partial pressure in furnace gases.

- (b) Electrochemical elements designed to study the temperature gradients in oxide melts (Pt sputtered zirconium electrodes are usually used for this task). The following galvanic element is used here



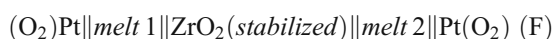
where T_1 and T_2 are the different temperatures in the regions of the melt with the same composition adjacent to the electrodes (usually, one of the electrodes is supplied with an additional heater). In this case, the EMF of the element is treated as isothermal EMF and is written as

$$\Delta E_{\Delta T} = E_T + [\varphi(T_2) - \varphi(T_1)] \quad (12)$$

where $\varphi(T_1)$ and $\varphi(T_2)$ are the potentials of the first and the second electrode, respectively, and E_T is the thermoelectric EMF determined by the following equation

$$E_T = \int_{T_1}^{T_2} \left(\frac{d\varphi_T}{dT} \right) dT \quad (13)$$

- (c) The third version of the zirconium electrode concerns attempts to determine oxygen activity in the melt by galvanic elements of the following type:



Let us consider these approaches in detail. Obviously, neither the first nor the second galvanic element could provide an opportunity to obtain data related to the changes in the oxygen ion activity. Provided that we neglect the possibility of the diffusion potential appearance in the YSZ membrane, the first element will give some constant EMF value according to:

$$E = \frac{RT}{2F} \left(\varphi_{Pt}^0 - \varphi_{ZrO_2}^0 \right) \quad (14)$$

The equation describing the EMF of the second element is more complex, since the EMF here depends on the nature of the studied melts (an example is given for sodium-containing melt)

$$E = \frac{RT}{2F} \ln \frac{a_{Na_2O}^2}{a_{Na_2O}^1} + E_{junc} \approx \frac{RT}{2F} \ln \frac{a_{O^{2-}}^2}{a_{O^{2-}}^1} + const, \quad (15)$$

where E_{junc} is the value of junction potential due to the presence of YSZ membrane, this potential is

$$E_{junc} = \int_{(1)}^{(2)} \sum_i \frac{t_i}{z_i} d \ln a_i \quad (16)$$

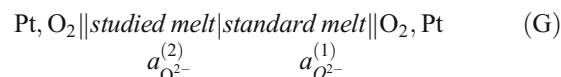
As can be seen from the above consideration, such elements are not suitable for the task of the determination of oxygen activity in oxide melts. Neither similar work with alundum membrane [60] can be considered as satisfactory.

The use of electrodes made of zirconium ceramics gives rise to some experimental problems due to the fact that the material is not chemically stable in the melts with high (more than 15–20 mol.%) content of alkaline or alkaline earth oxides. Dissolution of zirconium dioxide additionally contributes to the EMF of the galvanic element. Since the zirconium oxide dissolution increases the viscosity in the melt adjacent to the electrode, the dissolved electrode material is removed from this zone very slowly, making it impossible to control the contribution of this process to the EMF of the galvanic element. The use of electrodes produced from beryllium ceramics stabilized by calcium and magnesium oxides seems more attractive. The chemical stability of such material is some times higher than that of zirconium ceramics. This fact gives an opportunity to work with a wide range of melt compositions with sufficient measurement accuracy.

Paper [46] presents very interesting results for the electrode manufactured from glassy carbon; this interest is due to the fact that glassy carbon does not adsorb oxygen from the melt, so it can be used as a redox sensitive electrode for any oxidation–reduction ion pairs. On the other hand, the temperature range of its application is quite narrow (usually, lower than 650–700°C in air; inert atmosphere is necessary at higher temperatures).

Standardization of the pO scale

The following galvanic element is considered for pO measurements (to simplify this consideration, we shall discuss an element with Pt electrodes here; however, there is no obstacles for the use of YSZ electrodes for pO measurements).



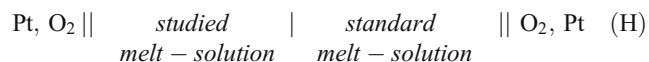
The EMF (ΔE) of this element is described by

$$\Delta E = \frac{RT}{2F} \ln \frac{a_{O^{2-}}^{(2)}}{a_{O^{2-}}^{(1)}} + E_{junc}, \quad (17)$$

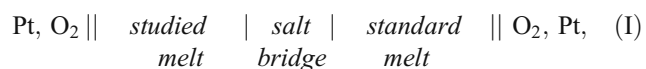
where, E_{junc} is the junction potential, R —universal gas constant, T —temperature, F —Faraday constant, and

$a_{\text{O}_2^-}^{(2)}$ and $a_{\text{O}_2^-}^{(1)}$ —activities of oxygen ions in the studied and the standard melts, respectively. As follows from Eq. 17, the problem of the standardization of the method concerns the determination of the diffusion potential. Hence, the state of liquid boundary in the above given galvanic element should provide an elimination of the diffusion potential or its constancy for all studied and sample melts.

This task can be solved by two ways: introduction of a solvent or application of a salt bridge. These approaches can be realized using the following galvanic elements:



where melt solution stands for high temperature solution of oxide samples in a nonoxygen solvent:



which includes the salt bridge from the molten substance with equal transport numbers for cation and anion.

The elimination of the diffusion potential in the galvanic element (G) is a result of the introduction of an excess amount of solvent satisfying the following requirements:

- 1) The solvent should not contain oxygen.
- 2) The transport numbers of the cations and anions of the solvent should be equal.
- 3) The (solvent)/(oxide melt) molar fraction ratio (n) should provide an excess of solvent. This condition means that the electricity transport in the galvanic element G is mainly provided by solvent ions, i.e., these ions should be the main electricity transport agents.
- 4) The solvent should have a relatively low melting temperature and the range between its melting and boiling temperatures should exceed 100 °C.
- 5) The solvent should be inert to oxidation by air oxygen.
- 6) It should be possible to easily purify the solvent from water and other admixtures.
- 7) The properties of solutions formed by this solvent should be similar to the properties of the initial reagents, i.e., these solutions should be close to ideal.

It was shown that KF is the most adequate substance satisfying the above requirements. For this reason it can be used as a solvent in the galvanic element (G) and as a salt bridge in galvanic element (B). It was demonstrated in [9, 38] that the EMF of the galvanic elements (H) and (I) in case of KF is:

$$\Delta E \approx \frac{RT \cdot 2.303}{2F} \log \frac{a_{\text{O}_2^-}^{(2)}}{a_{\text{O}_2^-}^{(1)}} + \textit{const}, \quad (18)$$

The theoretical basis of this formula was formulated and the procedure of pO measurements with these galvanic elements was described. Note that Eq. 6 for galvanic element (H) was derived for the condition of equal KF mole concentrations in the studied and the standard melt solutions.

Another important problem of pO scale development is the standardization of the measured values. This can be done within two principally different approaches: the first one, like in the US NBS standard for pH, assumes introduction of a set of standard melts covering all possible pO scale range; the second approach (as in BSI scale) sets one melt composition as a scale defined point; all other possible secondary melt composition should be introduced in relation to the pO value measured at that defined point. The second approach seems to be more accurate with respect to the fact that, in contrast to the BSI scale, which does not use a salt bridge, the discussed approach includes the estimation of diffusion potential and its elimination.

We suggest to use the state of oxygen ions in the pure silica melt as a defined scale point and to confer the pO value of 7 for this state; this corresponds $a_{\text{O}_2^-} = 10^{-7}$. At this standardization method, supposing the state of oxygen ions in pure silica melt as being close to ideal, one can determine SiO_2 dissociation constant, see Eq. 4, as equal to 6.32×10^{-11} . The choice of pure silica melt as a defined scale point for oxygen ions was made regarding the following ideas: First, silica is a rather well investigated substance; its structure and physicochemical properties are well known. Second, most technical glasses, metallurgical slags, nature minerals, and oxide coatings are based on silica.

Stating the standard state of oxygen ions, it is possible to introduce the primary standard of the pO scale for galvanic element (A). To determine the working content of silica in the solvent, we have studied the following galvanic element



where n was 1, 3, 5, 7, 10, 15, and 30. The EMF of this element is defined by the Nernst equation

$$\Delta E \approx \frac{RT \cdot 2.303}{2F} \log \frac{a_{\text{O}_2^-}^{(2)}}{a_{\text{O}_2^-}^{(1)}} \approx \frac{RT \cdot 2.303}{2F} \log \frac{x^{(1)}}{x^{(2)}}, \quad (19)$$

where $x^{(1)} = 1/(n+1)$ and $x^{(2)} = 0.125$ are the mole fractions of silica in the studied and the standard melts, respectively. Experimental results are depicted in Fig. 1.

As seen from Fig. 1, the curves $\Delta E - \log(n+1)$ can be subdivided into two regions, the first is for the melt composition range with n varying from 1 to 3–4 and the second one for $5 \leq n \leq 30$. The temperature coefficient of

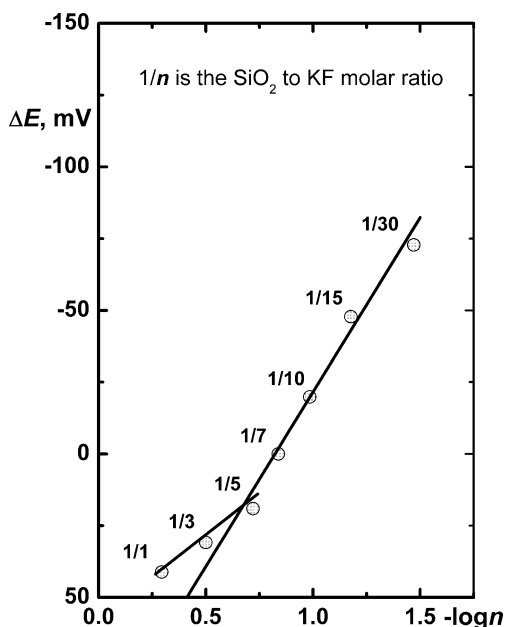


Fig. 1 The Nernst dependence of KF–SiO₂ melts measured with the galvanic element (B) at 1173K

ΔE calculated for the second region from the experimentally determined curve slope is $((10.6 \pm 0.7) \cdot 10^{-2} \text{ mV})$. Within the uncertainty limit, this value is the same as the theoretical value of $|9.9 \times 10^{-2}| \text{ mV}$ confirming that the interaction of KF and SiO₂ is quite close to ideal here. To confirm this fact, we have carried out a study of quenched KF–SiO₂ system samples by solution calorimetry, DTA, DSC, and quantitative XRD analysis [61]. The formation enthalpies were shown to be zero within the experimental error for $n\text{KF} \cdot 1\text{SiO}_2$ ($n > 2$) samples; no compounds were detected in this composition range. These results combined with the above data of the electrochemical study of the galvanic element (C) gave the opportunity to choose the primary standard for the pO scale: This was the composition $7\text{KF} \cdot 1\text{SiO}_2$ with the fixed pO value of 7. $n=7$ was chosen because for lower n values the compositions of the standard are close to the first region where the Nernstian dependence is not evident. On the other hand, the decrease in silica concentration increases the experimental errors and the accuracy of melt solution compositions.

Defining the primary standard, we are able to introduce a set of secondary standards: $x\text{Na}_2\text{O} \cdot (1-x)\text{SiO}_2$ melts, where $x = 0.25, 0.30,$ and 0.375 , and the mole fraction of Na₂O was 0.500. These sodium silica melts are situated in the glass-forming region of the Na₂O–SiO₂ system. There, the viscosity of the melts varies in a wide range. This fact gives the opportunity to operate with these melts at temperatures lower than the liquidus temperature (T_l) in $T_l - T_g$ range using galvanic elements of different constructions.

The pO values of secondary standards were determined using the galvanic element

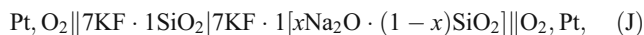
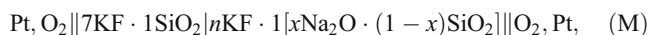


Figure 2 presents the result of the study. The measurements were performed in the temperature range of 1,153–1,293 K. In that range, we did not observe a significant dependence of pO on temperature. The measured deviations were smaller than the experimental error of the pO determination (± 0.04 pO scale unit). A set of preliminary experiments similar to that performed for KF–SiO₂ was carried out in order to apply the determined values to pure sodium silica melts without KF, i.e., melts with concentrations in the range $1[x\text{Na}_2\text{O}(1-x)\text{SiO}_2]n\text{KF}$. A calorimetric study of oxyfluoride samples at $n = 7$ showed zero values of the formation enthalpies from KF and $x\text{Na}_2\text{O} \cdot (1-x)\text{SiO}_2$, and XRD analyses also did not indicate any new compounds. The study of the Nernst dependencies was performed using the following galvanic element:



with $n = 1, 3, 5, 7, 10, 15,$ and 30 . The results of the study are depicted in Fig. 3.

All measured curves for $\Delta E - \log(n)$ at $n \geq 5$ were linear and parallel, they were also parallel to previously obtained curves for KF–SiO₂ system. Their temperature coefficient $(10.6 \pm 0.9) \times 10^{-2} \text{ mV/K}$ was within the limits of experimental errors the same as the theoretical one. These results

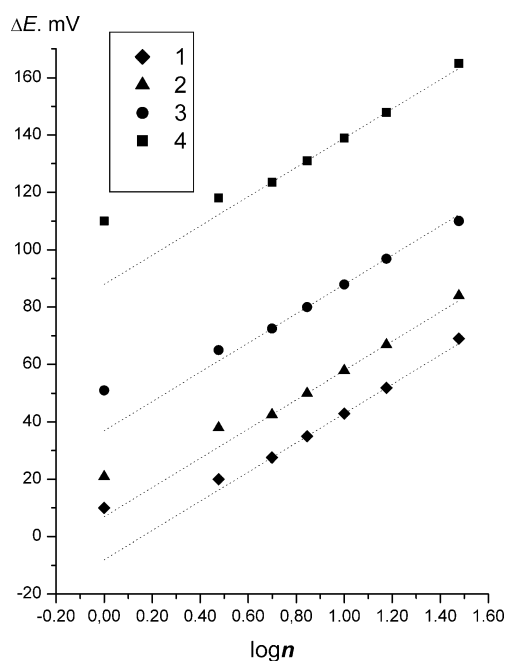


Fig. 2 pO study of Na₂O–SiO₂ applying the galvanic element (J)

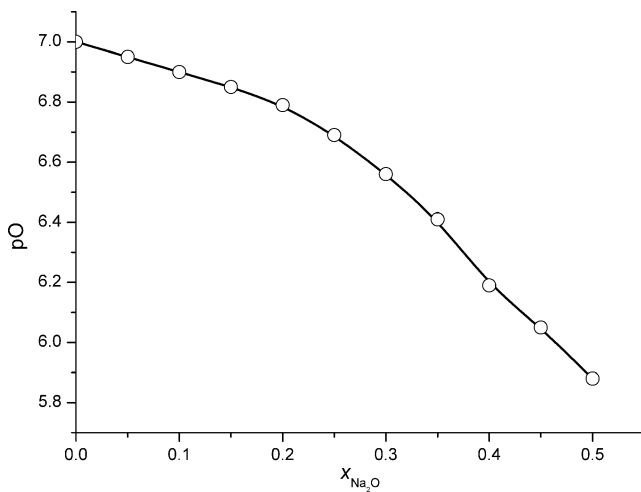


Fig. 3 Nernst dependencies for the secondary standards of the pO scale determined with the galvanic element (M). Numbers of the standards are the same as in Table 1

confirm the ideal behavior of $nKF \cdot 1[xNa_2O \cdot (1-x) SiO_2]$ melt solutions at $5 \leq n \leq 30$ and they also show that the preparation of solutions does not produce additional oxygen ions. This fact gives the opportunity to define the obtained experimental values of pO (galvanic element D) of pure sodium silica melts and of $7KF \cdot 1[xNa_2O \cdot (1-x) SiO_2]$ melt solutions. Thus, they can be used as secondary standards (see Table 1).

The pO values of the galvanic element (A) with the primary standard as a standard melt were calculated using to the following equation:

$$pO = 7 - \frac{\Delta E \cdot 2F}{2.303RT} \quad (20)$$

In case of measurements in galvanic elements (A) and (B) versus secondary standards, pO values were calculated as:

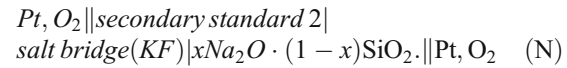
$$pO = pO_{\text{second.standard}} - \frac{\Delta E \cdot 2F}{2.303RT}, \quad (21)$$

where $pO_{\text{second.standard}}$ is the pO of the second standard used in a form of oxyfluoride solution or oxide melt (see Table 1).

Table 1 Secondary pO scale standards ($xNa_2O \cdot (1-x) SiO_2$)

X_{Na_2O} - Na_2O mole fraction	pO \pm 0.04
0.250	6.70
0.300	6.57
0.375	6.32
0.500	5.88

This equation is also applicable for the case of measurements using galvanic elements with a salt bridge (type B elements), e.g., in the element



The comparison of the results obtained using this galvanic element with the same data obtained by element (M) are presented in Fig. 4. As can be seen from this figure, the use of the second standards system in different galvanic elements results in a good agreement of the measured data.

Conclusion

Since the aim of this paper was to consider the theory of pO measurements and standardization with respect to the wide application practice of pH measurements, it was not reasonable to overload it by numerous experimental results. These results mutually agreed and were standardized according to the developed procedure. They can be found in the following papers: systems SiO_2 - B_2O_3 , GeO_2 - B_2O_3 , SiO_2 - GeO_2 [62–66], M_2O - SiO_2 (M–Li, Na, K) [67–71], M_2O - GeO_2 (M–Li, Na, K) [68–75], M_2O - B_2O_3 (M–Li, Na, K, Ba) [76–78], Na_2O - B_2O_3 - SiO_2 [79–81], Li_2O - K_2O - SiO_2 [82, 83].

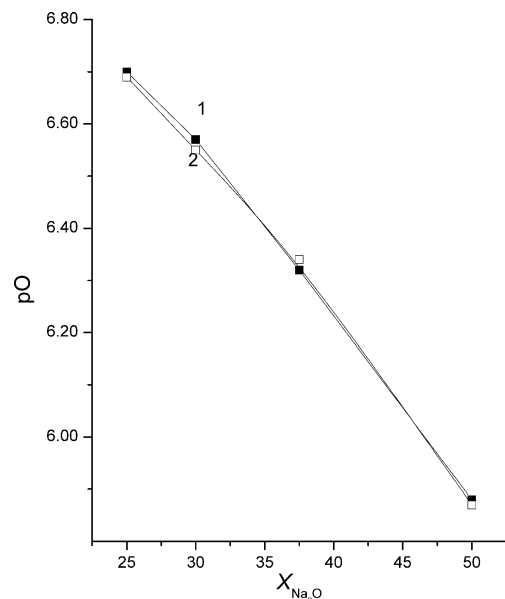


Fig. 4 Comparison of the results obtained for the relative pO values of secondary standards in the galvanic elements (J)—1 and (N)—2

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