

ACID-BASE PROPERTIES OF MELTS OF THE M_2O-GeO_2 SYSTEM (M= Li, Na, K)

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Abstract. This paper presents the most modern theories of acid-base interaction in oxide melts. Also a historic review of the development of approaches to describe the acid-base properties of melts is given. Generalized conception is suggested which describes these properties adequately within a wide concentration interval. Some quantitative procedures for estimation of acid-base properties of the oxygen-containing melts are considered. Alkali-germanate melts are chosen as a model system. Experimental results on the basicity of the M_2O-GeO_2 system are discussed and compared. The basicity of these melts is also compared with that of other alkali containing melts such as M_2O-SiO_2 and $M_2O-B_2O_3$.

1. INTRODUCTION

The development of technological production processes of glass, metal and cement implies the continuous control – monitoring of the proceeding of chemical conversions in technologic plants and assemblies. Among the processes to take into consideration there are:

- glass making processes: batch caking, glass cooking, cast glass, the interaction of glass forming melt with the refractory lining of the glass making furnace;
- metallurgic production: a wide set of equilibria between metal, slag and reaction atmosphere: the processes of decarboxylizing, desulfurizing, dephosphorizing, etc., the interaction of slag with the refractory materials of technologic assemblies;
- the cement production attended with the continuous control of gaseous atmosphere and the laboratory control of basicity.

Nowadays the main control parameters of high temperature technological processes are time and temperature. The observation of the physico-chemical processes of the purpose object at the high temperature technologic stages is carried out at the expense of sampling and analyzing. A similar situation was in the chemistry of aqueous solutions early in the 20th century. That time the development

of chemical technologies of solutions demanded to create some methods of the continuous observation of chemical process proceeding and the method of the state control of liquid medium within the temperature range of the aqueous solution existence. It was the technologic demand what gave rise to the international acceptance of the *pH* scale ($pH = -\lg a_{H^+}$) and afterwards to the creation of apparatus base to fulfil the *pH* control in terms of the existing modifications (the NBS and BSI scales) on an international scale [1, 2].

Having analyzed the situation already established in the high temperature chemistry of the oxygen containing substances, first of all it is necessary to mention that the idea to create the scale of acid-base properties of oxide melts as $pO = -\lg a_{O^{2-}}$ proposed by X.Lux in 1939 [3] has not possessed a total solution yet. The problem to create the system of measuring and normalizing the acid-base properties of oxide melts carries the following aspects:

- 1) the theory of the acid-base processes in oxide melts and determining the set of chemical conversions responsible for "the acid-base" properties of melt;
- 2) the principle of *pO*-scale introducing (one reference point or a set);
- 3) the determination of the galvanic cell type, the measuring regime and the range of applicability;

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- 4) the engineering of laboratory and technologic schemes for the pO determination;
- 5) the acceptance of the state standard to measure pO .

Creating the pO measurement system demands a wide number of investigation: both of the melted fluorides, which are the materials of galvanic cells, and of the processes of their chemical interaction with oxide melts, the development of porous ceramic electrochemical switches, as well as the creation of hermetics and adhesives inert to the oxide and oxyfluoride melts, etc. However the most important scientific problem is the interplay investigation of the basicity of oxide melts and the composition of gaseous atmosphere above them.

In this connection in the Institute of Silicate Chemistry of the Russian Academy of Sciences a new scientific line of inquiry has been developing. Its purpose is to create the measurement technique and the normalization of pO -index in oxide melts, and in the long run, the acceptance of the state standard of the Russian Federation to determine these values.

The article is devoted to the particular problem: the determination of basicity as pO -indexes for the alkali-germanate melts and then the comparison of their basicity with the basicity of a number of the alkali-silicate, alkali-borate and other melts studied earlier.

2. THEORY

2.1. The main acid-base conceptions as applied to the oxide melts

In the light of general structural-chemical concepts of the acid-base interactions in the oxide melts these interactions can be divided into three main groups. The first group takes into account the electroneutral components of melt as oxides and their salts. In this situation the acid-base interaction in an oxide melt, for example in an alkali-silicate one, is presented as follows:



$$K_1 = \frac{a_{M_2O}^x a_{SiO_2}^y}{a_{M_{2x}Si_yO_{2y+x}}}. \quad (2)$$

where K_1 is the dissociation constant and a_i is the activity of the corresponding substance.

This handy approach uses the parameters of basicity (acidity) of the components determined ex-

perimentally: they are activities or concentrations of electroneutral substances. In the glass manufacture the acidity of batch is determined as the ratio of the weight or mole fractions of acid oxides of glass-formers to the ones of alkali (alkaline-earth) modifier oxides. This approach is nothing more than guessing, for in its context there is no difference between oxides of lithium, sodium and potassium, which acid-base properties undeniably vary far and away. The attempts to solve this problem were undertaken in a number of studies [4-7]. Each of oxides was assigned an empirical coefficient which defined its contribution to the total basicity.

The chief drawback to this approach is the impossibility to compare the basicities of such objects as, for example, Li_2O-SiO_2 and $PbO-B_2O_3$, or $B_2O_3-SiO_2$ and Na_2O-GeO_2 , not having any common component the activity or concentration of which could be used as the point to compare.

Another approach to describe the acid-base interactions in oxide melts was using the complex of ion-molecular equilibria. As a case in point, let us consider the sodium silicate melt [8, 9]. For the melt components the following particles are considered:

$SiO_{4/2}$ – the silicon-oxygen tetrahedron including the bridging oxygen;

$[SiO_{3/2}]^+$ – the silicon-oxygen groupings charged positively and with one oxygen vacation;

$[SiO_{3/2}]O^-$ – the silicon-oxygen tetrahedron with a non-bridging oxygen;

$[SiO_{3/2}]O^-M^+$ – M^+ ion as a modifier connected with the bridging and non-bridging oxygens;

$([SiO_{3/2}]O^-)R^{2+} - R^{2+}$ ion as the modifier;

$[RO_{n/2}]M^+$ – the element-oxygen grouping as the net former;

$[RO_{n/2}]^-$ – the element-oxygen grouping charged negatively;

M^+ – the dissociated ion M^+ ;

M^{2+} – the dissociated ion M^{2+} ;

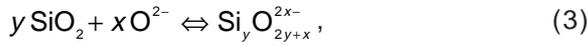
R^{n+} – the dissociated ion R^{n+} ;

O^{2-} – the vacant oxygen ion.

M^+ is an ion of univalent metal (as Na^+ , Li^+ , Ag^+); M^{2+} is an ion of bivalent metal (as Ca^{2+} , Ba^{2+} , Zn^{2+}); R is the element which takes part in the production of glass network (glass formers like B, Ge and P) and conditional glass formers (or conditional network formers according to the classification by M.M.Schultz) like Al, Sb and Bi.

When this takes place a more correct approach can be the activity determination of anyone of the general melt components. Such a component is O^{2-}

ion, which is the base from the point of view of theories by G. Lewis, and N.M. Usanovitch [10, 11]. Consequently, the O^{2-} activity or its concentration can be used as a measure of the acid-base properties of melt. At that the acid-base interaction in an alkali-silicate melt can be given as:



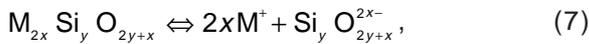
$$K_3 = \frac{a_{SiO_2}^y a_{O^{2-}}^x}{a_{Si_y O_{2y+x}^{2x-}}}. \quad (4)$$

This approach for the description of acid-base equilibria allows to compare all the oxygen containing melts one another, and the main part of models of acid-base interaction in oxide melts is built just using the ion-molecular approach.

It is enough easy to show the interrelation between equations (1) and (3) if we put the dissociation reactions of electro-neutral components (oxides and salts) by the following way:



$$K_5 = \frac{a_{M_2 O}}{a_{M^+}^2 a_{O^{2-}}}, \quad (6)$$



$$K_7 = \frac{a_{M_{2x} Si_y O_{2y+x}}}{a_{M^+}^{2x} a_{Si_y O_{2y+x}^{2x-}}}. \quad (8)$$

Then:

$$K_1 = K_3 \frac{K_5}{K_7}. \quad (9)$$

The third approach is the model suggested by Toop and Samis [12, 13]. Within the framework of this idea three forms of oxygen ions are considered to be the melt components: O^0 is the bridge oxygen, O^- is an end oxygen and O^{2-} is a free oxygen ion. At this rate the following equilibrium of these three oxygen forms in melt is taken into account:



$$K_{10} = \frac{a_{O^{2-}}}{a_{O^0} a_{O^-}}. \quad (11)$$

If this takes place the suggestions about the indifference of the O^0 state in SiO_2 and the silicates

formed are accepted as well as O^- in the latter ones. The distribution of oxygen particles in ratio to the value of K_{10} calculated for the melt of alkali-silicate system in [9] is given in Fig.1. At $K_{10}=0$ only free ions and bridging forms of oxygen can be present in melt. At $K_{10}=\infty$ only O^{2-} and O^- exist in the melt up to the composition of 33 mol.% M_2O , and after the composition the ions O^- and O^0 do. In case of $K_{10}=17$ all three forms of oxygen coexist in the melt.

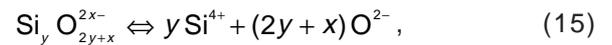
The interconnection of the second and the third approach can be done by the following equation:

$$K_3 = K_{10} \frac{K_{13}}{K_{15}}, \quad (12)$$

where the constants K_{13} and K_{15} play the parts of dissociation constants of ion-molecular combinations according to the reactions:



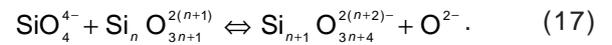
$$K_{13} = \frac{a_{Si^{4+}} a_{O^{2-}}^2}{a_{SiO_2}}, \quad (14)$$



$$K_{15} = \frac{a_{Si^{4+}}^y a_{O^{2-}}^{(2y+x)}}{a_{Si_y O_{2y+x}^{2x-}}}. \quad (16)$$

As it was mentioned above Toop and Samis's model was rather limited and could not serve for describing the acid-base interactions in the real oxide melts.

Some works [14-16] developed Toop and Samis's model. There the acid-base interaction was considered from the polymer-monomer equilibrium point of view by the reaction:



Both linear and branched Si-O-Si chains were taken into consideration according to the composition and the nature of the systems under investigation. From the theoretical principles the polymerisation of silicate melt with the formation of chains gives rise to the appearance of additional free oxygen ions. However this approach works only up to the 50 mol. % of glass forming oxide. And on the other hand the polymer models can not give any quantitative acid-base characteristics of melt.

The basis of Dron's theory was the statistical consideration of formation "bridging", "end" and free ions of O^{2-} [17-19]. As an object to apply the theory the system M_2O - SiO_2 was chosen within all the com-

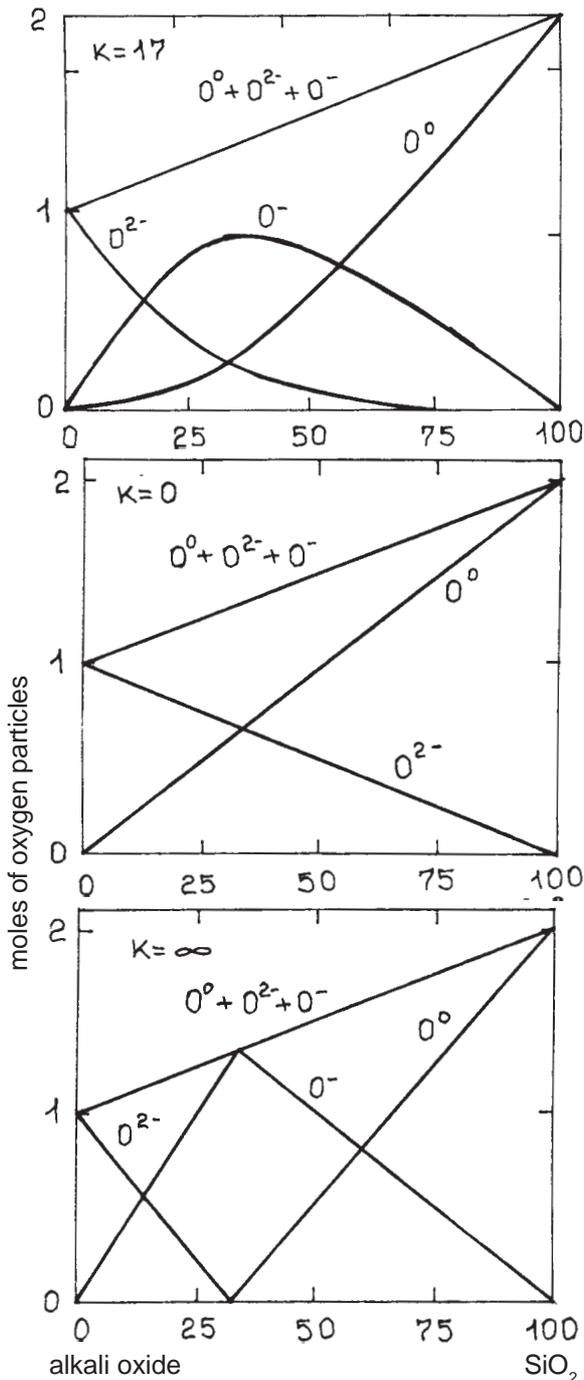


Fig. 1. Distribution of oxygen particles in alkali-silicate melts depending on the K_{10} value according to Toop and Samis's theory.

position region. At that the formation of groupings $\text{SiO}_{4/2}$ (A), $\text{SiO}_{3/2}\text{O}^-$ (B), $\text{SiO}_{2/2}\text{O}^{2-}$ (C), $\text{SiO}_{1/2}\text{O}_{3/2}^{3-}$ (D) and $\text{SiO}_{4/2}^{4-}$ (E) was taken into consideration.

According to the chosen groupings Dron put down a matrix of possible interparticle interactions of associates like AOA, AOB, AOC, etc. with oxygen ions and got a total set (within the limits of the particles under study: A, B, C, etc.) of all the possible acid-base interactions in oxide system. It in-

cluded 10 reactions. That set of interactions could be got into 4 independent semi-reactions:



$$K_{18} = \frac{a_B}{a_A a_{\text{O}^{2-}}^{1/2}}, \quad (19)$$



$$K_{20} = \frac{a_C}{a_B a_{\text{O}^{2-}}^{1/2}}, \quad (21)$$



$$K_{22} = \frac{a_D}{a_C a_{\text{O}^{2-}}^{1/2}}, \quad (23)$$



$$K_{24} = \frac{a_E}{a_D a_{\text{O}^{2-}}^{1/2}}. \quad (25)$$

To get numerical magnitudes characterizing the acid-base parameters of melt Dron made the following suggestions [17, 18]:

$$K_{18}=1; K_{20}=Q; K_{22}=Q^2; K_{24}=Q^3.$$

Having chosen the numerical values of an empirical parameter Q and taken into consideration some statistic thoughts which gave the concentrations of groupings A, B, C, D and E, the author managed to calculate the value $p\text{O} = -\lg a_{\text{O}^{2-}}$. The results of these calculations for various Q values are shown in Fig. 2. As one can see from the figure, at $Q=1$ K_{18} and K_{22} become equal and $p\text{O}$ does not practically depend on the composition. This result is quite interesting, because at $Q=1$ Dron's model goes to Toop and Samis's model with $K_{10}=1$. At $Q=100$ and 1000 one can see the turns in the concentrational dependences of $p\text{O}$ and these turns become more sharp with the increase in Q . This phenomenon has analogous to the titrating curves of the multibase acid with the base, if the dissociation constants for each step differ a lot (Fig. 3).

Together with undoubt merits of Dron's theory it has a substantial drawback. It is a free choice of Q

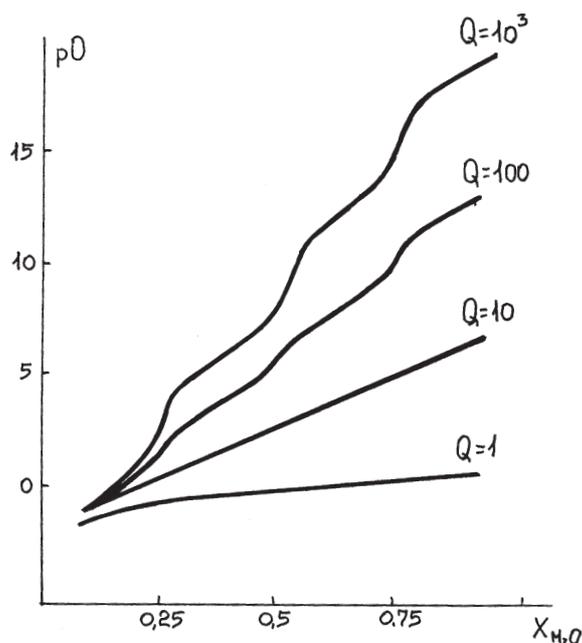
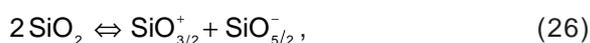


Fig. 2. pO dependence on the composition of alkali silicate system and the Q parameter chosen at will. The Q values are shown over each curves.

value. The criterion of its choosing is the “common sense” of gotten pO values. Besides within the limits of this model it is impossible to describe the following compounds: $3M_2O \cdot 5SiO_2$, $5M_2O \cdot 8SiO_2$, $M_2O \cdot 3SiO_2$, $M_2O \cdot 4SiO_2$, which exist in the alkali-silicate systems according to the phase diagrams [20, 21].

A particular place among the ideas about acid-base interactions in melts occupies Paul’s theory [22, 23]. The theory was founded on the ideas about the salvational processes in non-protonic media. From Paul’s point of view the main principle is the process of autoionization in a pure glassformer oxide. For B_2O_3 and silica it can be shown as:



The interaction between silica and alkali oxide is put as:



where $O_{1/2}$ is considered to be a bridging oxygen (O^0). Then equation (25) can be done as:

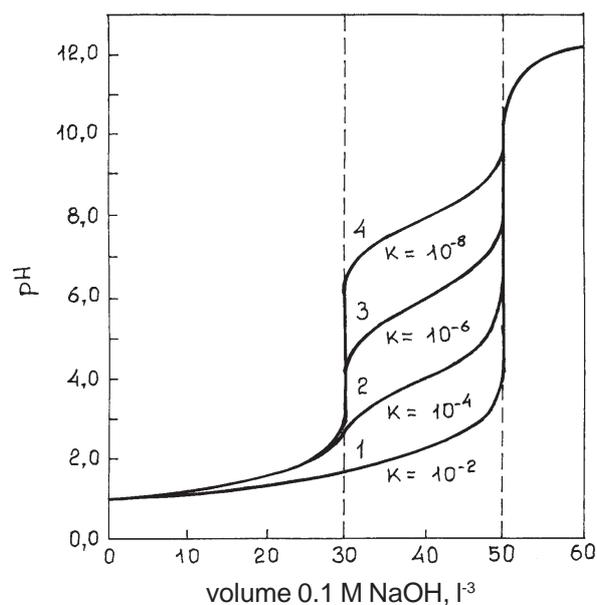
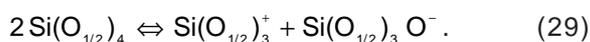


Fig. 3. Titration curve of 30 ml of a polybasic acid with sodium hydroxide. The difference in the dissociation constants by the first and the second steps was assigned. The figures under the curves are the differences between the first and the second dissociation constants.

For B_2O_3 Paul supposed a possibility to form three- and four-coordinated boron in bor-oxygen groupings according to the reactions:



For alkali-boron and alkali silicate melts of equamolar composition Paul suggested the following way of increasing the basicity of melts:



The basic step forward of Paul’s theory is the autoionization process of the glass former oxide. He supposed that both in pure SiO_2 and pure B_2O_3 the acid-base processes take place. However within the limits of Paul’s theory to determine the characteristics of these processes quantitatively is possible only using the activities of the products of autoionisation, ion constituents like $SiO_{3/2}^+$ and $SiO_{5/2}^-$ or BO^+ and BO_2^- . This leads us to the conclusion that it is impossible to compare the basicity of pure glass formers, because the carrier of basic properties, ion O^{2-} , is excluded from the mechanism. Moreover a closer examination of reaction (29) shows that it describes only the formation of bisilicate of alkali oxide and it does not describe the acid-base interaction in other composition regions. As a mea-

sure of basicity Paul assumed to use the concentration of $\text{Si}(\text{O}_{1/2})_3\text{O}^-$ groupings, the activity of which is thermodynamically undetermined along with the O^{2-} activity, but the use of this grouping basicity as a measure of the total basicity gives no way of comparing melts with distinct oxide glass formers.

Shultz's conception occupies a significant place among the concepts of the acid-base interactions in oxide melts [8, 24]. The acid-base interaction in oxide melts is represented as two parallel processes:



$$K_{32} = \frac{a_{\text{SiO}_{3/2}\text{O}^-}^2}{a_{\text{SiO}_{4/2}}^2 a_{\text{O}^{2-}}}, \quad (33)$$

and above-mentioned



$$K_5 = \frac{a_{\text{M}^+}^2 a_{\text{O}^{2-}}}{a_{\text{M}_2\text{O}}}, \quad (6)$$

where processes (5) and (32) are contributors of oxygen ions. The activity of oxygen ions in (5) and (32) can be displayed as follows:

$$a_{\text{O}^{2-}} = K_{32} \left(\frac{a_{\text{SiO}_{3/2}\text{O}^-}}{a_{\text{SiO}_{4/2}}} \right) \approx K_{32} \left(\frac{x_{\text{SiO}_{3/2}\text{O}^-}}{x_{\text{SiO}_{4/2}}} \right). \quad (34)$$

Also quite apparently that the main contributor of oxygen ions is the dissociation of alkali (M_2O) or alkaline-earth (MO) oxide according to the reaction of the (5) type. Then for a melt containing some alkali or alkaline-earth oxides the ratio:

$$a_{\text{O}^{2-}} = \frac{\sum_i K_i a_{\text{M}_{2/n_i}\text{O}}}{\sum_i a_{\text{M}^{n_i}}^{2/n_i}} \approx \frac{\sum_i K_i x_{\text{M}_{2/n_i}\text{O}}}{\sum_i x_{\text{M}^{n_i}}^{2/n_i}} \quad (35)$$

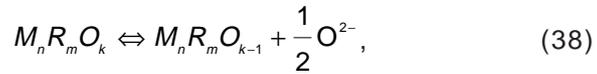
is correctly reasoned. K_i is the dissociation constant of an alkali or alkaline-earth oxide. As this takes place it is necessary to take into consideration that only the basicity of alkali or alkaline-earth oxides can be used in Eq. (35). However the glass formers have their own basicities which must be taken into consideration in the region of low contents of alkali oxides.

2.2. A unified concept of the acid-base interaction in oxide melts

A task of this review is the formulation of the generalized theory of the acid-base interaction in oxide melts which would give due consideration to all the available experience. The dissociation principle by S. A. Arrhenius is at the heart of the theory:



It supposes that any matter in liquid state can be undergone the dissociation, that is the detachment of positive or negative ions. In line with this, we can consider the oxide melts to be dissociating liquids which split or attach oxygen ions O^{2-} . First of all it is necessary to determine what is the unit act of the acid-base process. By way of example, in the chemistry of aqueous solutions in the processes of protolytic equilibrium the unit act of the acid-base equilibrium is the detachment or addition of H^+ (or H_3O^+). For the oxide melts the unit process is a detachment (or an addition) of 1/2 mole of oxygen ion O^{2-} , or the charge change of the element-oxygen grouping by 1. It can be depicted in the general view as:



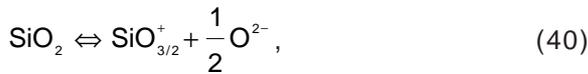
$$K_{38} = \frac{a_{\text{M}_n\text{R}_m\text{O}_{k-1}} a_{\text{O}^{2-}}^{1/2}}{a_{\text{M}_n\text{R}_m\text{O}_k}}. \quad (39)$$

In this case both alkali oxides, alkaline-earth oxides, their salts and pure glass former oxides are considered. In the latter case the dissociation are consistent with the breaking of one bridge bond M-O-M (as in Dron's theory) or the O^- detachment from the element-oxygen grouping (corresponding to Paul's autoionisation). As this takes place, in reaction (38) O^{2-} acts as the basis and the element-oxygen complex does as the mating acid. This approach has a number of advantages. In the first place, having determined uniquely the O^{2-} ion as the basis present in all the oxide melts, the problem of acid (the opposite ion) specification is solved. In a real melt all the element-oxygen complexes formed by the dissociation of salts, oxides or other element-oxygen complexes play the role of acids. The absence of necessity to determine the opposite ion fitting to O^{2-} allows to use this approach to describe the acid-base properties of all the oxide

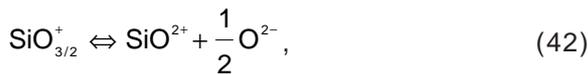
melts. Here, the concepts “acidity” and “basicity” become indivisible, because both are determined by the O^{2-} activity. And where should the boundary of acid and basic properties be drawn? That is the question of normalization and quantity determination of pO .

It is necessary to do a short remark and apply to the chemistry of aqueous solutions. In the context of this theory the proton H^+ (or protoxonium H_3O^+) sets against the hydroxyl ion OH^- (or hydroxonium $H_3O_2^+$). The idea of the counterion individualizing results from the particular properties of water. The water undergoes the different acid-base transformations depending on the basicity of other components of solution (the water is considered to be a component of the water-solute system). All these explanations are suited naturally for the chemistry of aqueous solutions when there is a possibility to operate exact conceptions of acid and base. However in the chemistry of non-aqueous and mixed (aqueous-organic) solutions these ideas failed. If so the problem of concreting the basis became unsolved at the consideration of all the systems in general. All that aided to create the generalized theories of acids and bases first by G. Lewis and then by M.I. Usanovitch, which was taken into consideration in chapter 2.1.

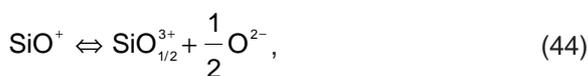
By this means in the context of the acid-base conceptions under consideration the glass former oxides and their salts are multibase acids (or, in dependence on the processes under consideration, bases). As an example, SiO_2 can be undergone to four stages of dissociation with the break-out of 1/2 mole of O^{2-} , B_2O_3 to six stages, P_2O_5 to ten. To site an example for SiO_2 :



$$K_{40} = \frac{a_{SiO_{3/2}^+} a_{O^{2-}}^{1/2}}{a_{SiO_2}}, \quad (41)$$



$$K_{42} = \frac{a_{SiO^{2+}} a_{O^{2-}}^{1/2}}{a_{SiO_{3/2}^+}}, \quad (43)$$



$$K_{44} = \frac{a_{SiO_{1/2}^{3+}} a_{O^{2-}}^{1/2}}{a_{SiO^+}}, \quad (45)$$



$$K_{46} = \frac{a_{Si^{4+}} a_{O^{2-}}^{1/2}}{a_{SiO_{1/2}^{3+}}}. \quad (47)$$

The relation of the values of dissociation constants must be subject to the following condition:

$$K_{40} > K_{42} > K_{44} > K_{46}.$$

An analogous equilibrium complex can be written for the other glass formers and their salts.

The next principle moment is the consideration of the process of dissociation of alkali and alkaline-earth oxides. The usual way to write down the dissociation reaction as follows:



$$K_5 = \frac{a_M^2 a_{O^{2-}}}{a_{M_2O}}, \quad (6)$$



$$K_{48} = \frac{a_{M^+} a_{O^{2-}}}{a_{MO}}. \quad (49)$$

If in this case the unit act of acid-base dissociation is considered to be the detachment of 1/2 mole of oxygen ions O^{2-} , we should consider the following structural-chemical groupings: $[M_2O_{1/2}]^{0.5+}$ or $[MO_{1/2}]^{0.5+}$. Besides in terms of the dissociation processes of M^+ or M^{2+} detachment some structural-chemical groupings like $[MO_{1/2}]^-$ are added. On the other hand, for alkali or alkaline-earth oxides it is more comfortable to use reactions similar to (5) and (40), supposing the total dissociation of oxides. It is quite correctly reasoned because their basicity is much more high than the basicity of glass formers oxides. The analogous reasonings are quite correct when comparing the alkali and alkaline-earth oxides to the oxides like Al_2O_3 , PbO , Bi_2O_3 , etc.

By this means in the framework of the considered concepts the oxide melt of any composition is a set of structural-chemical groupings and oxides undergo the dissociation processes with the detachment of O^{2-} ions and the contents of oxygen ions

(the basicity of melt) are determined by the dissociation constants of these groupings and oxides.

2.3. Estimation of acid-base properties of oxide melts

The classical ideas about acid-base properties of oxides are started from their capacity to form salts. The measure of salt strength is the absolute value of free energy at the formation of the compound from oxides. The smaller the value the greater the relative basicity of salt [25].

In general all the approaches to the estimation of acid-base properties can be divided into several lines:

- the thermodynamic line which uses the values of ΔH and ΔG as the measure of acid-base characteristics;
- the chemical approach. It uses such ideas of chemical interactions between melt components as electronegativity, salting, phase transition;
- the ion-ionizer line. It uses such ideas as ionisation potential, modified electronegativity, etc;
- the optical basicity.

Let us take up all these approaches.

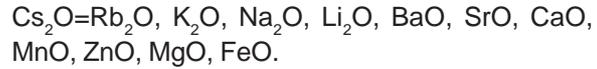
A most typical representative of the thermodynamic line is L.A. Shvartzman and I.A. Tomilin's work on the estimation of the acid-base properties of metallurgy slags [26]. The measure of oxide basicity was considered to be the value of ΔH related to the typical coordination number of the glass forming element in melt:



That is essentially Sun's criterion was taken as the measure of acid-base properties [27]. The more strength the acceptor-acid confines the electron pair of oxygen the more complete reaction (49) must proceed [26]. Data on the values of bond strength of element-oxygen are given in Table 1. As may be seen from the table the increase in basicity (the decrease in the value of binding energy, R-O) goes from the typical glass forming oxides, SiO_2 , B_2O_3 , GeO_2 , P_2O_5 , to the conditional ones, Al_2O_3 , V_2O_5 , As_2O_5 , Sb_2O_5 . The more basic are alkali and alkali-earth oxides.

The chemical approach has a number of lines. M.Rey [28] considered the form of the phase diagrams of binary oxide systems. The more acid the oxide introducing in SiO_2 the more the inclination to the phase separation in the forming melt. Accord-

ing to Rey the ideal solutions are Cs_2O-SiO_2 and Rb_2O-SiO_2 . Deviations from the ideality are building up to the systems Li_2O-SiO_2 and $BaO-SiO_2$. And as a result all the oxides can be arranged in a row after the decrease in basicity:



Let us consider the drawbacks of Rey's theory. In action Cs_2O-SiO_2 and Rb_2O-SiO_2 are far cry from the ideality [29]. According to the ideas of Rey the systems $B_2O_3-SiO_2$, $B_2O_3-GeO_2$ and SiO_2-GeO_2 must have a great region of phase separation, whereas they are a step to the ideality [20, 30, 31].

A particular place between the chemical approaches is occupied by the idea of electronegativity. The basis of this theory is the supposition about the electric nature of all the chemical "forces". The electronegativity is the difference between the energy of real bond and the energy of covalent one [32]. Later this theory was developed in works [33, 34]. Some quantum-chemical calculations estimating the type and the hybridization degree of electron clouds of radicals and associates were used as the basis of this theory. The values of electronegativity of metals in free radicals are given in Table 2.

The authors of work [35] suggested the method of quantum-chemical electronegativity. This method takes into consideration the values of affinity to the electron and the degree of binding hybridization. It was focused on the determination of orbital electronegativity of each element.

The crystal electronegativity is aligned with the spatial arrangement of the nearest neighbours and the binding length [33, 36]. The most important question of this method is the coordination number of element in crystal.

Gordy suggested the conception of spectroscopic electronegativity which characterizes the interrelation between electronegativity and spectral characteristics [37]. It is necessary to mention that the values of spectroscopic electronegativity correlate well with the thermochemical and geometrical values of electronegativity [38, 39].

Having considered the general types of electronegativity, due attention should be given to the boundaries of applicability of this approach. In the modern chemistry the electronegativity is the most general and prevalent characteristic of the acid-base properties of the element. Along with it the applicability of these values to the particular classes of substances demands a special attention. Electronegativity allows to estimate only the asymmetry of electron cloud of the bond. That means on what atom

Table 1. Binding energy values of R-O [26-28].

R	valency	coordination number	ΔH_{R-O} kcal/mol
B	3	3	119
	3	4	89
Si	4	4	106
Ge	4	4	108
Al	3	3	101
	3	4	79
	3	6	53
P	5	4	111
	5	5	88
V	5	5	112
	5	4	90
As	5	5	70
	5	4	87
Sb	5	4	85
	5	5	68
Zr	4	6	81
	4	8	61
Ti	4	6	73
Zn	2	2	72
	2	4	36
Pb	2	2	73
	4	6	39
	2	4	36
Th	4	8	65
	4	12	43
Be	2	4	63
Cd	2	2	60
Sc	3	6	60
La	3	7	58
Y	3	8	50
Sn	4	6	46
Ga	3	6	45
In	3	6	43
Mg	2	6	37
Li	1	4	36
Ba	2	8	33
Ca	2	8	32
Sr	2	8	32
Cd	2	4	30
Na	1	6	20
Cd	2	6	20
K	1	9	13
Rb	1	10	10
Hg	2	6	11
Cs	1	12	10

forming the bond the positive (or negative) charge can be expected and then to estimate the charge.

Table 2. Electronegativity values of metals (X_{A^*} is the electronegativity of atom in free radical, X_A is the electronegativity of atom).

R	X_{A^*}	X_A
Be	1.3	1.5
Cd	1.5	1.7
Mg	1.2	1.2
B	1.6	2.0
Ca	1.2	1.0
Al	1.3	1.5
Sr	1.2	1.0
Ga	1.2	1.5
Ba	1.2	0.9
In	1.2	1.7
Zn	1.5	1.7

The method of electronegativity can be taken directly only to the molecules. For the crystal it is necessary to take into account the coordinational numbers of atoms, the bonding order and the length of bond. That is why the application of the method of electronegativity to the liquids (melts) is a rather difficult challenge.

The ion-ionizer line is well presented in works of "the metallurgical school". Its basis is also the concept of electronegativity of elements forming oxides. However as it was abovementioned the concept of electronegativity can be used only for rough estimations of the acid-base properties of oxide systems. That is why in the physical chemistry of high-temperature slags and salt melts the acid-base properties of elements are characterized by the determination of their electron shell structure [40]. The process of acid-base interaction can be given by the following equation:



where M is the basis, M^{n+} is the acid and e is a electron. The measure of acid-base properties of the element is the ionization potential or the electron affinity of the electroneutral atom [41]. And for the anions the measure of basicity is:

$$\gamma_{orb} = \frac{F}{R_{orb}}, \quad (51)$$

where F is the electron affinity, R_{orb} is the value of orbital radius. Correspondingly for the cations:

Table 3. Strong bases.

<i>Ion</i>	I_n, eV
K ⁺	7.33
Ba ⁺	11.55
Pb ²⁺	15.24
Na ⁺	18.48

Table 4. Bases.

<i>Ion</i>	I_n, eV
Bi ³⁺	27.43
Li ⁺	28.52
Mg ²⁺	61.1

Table 5. Weak Bases.

<i>Ion</i>	I_n, eV
Mn ²⁺	40.31
Fe ²⁺	44.45
Co ²⁺	49.71
Ni ²⁺	55.85
Zn ²⁺	61.3
Fe ³⁺	86.31

Table 6. Amphoteric cations.

<i>Ion</i>	I_n, eV
Cu ²⁺	65.88
W ⁶⁺	107.02
Mo ⁶⁺	123.62
Al ³⁺	123.69

Table 7. Weak and strong anhydrides

<i>Ion</i>	I_n, eV
V ⁵⁺	153.77
P ⁵⁺	361.17

$$\gamma_{orb}^{n+} = \frac{I_n}{R_{orb}}, \quad (52)$$

where I_n is the n -th ionization potential of the ion with n charges. The basicity distribution of ions can be arranged in the Tables 3 – 7 [42].

When Tables 3-7 are compared with the data of Tables 1 and 2, it is apparent that there is a good correlation between them. It comes as no surprise, because the estimation of basicity in these tables

lean upon the periodic law which determines the arrangement order of elements in the rows of basicity.

However this approach could not serve demands for the determination of acid-base characteristics of oxides. It did not take into consideration the coordination surrounding of the ion in a real melt, the possibility of valence and charge change.

Sometimes to characterize the acid-base properties of elements the value of electron affinity is used [43]:

$$E_x = \frac{N_x}{\sigma + \pi + ne} \left(\frac{\sigma + \pi + ne}{2} \right)^{\frac{1}{ne+2}}, \quad (53)$$

where σ is the number of σ bonds, π is the number of π bonds, ne is the number of free electrons in the valence shell. In the work [41] the number of parameters used for characterizing the acid-base properties of elements were extended. These data are given in Table 8.

One can see that in dependence of the chosen parameter the elements can hold different positions. The same picture is for the scales of electronegativity. That is why these parameters can be used only for an approximate estimation of the acid-base properties of element. Besides the oxygen surrounding which exists in the real melt was not taken into consideration.

The method of determination which was called "the optical basicity" is rather modern [44-48]. The basis for this method is the determination of optical electronegativity [36, 37, 49, 50]. The result is numerical values characterizing the basicity of substances, ions, element-oxygen groupings. The glass network is considered as an interacting continuum involving high-polarized Si⁴⁺ and O²⁻ ions. When interacting O²⁻ and Si⁴⁺ the electron density and charge are redistributed so that it gives rise to the appearance of groupings Si-O-Si and Si-O. The addition of other ions gives rise to a certain changes of the continuum. The general donor ability or the basicity of glass is determined by the relation between different types of oxygen, similar to Toope and Samis's model.

The optical basicity is determined as:

$$\lambda = \frac{v_{fr,ion} - v_{gl}}{v_{fr,ion} - v_{O^{2-}}} = \frac{\Delta v_{gl}}{\Delta v_{O^{2-}}}, \quad (54)$$

where $v_{fr,ion}$ is the hypothetical frequency of ultraviolet rays absorption by the free indicator ion; $v_{O^{2-}}$ is the hypothetical frequency of ultraviolet rays absorption by the oxygen ion; the frequency of ultraviolet

Table 8. Parameters characterizing the acid-base properties of elements, [40-43].

R	Oxidation state	ΣI_n eV	R_{orb} Å	g_{orb}^{n+} ev/Å	χ eV	χ/R_{orb} ev/Å	I_n eV	I'	E_x eV	coordination
K	1	4.34	2.162	7.33	2.32	1.07	4.34	0.32	0.320	–
Na	1	5.14	1.713	18.48	2.47	1.60	5.14	0.38	0.380	
Li	1	5.39	1.586	28.52	2.99	1.89	5.39	0.40	0.400	–
Mg	2	22.69	1.279	61.10	3.81	2.98	15.04	0.83	0.560 0.680	–Mg– Mg=
Mn	2	23.08	1.278	40.31	3.33	2.60	15.64	0.85	0.567 0.671	–Mn– Mn=
Fe	2	–	–	–	4.24	3.47	24.07	0.89	0.600 0.600	–Fe– Fe=
Co	2	24.93	1.181	49.71	4.40	3.72	17.06	0.92	0.617 0.620	Co Co=
Ni	2	25.78	1.139	55.85	4.46	3.92	18.15	0.95	0.633 0.637	Ni Ni=
Cu	2	28.02	1.191	65.88	4.48	3.76	20.29	1.03	0.670 0.672	–Cu– Cu=
Zn	2	27.35	1.065	61.10	4.74	4.45	17.96	1.01	0.660 0.662	–Zn– Zn=
Pb	2	22.44	1.215	15.24	4.22	3.47	15.03	0.83	0.620 0.640	–Pb– Pb=
Bi	3	49.35	1.295	27.43	4.10	5.84	25.60	1.21	0.710 0.730	Bi< –Bi=
Fe	3	54.71	1.277	85.31	4.24	3.47	30.64	1.34	0.710 0.730	Fe< –Fe=
Ca	2	17.98	1.690	22.06	2.08	1.23	11.87	0.66	0.440 0.530	–Ca– Ca=

ΣI_n – the sum of ionization potentials up to n -degree, R_{orb} – the orbital radius, g_{orb}^{n+} – the ratio of the ionization potential of i -degree to the orbital radius, χ – electron affinity, I_n – ionization potential of n -degree, $I'=I_n/R_{orb}$, E_x – the difference of electron affinities between the first and the second stages.

rays absorption by the indicator ion in the glass. ν_{gl} is determined experimentally. In the real experiment $\Delta\nu_{gl}$ is determined and adjusted to the standard state. The standard state is the chosen glass of certain composition. $\nu_{O^{2-}}$ is the value which is ascribed to each indicator ion. For example, for Pb^{2+} $\nu_{O^{2-}}$ is equal to 31000 cm^{-1} [48].

With the values of optical basicity it is possible to speak about the state change of oxygen particles in the glass under study in comparison with the standard one. In so doing the quantitatively agreed values can be obtained. As a result Duffy made the following row of basicity for the glassforming oxides:



The basicity grows from left to right.

On the one hand, the data on the optical basicity are quite useful to gain a better understanding of the donor-acceptor interaction in glasses. On the other hand, they do not give the values of activity of O^{2-} ions in glass and especially in melt. To solve this problem Duffy introduced the parameter γ^* , which accounts for the ability of cations to maintain the electron cloud of oxygen. The higher the value of γ^* , the more acid the element is. The values of γ^* for the elements studied by Duffy are given in Table 9.

Table 9. The value of γ^* for some elements.

R	N	S	P	B	Si
γ^*	3.73	3.04	2.50	2.36	2.09
R	Zn	Al	Mg	Li	
γ^*	1.82	1.65	1.28	1.00	

In general the method of optical basicity is rather promising for the investigation of the optically transparent objects at room temperature, when on frequent occasions the usual methods of the study of acid-base properties of glass break down.

3. METHODS OF MELT BASICITY DETERMINATION

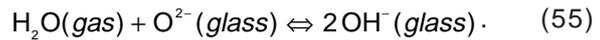
Lux was the first who put the question on the experimental determination of the basicity of oxide melts [3]. The general approach to solve it has not existed to this day. The various of approaches demonstrates not only the complexity but the actuality of this problem as well. Now there are some experimental methods of basicity determination for the oxide melts. They are:

- the method of gas solubility;
- the method of indicators;

– the EMF method.

The method of gas solubility suggests the chemical interaction of the oxide melt with the gas agent. H_2O , SO_2 , CO_2 or mercury vapour are used as the gas agent. The O^{2-} concentration in melt is determined after the results of this interaction using the spectrum analysis.

The authors of the works [51-53] used water as the gas agent. The interaction between melt and water vapor can be shown as:

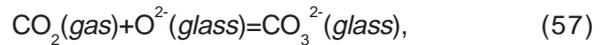


The formation of OH^- groupings was considered as the presence of $=Si-OH$ and $=Si-OH...O-Si=$ ones. The determination of hydroxyl groupings contents was carried out using the IR spectroscopy. The constant of reaction (55) was shown up as:

$$K_{55} = \frac{[OH^-]^2}{f_{H_2O}[O^{2-}]}. \quad (56)$$

where f_{H_2O} is the fugacity of water vapour.

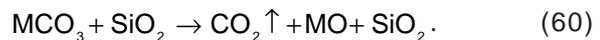
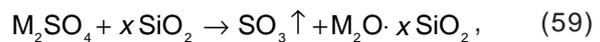
When CO_2 is used as the gas agent, its solubility in melt can be shown as [54]:



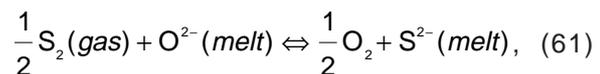
$$K_{57} = \frac{[CO_3^{2-}]}{p_{CO_2}[O^{2-}]}, \quad (58)$$

where p_{CO_2} is the pressure of CO_2 vapour.

At bulk melting as a result of interaction the following reactions can take place [55]:

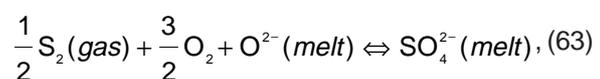


Sulfur can dissolve in glass giving either sulfide or sulfate with the partial pressure of oxygen in the stove atmosphere. The reactions of sulfur solution can be shown as [22, 56]:



$$[O^{2-}] = \frac{[O_2]^{1/2}[S^{2-}]}{K_{61}[S_2]^{1/2}} \quad (62)$$

and

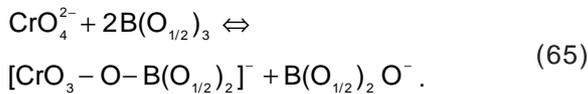


$$[O^{2-}] = \frac{[SO_4^{2-}]}{[S_2]^{1/2} P_{O_2}^{3/2} K_{63}} \quad (64)$$

It is necessary to mention that the reaction constant depends on the melt nature [57]. If the oxygen and sulfur pressures are constant, the sulfur solubility increases as the activity of oxygen ion increases.

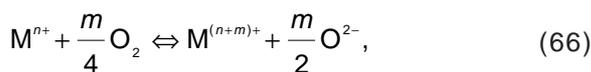
So, the increase in the gas solubility in melt can be interpreted as the increase in the basicity of melt. But the main drawback of this method is the following fact. The point is that the authors could not determine the activity of oxygen. In reality they determined the concentration of oxygen ions. Besides it is necessary to mention that the coefficients K_{61} and K_{63} are not constant, because they depend on the composition of oxide system [55].

The indicator method uses ions of transition metals as the indicator to determine the acid-base relations in borate and silicate glasses. Weyl's ideas about the interrelation nature between acid-base and redox equilibria in oxide melts were the basis for the method [58]. The coordination of these ions depends on the state of oxygen ion in melt [22, 23, 58-60]. The indicator ion in oxide melt is subjected to some chemical interaction. By way of illustration for the pair Cr^{3+}/Cr^{6+} in borate glass:



The transition ions can give colored paramagnetic ions [58] in melt and the type and nature of the formed compounds can be determined with the help of spectroscopy. For some glass forming systems there are rows of transition metals, for example Ti^{3+}/Ti^{4+} , Fe^{2+}/Fe^{3+} , V^{4+}/V^{5+} , Cu^{1+}/Cu^{2+} , Cr^{3+}/Cr^{6+} , Mn^{2+}/Mn^{3+} , Co^{2+}/Co^{3+} , Ce^{4+}/Ce^{3+} [58, 59, 61-65]. These transition metals give different spectroscopic coloring depending on the basicity of melt, namely, the contents of alkali metal in it.

The process of acid-base interaction can be given as the following reaction [59, 66]:



$$K_{66} = \frac{[M^{(n+m)+}]}{[M^{n+}]} \cdot \frac{a_{O^{2-}}^{m/2}}{P_{O_2}^{m/4}}, \quad (67)$$

where $n+$ is the lower valence state, $(n+m)+$ is the higher valence state.

Up to now the only method which is handy and working just in melt is the Electro Moving Forces (EMF) method [22, 67, 68]. H. Lux was one of the very first who used this method to determine the concentration of free oxygen ions, or the basicity of the system, in melted salts [3].

This method allows to get the pO values, where $pO = -\lg a_{O^{2-}}$. (68)

The principle of the method is in the use of reversible electrochemical circuit. The potential forming reaction of this circuit agrees with the reaction under study. To study the oxide melts the following galvanic cell is used [69-71]:



The platinum electrode is used as an electrode reversible on oxygen ions [72-74]. The following reaction takes place on the electrode:



The authors [72-76] proved the oxygenous electron function and the reversibility of the platinum electrode dipped into the ion melt for different alkali-silicate, alkali-borate, alkali-phosphate and alkali-germanate glasses. The EMF of this cell is given the following equation [77-79]:

$$E = \frac{RT}{2F} \ln \frac{a_{O^{2-}}^I}{a_{O^{2-}}^{II}} + E_{diff}, \quad (70)$$

where R is the universal gas constant, F is the faraday (electrochemical constant), $a_{O^{2-}}^I$ is the activity of oxygen ions in the melt under study, $a_{O^{2-}}^{II}$ is the activity of oxygen ions in the standard melt. E_{diff} is the diffusion potential, which is an additional change of potential at the boundary of two melts in contact. It results from the difference in the diffusion rates and has the following equation:

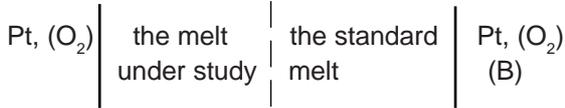
$$E_{diff} = -\frac{RT}{F} \int \sum_i \frac{t_i}{z_i} d \ln a_i, \quad (71)$$

where t_i is the transport number, z_i is the charge of i^{th} ion.

Nowadays the EMF method is the basis for the construction of the unified pO scale for the oxide melts.

4. THEORETIC GROUND FOR THE pO TECHNIQUE BASED ON THE EMF METHOD

To investigate the activity of the potassium oxide in melt the following galvanic cell was made:



Binary oxides containing an alkaline oxide (for example, M_2O - SiO_2 , M_2O - GeO_2 , M_2O - B_2O_3) with different concentrations of alkaline oxide are used as the standard melts and the melt under study. The process in the galvanic cell (B) is in the transfer of K^+ ions from one melt to the other. The activities of these two melts are different:

$$\Delta E = \frac{RT}{2F} \ln \frac{a''_{M_2O}}{a'_{M_2O}} = \mu''_{M_2O} - \mu'_{M_2O}, \quad (72)$$

where μ is the chemical potential, the symbols (*I*) and (*II*) signify the melt under study and the standard melt correspondingly.

With the temperature dependencies of concentration for the EMF it is possible to calculate the chemical potential of the potassium oxide according to the following equation:

$$\Delta\mu_{M_2O} = -2F\Delta E. \quad (73)$$

The chemical potential is normalized to the standard electrode. The measurement precision was better than ± 2 kJ/mol.

The direct determination of the activity of ions of one sort is impossible. However, this problem of quantitative determination of the acid-base characteristics of oxide melts could be solved on the basis of definite agreement about the ways of measurement and the normalization of pO values.

To determine the values treated as $a_{O^{2-}}$ it is necessary to eliminate the diffusional potential (see Eq. (70)). The procedure of experiment is determined by the type and construction of the galvanic cell [80]. Two types of galvanic cells were used: with the salt bridge (C) and with the melt-solvent (KF-oxide melt) (D):



The choice of the material of salt bridge and the melt-solvent was carried out reasoning from the following principles. First, the transport numbers of cation and anion of the material of salt bridge and the melt-solvent must be equal. Second, for the galvanic cell (D) the interaction of the system under study and the solvent must be absent. Third, it is necessary to have the excess of solvent. Fourth, oxygen must not enter the composition of both the solvent and the salt bridge and they must not be oxidized with the oxygen of air. The fulfillment of all these conditions gives rise to the elimination of the diffusional potential [69, 80]. The KF melt meets all these conditions [69, 81, 82].

The elimination condition of the diffusional potential for the galvanic cell (C) is the total change of the carriers of charges at the boundary of matter - salt bridge and the equality of mobilities of cation and anion of the salt bridge.

The transport numbers of K^+ and F^- are equal: $t_{K^+}=0.505$, $t_{F^-}=0.495$ [83, 84]. Thus it may be deduced that the value of the diffusional potential goes to zero. So, the EMF of the galvanic cell will be determined only by the change in activity of oxygen ions:

$$\Delta E = \frac{RT}{2F} \ln \frac{a''_{O^{2-}}}{a'_{O^{2-}}}. \quad (74)$$

The normalization of the experimental pO values was performed by the following procedure. The state of oxygen ions O^{2-} in the pure SiO_2 is assumed to be their standard state (primary standard) at the given temperature and pressure. According to [79]:

$$pO_{SiO_2} = 7, \quad (75)$$

that is

$$a_{O^{2-}} = 10^{-7}. \quad (76)$$

The unit event of dissociation equilibrium is the break-off of a semimole of oxygen ions from one mole of $SiO_{4/2}$. That is the change of summary charge of the oxygen silicate tetrahedron by one. The process of SiO_2 dissociation has four stages. As a result the Si^{4+} ion forms. However, [79] taking into consideration the nature of donor-acceptor interactions we can consider only the first stage, because all the constants of all the other further reactions are markedly lower:



and the equilibrium constant of this reaction is:

$$K_{40} = \frac{a_{SiO^{3/2}^+} a_{O^{2-}}^{1/2}}{a_{SiO_2}} = \frac{x_{SiO^{3/2}^+} x_{O^{2-}}^{1/2}}{x_{SiO_2}} \quad (77)$$

The dissociation constant can be obtained from equation (41) if the admission is taken and the ideality of solution consisted of ions and molecular particles is supposed. The K_{40} constant can be written with the help of mole parts of components and then the equation of charge conservation is:

$$2x_{O^{2-}} = x_{SiO^{3/2}^+} \quad (78)$$

For one mole of SiO_2 K_{40} is equal to $6.32 \cdot 10^{-11}$.

To calculate the pO values for the galvanic cell (C) within the working intervals of oxide system concentrations in KF the following equation was used:

$$pO = 7 - \frac{\Delta E \cdot 2F}{2.303 \cdot RT} \quad (79)$$

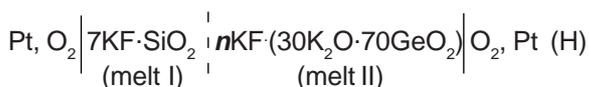
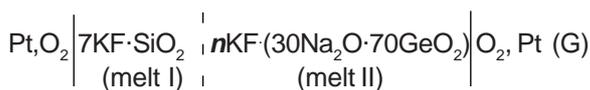
For the galvanic cell (D) the calculation of pO values was carried out by the equation:

$$pO = pO_{standard} - \frac{\Delta E \cdot 2F}{2.303 \cdot RT} \quad (80)$$

where $pO_{standard}$ is the pO value determined for the secondary standard. The secondary standard was the melt of $30Na_2O$ - $70SiO_2$. It was equal to 5.56 [69].

5. EXPERIMENTAL

To determine the working concentration intervals by solvent Nernst's dependencies were studied. The following galvanic cells were made:



The values of EMF of the galvanic cells (E) - (H) are determined by Nernst's equation:

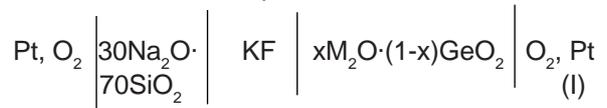
$$E = \frac{RT}{2F} \ln \frac{c_{melt}^{II}}{c_{melt}^I} \cong \frac{RT}{2F} \ln \frac{c_{O^{2-}}^{II}}{c_{O^{2-}}^I} \quad (82)$$

The concentration of oxide systems in KF is in direct proportion to the concentration of oxygen ions in this system. The composition of the comparison melt was the same, $7KF$ - $1SiO_2$. The composition of the melt under study was changed. The values of n in the melts under study were: 1, 3, 5, 7, 10, 15 and 30. The results of experiments are shown in Fig. 4. One can see that the experimental concentration dependencies of EMF for oxide systems in KF are parallel within the limits of experimental error. In the range from 5 to 30 n the dependencies coincide with Nernst's one within the experimental error. The theoretic angle coefficient must not exceed $5.05 \cdot 10^{-2}$. For the dependencies it was $(4.8 \pm 0.3) \cdot 10^{-2}$.

The parallelism of these dependencies testifies that the interaction in these systems is close to the ideality [67, 69]. It is believed that in the concentration limits of n from 5 to 30 the phenomenon of currency transfer is fulfilled by the solvent ions [78].

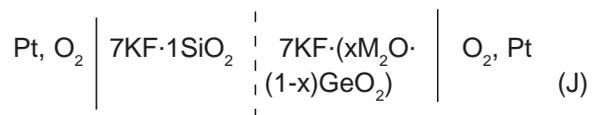
The investigation of all the samples of glasses was carried out in both types of galvanic cells.

For the galvanic cell (C) the $30Na_2O$ - $70SiO_2$ melt was used as the comparison melt:



The EMF values were renormalized to the pure SiO_2 . The value of $pO_{standard}$ for the comparison system was used. It was equal to 5.56 [69]. The calculation of pO was carried out by Eq. (80).

For the galvanic cell (D) the $7KF$ - $1SiO_2$ melt was chosen as the comparison melt. So this galvanic cell can be written as:



For this galvanic cell the calculation of the pO values was carried out by Eq. (79).

The concentrational dependencies of pO for both types of galvanic cells ((I) and (J)) are shown in Fig. 5. The data were obtained at the same temperature, $950^\circ C$. It is evident from Fig. 5 that the values of pO for both galvanic cells coincide within the limits of experimental error. It testifies once again about the absence of interaction between the solvent, which is KF, and the oxide systems under study. That is why this system can be considered to be quasineutral [67, 78, 82].

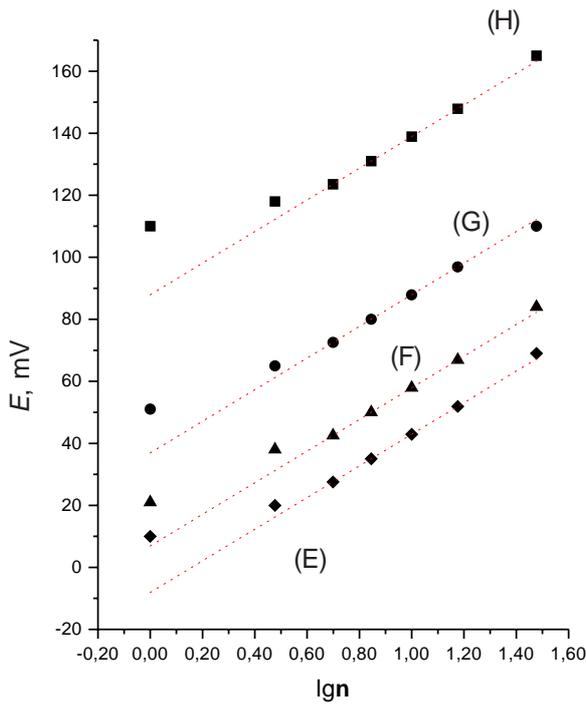


Fig. 4. Nernst's dependencies realized in the galvanic cells (E-H).

One of the challenges of the work was to investigate the influence of the cation change on the basicity of binary germanate melts. The objects under study were the systems: $\text{Li}_2\text{O-GeO}_2$, $\text{Na}_2\text{O-GeO}_2$ and $\text{K}_2\text{O-GeO}_2$. The region of composition was from 0 to 50 mol.% of alkali oxide. The samples of glasses were studied by the abovementioned procedure in both types of galvanic cells. The measurements of EMF were carried out in the temperature range from 900 to 1000 °C. The convergence of experimental values of $p\text{O}$ in the series of 10 measurements was ± 0.04 of the unit of $p\text{O}$.

In Fig. 6 one can see the concentration dependencies of $p\text{O}$ for the melts of the systems under study. With the increase in the contents of the alkali metal oxide the increase in the basicity of melts of equimolar compositions of R_2O . The basicity grows and correspondingly $p\text{O}$ decreases in the following row:



The investigation of chemical potentials in the $\text{K}_2\text{O-GeO}_2$ system was carried out. The EMF was measured in the cooling regime when the feeding switch off in the range from 1100 to 700 °C. The values of EMF were recorded every 10 degrees. It is

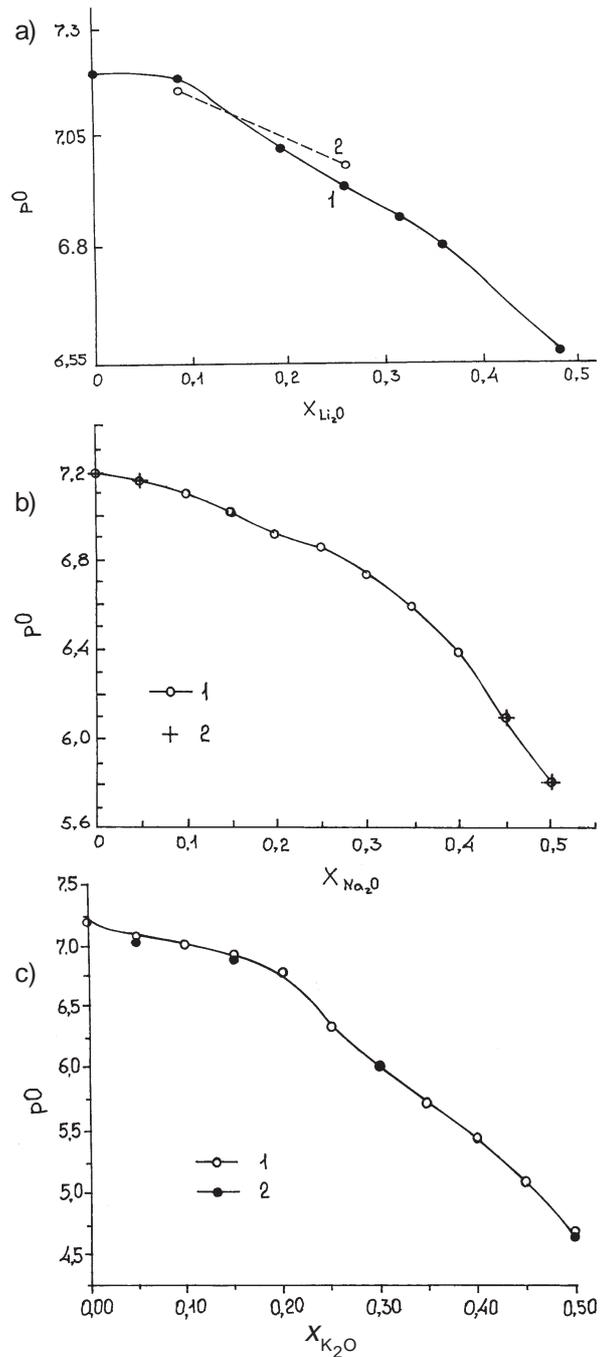


Fig. 5. Comparison between the results of $p\text{O}$ determination in the galvanic cells (I) – (1) and (J) – (2) for the systems: (a) – $\text{Li}_2\text{O-GeO}_2$; (b) – $\text{Na}_2\text{O-GeO}_2$; (c) – $\text{K}_2\text{O-GeO}_2$.

neccasary to mention that all the samples under study were stored in the exsiccator. The standard melt was $27.5\text{K}_2\text{O-6Al}_2\text{O}_3\text{-66.5SiO}_2$. The composition was chosen according to the following reasons. In the first place the unipolar principle must be met [80, 81]. Secondly, the viscosity of the standard melt must be higher than 10^4 Ps within the temperature range. This viscosity is enough for the standard melt and the melt under study not to mix. Thirdly, we

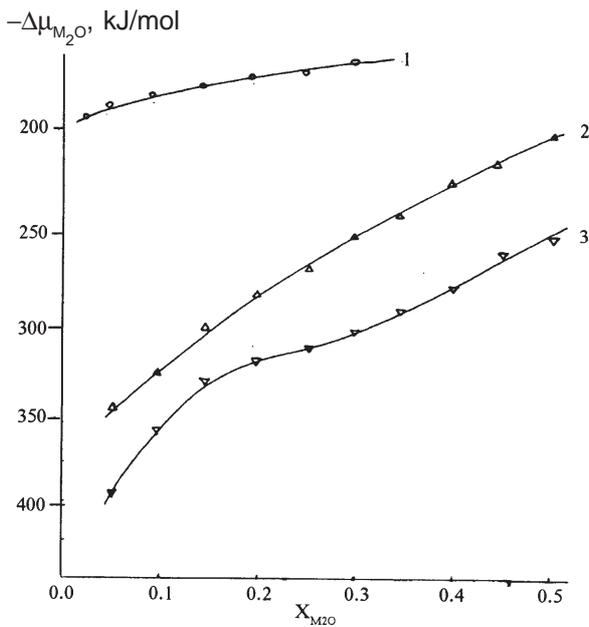


Fig. 8. Dependencies of μ_{K_2O} for the melts of the systems: 1 – $\text{Li}_2\text{O-GeO}_2$ [86], 2 – $\text{Na}_2\text{O-GeO}_2$ [86], 3 – $\text{K}_2\text{O-GeO}_2$ [87]. $T = 950\text{ }^\circ\text{C}$

tion of the constants of forming reactions. So, it can testify about the change in the chemical structure of melt.

The lower the value of activity a_{M_2O} , where

$$\mu_{M_2O} = \mu_{M_2O}^\circ + \ln a_{M_2O} \quad (83)$$

the more basic is the melt. That means that the oxides of binary system interact one with the other stronger and consequently the acid-base properties of oxides that form this system differ greater. It corresponds to the certain order of basicity in the row:

$\text{Li} > \text{Na} > \text{K}$.

In the region of high concentration of alkali oxide the basicity of the melt is determined by the processes of its dissociation and the pO values are in good agreement with the values of electronegativity (see table 8, [40-43]). Reasoning from pO values the greater the difference between the acid-base properties of the oxides forming the binary system the greater the effects of their interactions. Let's apply the concept of electronegativity to the consideration of the systems: $\text{Li}_2\text{O-GeO}_2$, $\text{Na}_2\text{O-GeO}_2$ and $\text{K}_2\text{O-GeO}_2$. The greater the interaction of oxides in the binary system composed from the alkali oxide and germanium oxide the greater the energy effects in such system. When passing from Li to K the electronegativity of element decreases. The greatest difference in the values of electronegativity for

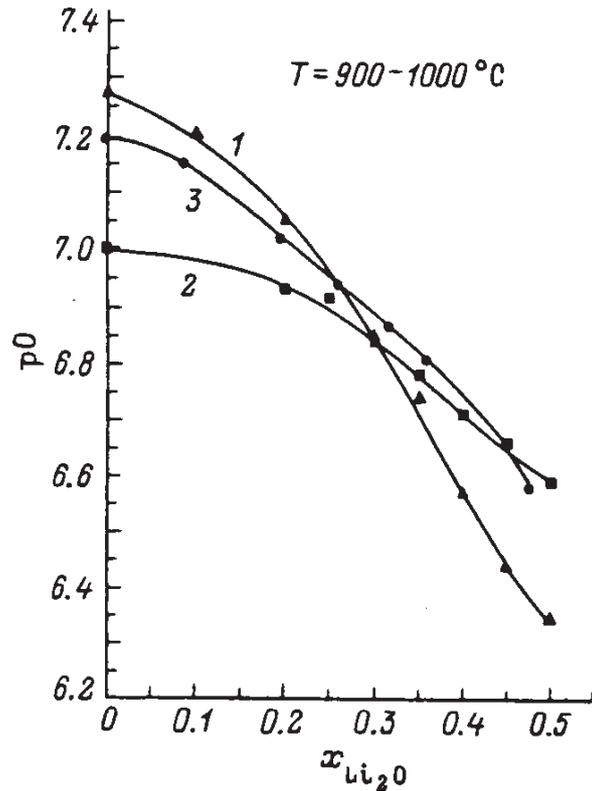


Fig. 9. Comparison of experimental concentration dependencies of pO for the melts of the systems: 1 – $\text{Li}_2\text{O-B}_2\text{O}_3$, 2 – $\text{Li}_2\text{O-SiO}_2$, 3 – $\text{Li}_2\text{O-GeO}_2$.

these three systems is observed for potassium and germanium. Respectively for lithium and germanium it is the lowest. So, when the difference in acid-base properties of oxides forming the system is great it is possible to use any method of their estimation: in the pO terms or using the chemical potential.

Another challenge of the work was the investigation of basicity influence on the summary basicity of melt. The $\text{Li}_2\text{O-B}_2\text{O}_3$, $\text{Li}_2\text{O-SiO}_2$ and $\text{Li}_2\text{O-GeO}_2$ were used to illustrate. The concentration dependencies of pO for these systems are shown in Fig. 9. The information about the basicity for the $\text{Li}_2\text{O-B}_2\text{O}_3$ and $\text{Li}_2\text{O-SiO}_2$ systems were taken in [78] and [82] correspondingly.

The lithium borate melts initially more acid show sharper increase in basicity than the lithium silicate melts and the lithium germanate ones. It is well-known that in the row of glass former oxides, $\text{SiO}_2 - \text{GeO}_2 - \text{B}_2\text{O}_3$, the basicity falls from silica to boron oxide [79, 88]. It is just their basicity that determines the initial value of pO at the low concentrations of alkali oxide. With increasing mole part of alkali oxide the summary basicity of systems begins to change. The change in acid-base properties is the most for the lithium borate system: $\Delta pO = 0.9$.

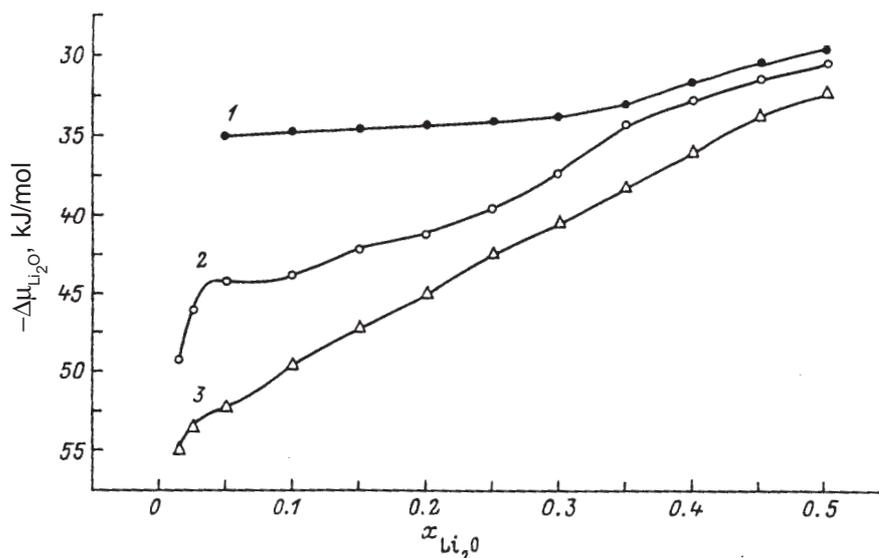


Fig. 10. Comparison of concentration dependencies of chemical potentials of melts for the systems: 1 – Li_2O - SiO_2 , 2 – Li_2O - GeO_2 , 3 – Li_2O - B_2O_3 .

In the region with low concentration of lithium oxide the pO values correlate well with the values of electronegativity of the glass forming elements, which go down from boron to silicon. There the basicity of melt is determined by the acidity of glass forming oxide.

Fig. 10 shows the concentration dependencies of chemical potential of alkali oxide for the Li_2O - B_2O_3 , Li_2O - SiO_2 and Li_2O - GeO_2 systems. The information about the chemical potential of alkali oxide for the Li_2O - B_2O_3 and Li_2O - SiO_2 systems were taken in [89] and [90] correspondingly. The strongest interaction, that means the lowest values of $\Delta\mu_{Li_2O}$, has the melts of lithium borate system. Its behaviour is in good agreement with our views about the greatest difference between the acid-base properties of lithium and boron. The more values of $\Delta\mu_{Li_2O}$ were obtained for the melts of lithium silicate and the lithium germanate systems. It accords with the order in basicity in the row of glassforming oxides determined earlier [79]. The lower the value of activity the stronger the interaction between the oxides of binary system. Therefore, their acid-base properties differ greater. However the quality estimation of chemical potential of alkali oxide testifies only about the strength of interaction and does not account the contribution of each component into the summary basicity of the system.

The similar conclusion can be made from the concentration dependencies of the formation enthalpy of lithium germanate glasses from crystal oxides (Fig. 11). The data on $\Delta H_{Li_2O-R_xO_y}$ were taken in the

works [91-93]. In the construction of Fig. 11, the calculation of $\Delta H_{Li_2O-R_xO_y}$ was carried out for the substance quantity which sum of mole fraction of all the oxides is equal to 1. This normalization allows to compare adequately the thermodynamic data. It can be seen from the figure that the acid-base interaction of components is best manifested in the lithium borate system. For this system the enthalpy is the most negative. It correlates quite well with the greatest change of the pO magnitude (Fig. 9) and with the most acid character of boron oxide in the row of the glass forming oxide under study.

The same regularity in properties can be followed for the Na_2O - B_2O_3 , Na_2O - SiO_2 , Na_2O - GeO_2 and K_2O - B_2O_3 , K_2O - SiO_2 , K_2O - GeO_2 systems. The concentration dependencies of pO values of these systems are shown in Fig. 12 and 13 correspondingly. The concentration dependencies of chemical potentials of alkali oxides are given in Fig. 14 and 15 correspondingly. All the necessary data were taken in the works [69, 82, 86, 87, 94-96].

Thus, the basicity given in pO terms is the most general characteristic which demonstrates the sum of contributions of all possible components of the melt for the system under study.

The next challenge of our study of the acid-base properties of oxide melts of the R_2O - GeO_2 ($M=Li, Na, K$) systems was the simulation of concentration dependencies of basicity for these systems to determine the interrelation between thermodynamic and acid-base properties of oxide melts. It is necessary to mention that earlier any attempt to simu-

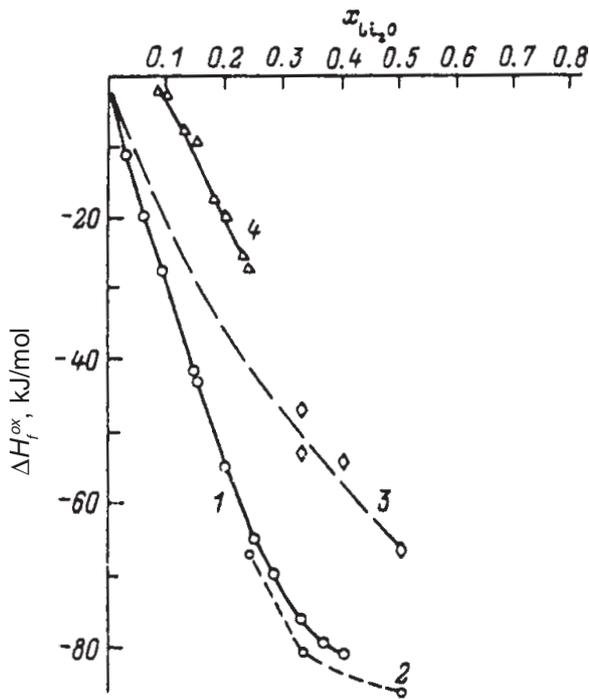


Fig. 11. Comparison of formation enthalpy of glasses and crystals for the systems: 1 – $Li_2O-B_2O_3$ (glass), 2 – $Li_2O-B_2O_3$ (crystal), 3 – Li_2O-SiO_2 (glass), 4 – Li_2O-GeO_2 (glass), $T = 25$ °C.

late the basicity index in the terms of pO was not undertaken. Only some thermodynamic properties of oxide melts were calculated.

As already noted, considering the acid-base interaction in the systems of two oxides the use of such a characteristic as the formation enthalpy from oxides, ΔH_f was very successful. To correlate we put to use the data on the formation enthalpies of sodium borate [97], sodium silicate [98-101], sodium germanate [93] and potassium borate [102, 103], potassium silicate [92], potassium germanate [93]. Fig. 16 and 17 show the concentration dependencies of formation enthalpies from crystal oxides of sodium and potassium borates, silicates and germanates. Referring to the figures it will be observed that the acid-base interaction of components is best manifested in the sodium borate and potassium borate systems. These systems have the most negative formation enthalpies, which well correlates with the greatest range of ΔpO (see Figs. 12 and 13) and with the more acid character of borone oxide in the row of the glass forming oxide under study. The obtained correlation between the formation enthalpies and pO of binary melts containing an alkaline oxide are not accidental and have a profound physico-chemical base. Both ΔH_f and pO are integral functions which reflect the state of melt

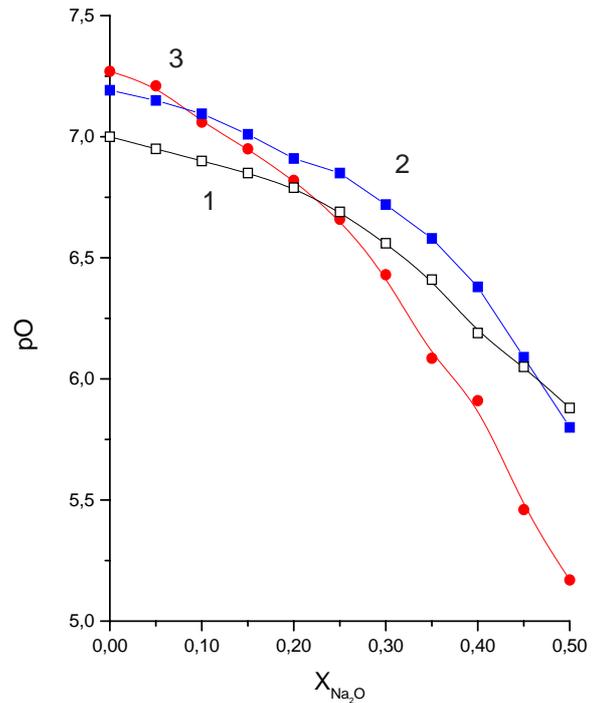


Fig. 12. pO dependencies on the composition for the systems: 1 – Na_2O-SiO_2 , 2 – Na_2O-GeO_2 , 3 – $Na_2O-B_2O_3$.

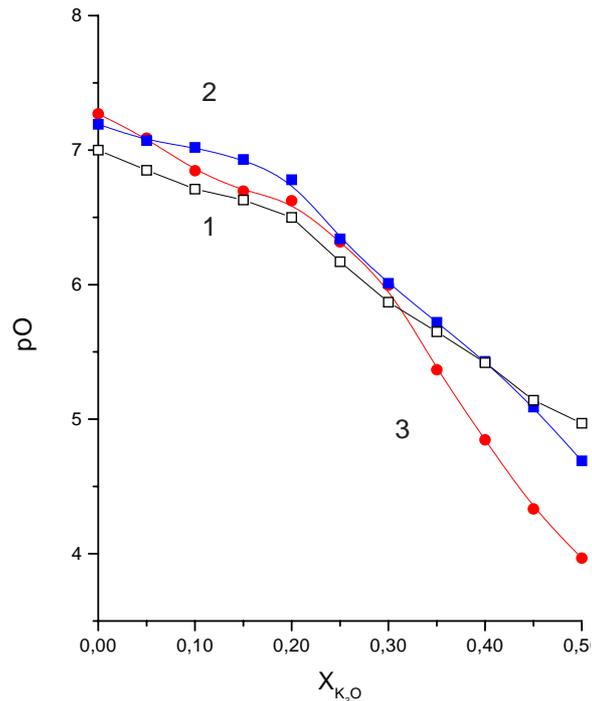


Fig. 13. pO dependencies on the composition for the systems: 1 – K_2O-SiO_2 , 2 – K_2O-GeO_2 , 3 – $K_2O-B_2O_3$.

(quenched glass) in general. ΔH_f is the heat effect of the formation reaction of the composition in question at the interaction of a particular acid and a particular base. pO is an integral characteristic of the basicity of the melt formed with evolution or absorp-

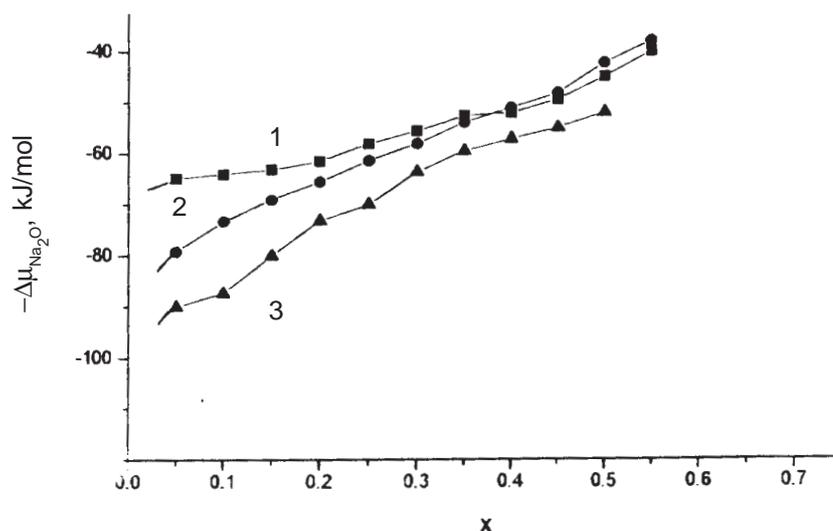


Fig. 14. Dependencies of chemical potentials of sodium oxide on the composition for the systems: 1 – Na_2O-SiO_2 , 2 – Na_2O-GeO_2 , 3 – $Na_2O-B_2O_3$.

tion of a particular heat quantity related to the basicity of standard melt. The former determines the energy character of the interaction of acid and base in the rows of analogous interactions of oxides close in properties. The latter, pO , characterises the basicity of the product of this interaction.

As for now there are two ways of simulating the changes of pO values.

The first simulation way proceed from the information about the activity of alkali oxide in the melt under study [69, 78, 104-106]. The basicity of melt is supposed to be determined only by the dissociation of alkali oxide.

The second way is the simulation of acid-base properties on the basis of the existing information about the chemical structure of the melts under study

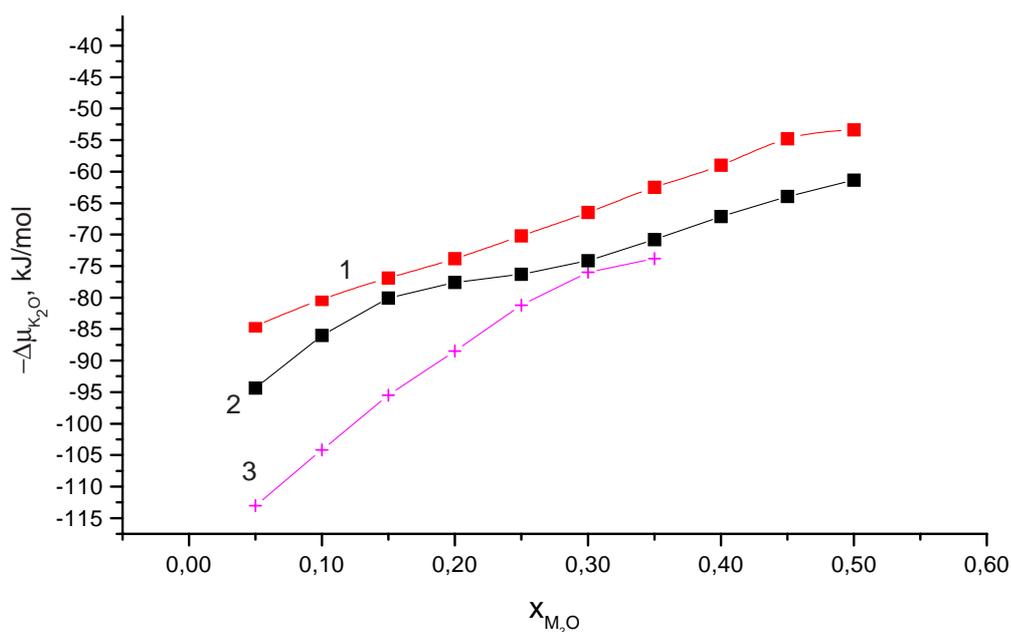


Fig. 15. Concentration dependencies of chemical potentials for the systems: 1 – K_2O-SiO_2 , 2 – K_2O-GeO_2 , 3 – $K_2O-B_2O_3$.

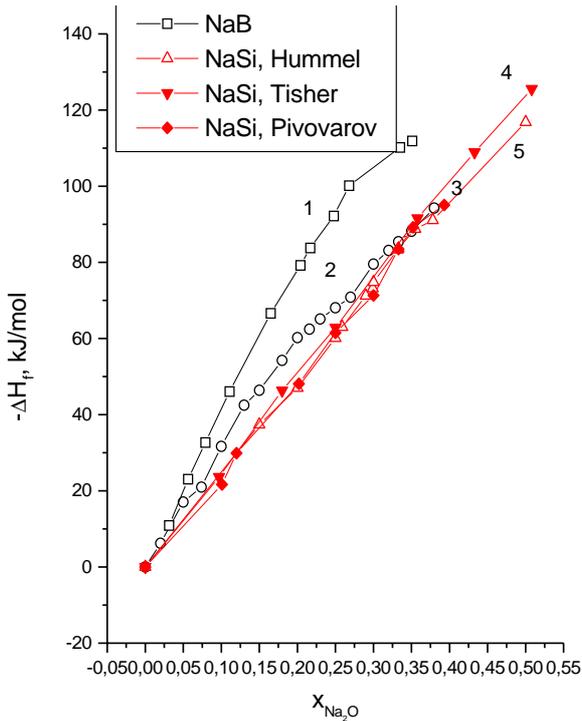


Fig. 16. Dependencies of enthalpies of formation on the composition for the systems: 1 – $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$, 2 – $\text{Na}_2\text{O}-\text{GeO}_2$, 3 – $\text{Na}_2\text{O}-\text{SiO}_2$ (Hummel's data), 4 – $\text{Na}_2\text{O}-\text{SiO}_2$ (Tisher's data), 5 – $\text{Na}_2\text{O}-\text{SiO}_2$ (Pivovarov's data). $T = 25^\circ\text{C}$.

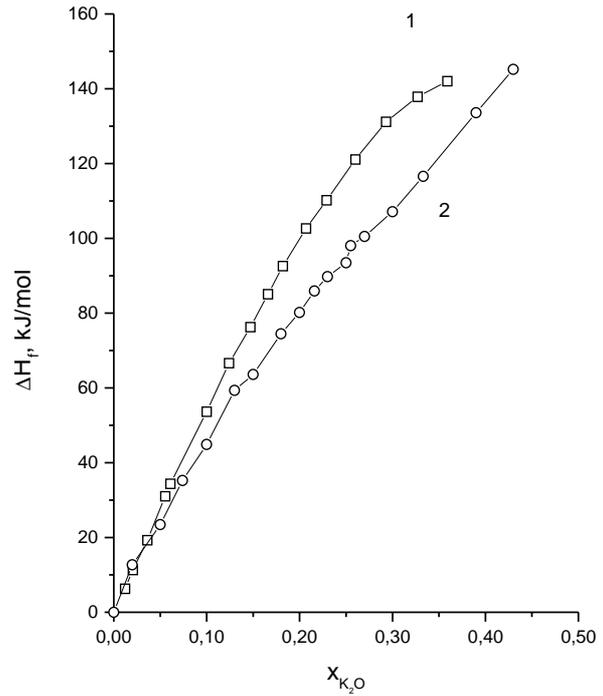


Fig. 17. Dependencies of enthalpies of formation on the composition for the systems: 1 – $\text{K}_2\text{O}-\text{B}_2\text{O}_3$, 2 – $\text{K}_2\text{O}-\text{GeO}_2$. $T = 25^\circ\text{C}$.

reasoning from the model of ideal associated solutions [82].

Let us consider the first simulation way. The dissociation equation of alkali oxide is:



The dissociation constant of this equation within the ideal approximation is:

$$K_5 = \frac{x_{\text{M}^+}^2 \cdot x_{\text{O}^{2-}}}{a_{\text{M}_2\text{O}}}. \quad (84)$$

The mole part of alkali oxide $x_{\text{M}_2\text{O}}$ is considered to be the real mole part of the oxide in melt, it means that it is its activity. The equation of charge conservation for this reaction is:

$$2x_{\text{O}^{2-}} = x_{\text{M}^+}. \quad (85)$$

Having combined equations (84) and (85) we have:

$$x_{\text{O}^{2-}} = \sqrt[3]{\frac{K_{\text{M}_2\text{O}} \cdot a_{\text{M}_2\text{O}}}{4}}. \quad (86)$$

From the one hand the dissociation constant of alkali oxide is unknown, on the other the normaliza-

tion ways of the values of $p\text{O}$ and $a_{\text{M}_2\text{O}}$ are different, it is possible to compare the relative change of $p\text{O}$, $\Delta^*p\text{O}$, according to the following equation:

$$\Delta^*p\text{O} = -\lg_3 \sqrt{\frac{a_{\text{M}_2\text{O}}}{a_{\text{M}_2\text{O}}^*}}, \quad (87)$$

where $a_{\text{M}_2\text{O}}^*$ is the reference point to compare the changes of $p\text{O}$ values.

The values of chemical potentials of lithium oxide and sodium oxide were taken in the work [86]. The extrapolation was carried out from the 1000 °C to the experiment temperature which was 950 °C. The results of calculations according to this model for all the systems are shown in Fig. 18. The values of $\Delta^*p\text{O}$ obtained also are shown here. To compare the experimental and calculated values of $\Delta^*p\text{O}$ they were renormalized to the following compositions: 33Li₂O-GeO₂, 50Na₂O-GeO₂, 50K₂O-GeO₂. These compositions were accepted as the reference points for the corresponding compositions. So, $a_{\text{M}_2\text{O}}^*$ was the activity just in this melt.

One can see from the figure that in the region with high contents of alkali oxide there is a good agreement between calculated and experimental

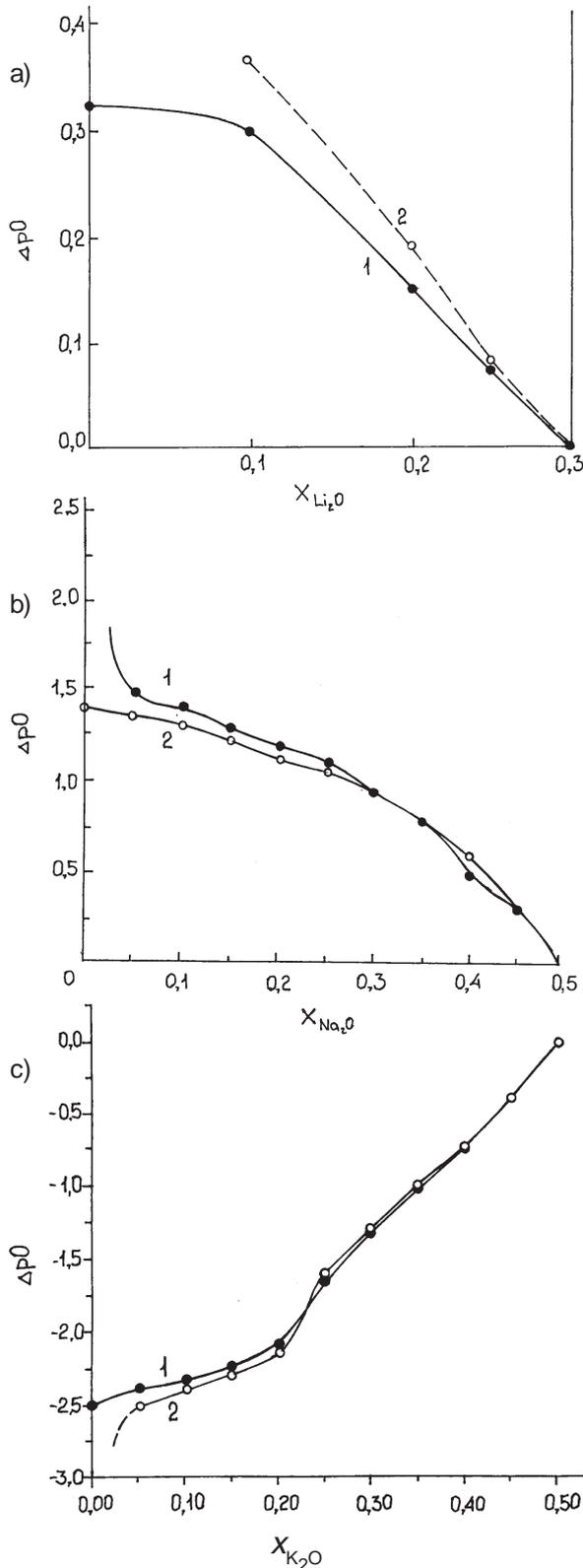


Fig. 18. Comparison of experimental (1) and simulated on model 1 (2) dependencies of the pO on the composition of the melts for the systems: a) – Li_2O-GeO_2 , b) – Na_2O-GeO_2 , c) – K_2O-GeO_2 . $T = 950^\circ C$

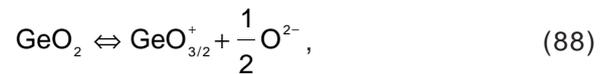
dependencies. That means that the changes in basicity of the system principally occur at the expense

of the dissociation of free alkali oxide. However, when decreasing its contents the basicity of glass former oxide begins to influence. The increase in deviations of the calculated values of ΔpO from the experimental ones testify about it.

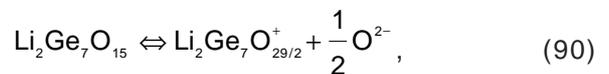
So, it is possible to state that this model to a first approximation points to the composition intervals where the basicity is determined just by the alkali oxide and where by the processes of the dissociation of glassformer oxide. This method of calculation is enough crude. It gives a quality estimation of the process going on in melt. It just indicates the regularity that the lower the basicity of melt the greater the influence of glass former oxide on the processes at work and the worse the model works. The deviations between experimental and calculated data could be explained by the main supposition of the model that the basicity of melt is determined only by the dissociation of alkali oxide.

Let us consider the second way of simulation. On the basis of this approach it is possible to take into account the influence of glass former oxide on the basicity of melt. According to the phase diagrams all the set of dissociative equilibria and corresponding equation constants is composed from the model of ideal associated solutions.

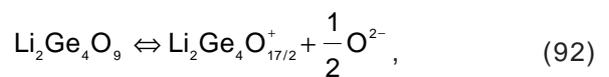
Let us consider the Li_2O-GeO_2 system. According to the phase diagrams [20] it is possible to write all the dissociation reactions and corresponding constants having regard to the existence in melt the following structure-chemical groupings: $Li_2O \cdot 7GeO_2$, $Li_2O \cdot 4GeO_2$, $Li_2O \cdot GeO_2$ [92]:



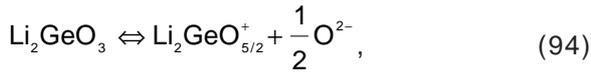
$$K_{GeO_2} = \frac{x_{GeO_{3/2}^+} \cdot x_{O^{2-}}^{1/2}}{x_{GeO_2}}, \quad (89)$$



$$K_{Li_2O \cdot 7GeO_2} = \frac{x_{Li_2Ge_7O_{29/2}^+} \cdot x_{O^{2-}}^{1/2}}{x_{Li_2O \cdot 7GeO_2}}, \quad (91)$$



$$K_{Li_2O \cdot 4GeO_2} = \frac{x_{Li_2Ge_4O_{17/2}^+} \cdot x_{O^{2-}}^{1/2}}{x_{Li_2O \cdot 4GeO_2}}, \quad (93)$$



$$K_{\text{Li}_2\text{O} \cdot \text{GeO}_2} = \frac{x_{\text{Li}_2\text{GeO}_{5/2}^+} \cdot x_{\text{O}^{2-}}^{1/2}}{x_{\text{Li}_2\text{O} \cdot \text{GeO}_2}}, \quad (95)$$



$$K_{\text{Li}_2\text{O}} = \frac{x_{\text{Li}^+}^2 \cdot x_{\text{O}^{2-}}}{x_{\text{Li}_2\text{O}}}. \quad (97)$$

Taking x_j to be the equilibrium concentration of components involving in the reaction, the equation of charge conservation for this reaction is:

$$2x_{\text{O}^{2-}} = x_{\text{GeO}_{3/2}^+} + x_{\text{Li}_2\text{Ge}_7\text{O}_{29/2}^+} + x_{\text{Li}_2\text{Ge}_4\text{O}_{17/2}^+} + x_{\text{Li}_2\text{GeO}_{5/2}^+} + x_{\text{Li}^+}. \quad (98)$$

The solution of the presented equations and the calculation of dissociation constants of structure-chemical groupings in melt were carried out by the minimization method of root-mean-square deviations of the calculated $p\text{O}$ values from the experimental ones. The information about the chemical structure of the melt was taken in the work [107].

The results of comparison of experimental and calculated dependencies of $p\text{O}$ on the composition of the system $\text{Li}_2\text{O}-\text{GeO}_2$ are shown in Fig. 19. In the high alkali region the calculated values of $p\text{O}$ differ from the experimental ones. This deviation could be explained. As a matter of fact when simulating the authors of the above mentioned work did not take into consideration the existence of the composition $2\text{Li}_2\text{O}-\text{GeO}_2$ in melt. Its contribution into the summary basicity of melt can be quite noticeable, even in spite of its insignificant amount, by virtue of the fact that the dissociation constant of this grouping is higher than the dissociation constant of lithium methagermanate.

The obtained values of dissociation constants are given in Table 10. The dissociation constants of the compositions $\text{Li}_2\text{O} \cdot 7\text{GeO}_2$ and $\text{Li}_2\text{O} \cdot 4\text{GeO}_2$ are well below the dissociation constant of pure GeO_2 . It is particularly remarkable. In the chemistry of aqueous solutions at interacting an acid and a base the salt which forms always has the basicity of intermediate value between the acid and the base. For the aqueous solutions the acid-base interaction of the acid and the base proceeds through the hydrate shell surrounding them. This shell determines both

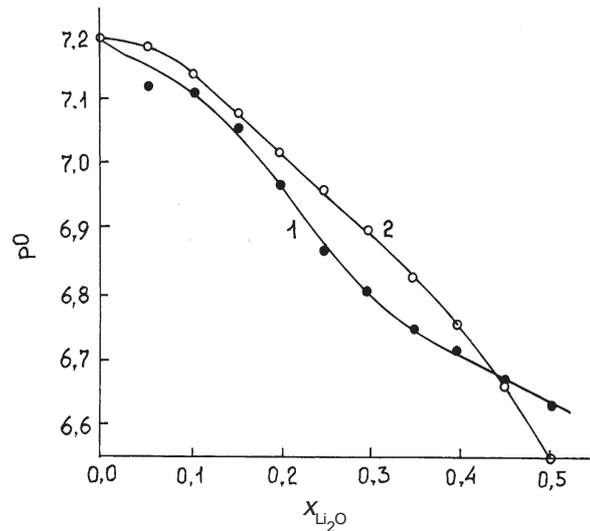


Fig. 19. Comparison of experimental (1) and simulated on model 2 (2) dependencies of the $p\text{O}$ on the composition of the melts for the $\text{Li}_2\text{O}-\text{GeO}_2$ system.

the character of interaction passing and the coordination state of interacting ions.

In the melt the acid-base interaction is the change of the state of structure-chemical groupings with the chemical composition and temperature. As this takes place the coordination state of the element of grouping is determined by the melt composition.

In our case the decrease in dissociation constant is attached to the formation the structure-chemical groupings with higher acidity in melt. The oxygen ion in such a grouping is held much more stronger. This phenomenon testifies about the existence of more acid compositions in this interval, namely the compositions containing the sixcoordinated germanium $[\text{GeO}_{6/2}]^{2-}$. Authors of a number of works used other methods of investigation and also mentioned the existence of the sixcoordinated germanium $[\text{GeO}_{6/2}]^{2-}$ in this concentrational region [108-110]. The dissociation of this composition at the break-off of the charged O^{2-} ion is hampered at a sacrifice in a stronger interaction of $[\text{GeO}_{6/2}]^{2-}$ with oxygen ions.

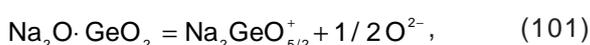
Let us consider the $\text{Na}_2\text{O}-\text{GeO}_2$ system. According to the work [86] in the melt of this system there are the structure-chemical groupings of $2\text{Na}_2\text{O} \cdot 9\text{GeO}_2$ and $\text{Na}_2\text{O} \cdot \text{GeO}_2$. According to this work and the phase diagrams [20] the set of dissociation equilibria and their equilibrium constants is:



Table 10. Dissociation constant of oxides and structure-chemical groupings of in alkali-germanate melts.

Oxide, struct.-chem. groupings	K	Oxide, struct.-chem. groupings	K
$Li_2O \cdot 7GeO_2$	$1.19 \cdot 10^{-11}$	$K_2O \cdot 4GeO_2$	$11.8 \cdot 10^{-11}$
$Li_2O \cdot 4GeO_2$	$2.31 \cdot 10^{-11}$	$Li_2O \cdot GeO_2$	$22.3 \cdot 10^{-11}$
GeO_2	$3.26 \cdot 10^{-11}$	$Na_2O \cdot GeO_2$	$62 \cdot 10^{-11}$
$K_2O \cdot 7GeO_2$	$4.1 \cdot 10^{-11}$	$K_2O \cdot 2GeO_2$	$98 \cdot 10^{-11}$
$2Na_2O \cdot 9GeO_2$	$6.49 \cdot 10^{-11}$	$K_2O \cdot GeO_2$	$5298 \cdot 10^{-11}$

$$K_{2Na_2O \cdot 9GeO_2} = \frac{X_{Na_4Ge_9O_{19/2}} \cdot X_{O^{2-}}^{1/2}}{X_{2Na_2O \cdot 9GeO_2}}, \quad (100)$$



$$K_{Na_2O \cdot GeO_2} = \frac{X_{Na_2GeO_{5/2}} \cdot X_{O^{2-}}^{1/2}}{X_{Na_2O \cdot GeO_2}}, \quad (102)$$



$$K_{Na_2O} = \frac{X_{Na^+}^2 \cdot X_{O^{2-}}}{X_{Na_2O}}. \quad (104)$$

The dissociation equation of germanium oxide and its equilibrium constant are similar to (89) and (90). Then the equation of charge conservation for the sodium germanate system is:

$$2X_{O^{2-}} = X_{GeO_{3/2}} + X_{Na_4Ge_9O_{19/2}} + X_{Na_2GeO_{5/2}} + X_{Na^+}. \quad (105)$$

The solution of the equation system and the calculation of dissociation constants were carried out by the same procedure as for the lithium germanate system. Table 10 shows the values of the dissociation constants of the structure-chemical groupings existing in this system. The results of comparing the experimental and calculated dependencies of pO are given in Fig. 20.

The authors of the work [86] did not take into consideration the possibility of the existence of the composition $2Na_2O-GeO_2$ in the melt. The calculation was carried out without this compound, that is why one can observe some deviations of the calculated values of pO from the experimental ones.

When considering the dissociation constants of the structure-chemical groupings of the sodium germanate system, one can see that the formation of sixcoordinated germanium does not give rise to an appreciable decrease in the dissociation con-

stants of these groupings in comparison with the lithium germanate system. The region after 30-35 mol. % of sodium oxide is characterized by a sharp increase in basicity, by 9 times. It can be explained by the fact that in this region a detectable decrease in the concentration of groupings contained the sixcoordinated germanium occurs. It is in good agreement with the data of [109-113].

Let us consider the potassium germanate system. In the literature there is not any information about the chemical structure of this system, namely, the data about the structural-chemical groupings in melt. The thorough calculation of these groupings is shown below.

To simulate the chemical structure of potassium germanate melts, namely to estimate the quanti-

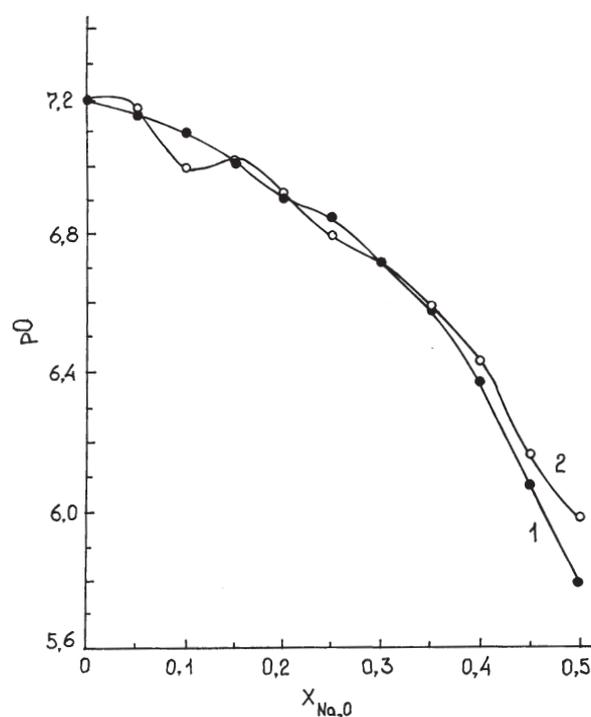


Fig. 20. Comparison of experimental (1) and simulated on model 2 (2) dependencies of the pO on the composition of the melts for the Na_2O-GeO_2 system.

ties of different structure-chemical groupings, the theory of the ideal associated solutions was used. The procedure of composing a set of equations linking the mole parts of structure components was described in [94]. According to the model the melts are considered to be the ideal solutions involving the structure-chemical groupings which are formed in the system from the initial oxides and are thermodynamically stable by the phase diagrams and also the remains of unreacted initial oxides. A set of equations is made. The set links the quantity of moles of the formed compounds (n_i) and the unreacted initial oxides from the law of mass action and the equations of material balance. The parameters linking the quantity of structure-chemical groupings are the constants of formation reactions of the i^{th} composition from oxides which were determined experimentally.

To simulate the chemical structure of potassium germanate melts in the interval from 0 to 50 mol. % of alkali oxide at 950 °C the following compositions are taken into consideration: $\text{K}_2\text{O}\cdot 7\text{GeO}_2$ (1:7), $\text{K}_2\text{O}\cdot 4\text{GeO}_2$ (1:4), $\text{K}_2\text{O}\cdot 2\text{GeO}_2$ (1:2), $\text{K}_2\text{O}\cdot \text{GeO}_2$ (1:1). We have the following set of equations:

$$\left\{ \begin{array}{l} K_{1:1} = \frac{n_{1:1}}{a_{\text{K}_2\text{O}} n_{\text{GeO}_2}} = 1.3792 \cdot 10^{13} \\ K_{1:2} = \frac{n_{1:2} \left(\sum_i n_i \right)^2}{a_{\text{K}_2\text{O}} n_{\text{GeO}_2}^2} = 2.2277 \cdot 10^{14} \\ K_{1:4} = \frac{n_{1:4} \left(\sum_i n_i \right)^3}{a_{\text{K}_2\text{O}} n_{\text{GeO}_2}^4} = 4.103 \cdot 10^{15} \\ K_{1:7} = \frac{n_{1:7} \left(\sum_i n_i \right)^6}{a_{\text{K}_2\text{O}} n_{\text{GeO}_2}^7} = 5.35 \cdot 10^{16} \\ x_i = \frac{n_i}{\sum_i n_i} \\ x_{\text{K}_2\text{O}}^* = n_{1:1} + n_{1:2} + n_{1:4} + n_{1:7} + n_{\text{K}_2\text{O}} \\ x_{\text{GeO}_2}^* = n_{1:1} + 2n_{1:2} + 4n_{1:4} + 7n_{1:7} + n_{\text{GeO}_2} \end{array} \right. \quad (106)$$

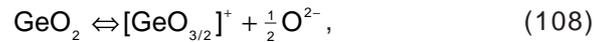
where X^* is the gross mole part of oxide. The initial values of K_p were calculated from the experimental values of Gibbs's potential by the following equation:

$$K_p = \exp\left(-\frac{\Delta G^\circ}{RT}\right). \quad (107)$$

Then the difference between the calculated and experimental values of chemical potential of potassium oxide was minimized up to 10^{-10} . The chemical structure for the $\text{K}_2\text{O}\text{-GeO}_2$ system (the distribution of structure-chemical groupings) is shown in Fig. 21.

For the potassium germanate system the extent of the composition region where the melt structure is determined by the compositions involving the sixcoordinated germanium is up to 27 mol.% of alkali oxide. After that the structures of bigermanate and methagermanate begin to prevail.

So, to calculate the pO values after the second way we accept that in this system there are the following stoichiometric compositions of compounds: $\text{K}_2\text{O}\cdot 7\text{GeO}_2$, $\text{K}_2\text{O}\cdot 4\text{GeO}_2$, $\text{K}_2\text{O}\cdot 2\text{GeO}_2$, $\text{K}_2\text{O}\cdot \text{GeO}_2$ and also the unreacted parts of initial components: K_2O and GeO_2 . The dissociation equation of germanium oxide and its equilibrium constant are similar to (89) and (90). All the other dissociation equilibria taking part in the system and their equilibrium constants are:



$$K_{\text{GeO}_2} = \frac{x_{\text{GeO}_{3/2}^+} \cdot x_{\text{O}^{2-}}^{1/2}}{x_{\text{GeO}_2}}, \quad (109)$$

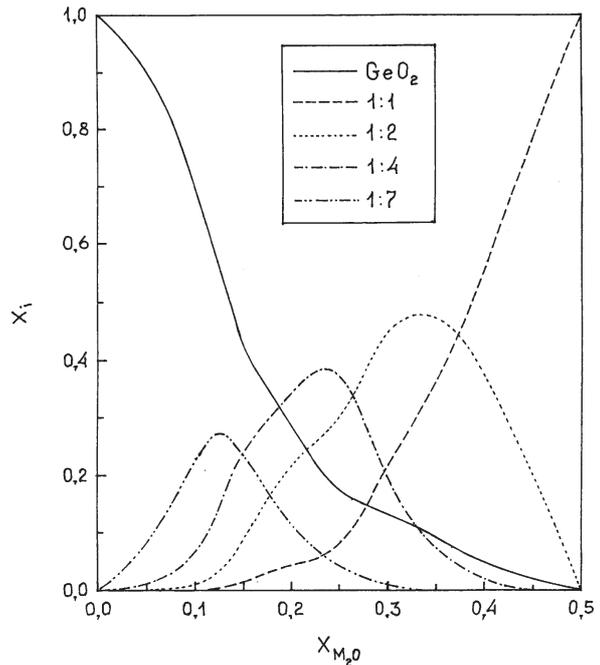
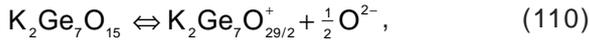
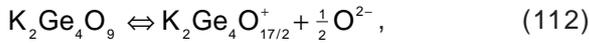


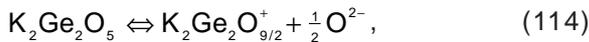
Fig. 21. Chemical structure of the melts for the $\text{K}_2\text{O}\text{-GeO}_2$ system.



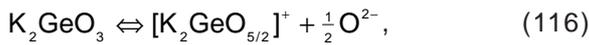
$$K_{K_2Ge_7O_{15}} = \frac{X_{K_2Ge_7O_{29/2}^+} \cdot X_{O^{2-}}^{1/2}}{X_{K_2O \cdot 7 GeO_2}}, \quad (111)$$



$$K_{K_2Ge_4O_9} = \frac{X_{K_2Ge_4O_{17/2}^+} \cdot X_{O^{2-}}^{1/2}}{X_{K_2O \cdot 4 GeO_2}}, \quad (113)$$



$$K_{K_2Ge_2O_5} = \frac{X_{K_2Ge_2O_{9/2}^+} \cdot X_{O^{2-}}^{1/2}}{X_{K_2O \cdot 2 GeO_2}}, \quad (115)$$



$$K_{K_2GeO_3} = \frac{X_{K_2GeO_{5/2}^+} \cdot X_{O^{2-}}^{1/2}}{X_{K_2O \cdot GeO_2}}, \quad (117)$$



$$K_{K_2O} = \frac{X_{K^+}^2 \cdot X_{O^{2-}}}{X_{K_2O}}. \quad (129)$$

Then the equation of charge conservation for the potassium germanate system is:

$$2X_{O^{2-}} = X_{GeO_{3/2}^+} + X_{K_2Ge_7O_{29/2}^+} + X_{K_2Ge_4O_{17/2}^+} + X_{K_2Ge_2O_{9/2}^+} + X_{K_2GeO_{5/2}^+} + X_{K^+}. \quad (116)$$

The solution of this set of equations and the acquisition of dissociation constants of structural groupings in melt were carried out numerically with the procedure akin to that used for the lithium germanate and sodium germanate systems. Fig. 22 shows the results of comparing the experimental and calculated dependencies of pO for the potassium germanate system. Table 10 shows the values of the dissociation constants of the structure-chemical groupings existing in the system.

In the region with high contents of potassium oxide minor deviations of the calculated data from the experimental ones are observed. It is possible

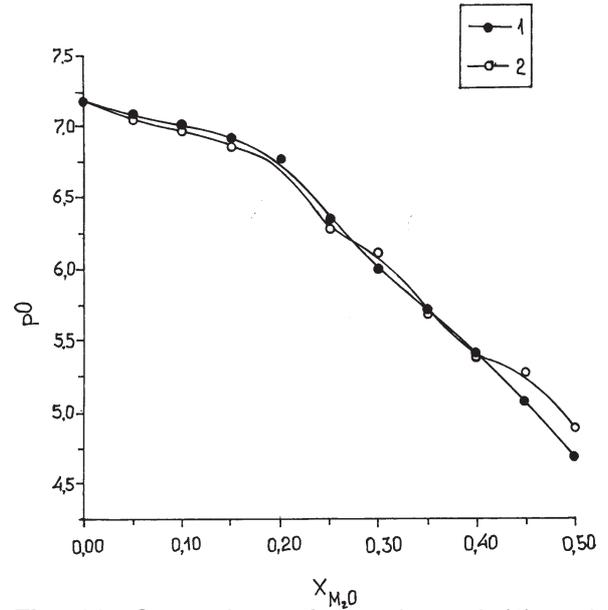


Fig. 22. Comparison of experimental (1) and simulated on model 2 (2) dependencies of the pO on the composition of the melts for the K_2O-GeO_2 system

to suppose the existence of a composition or some compositions in this region which we have not taken into consideration.

At the examination the dissociation constants of structure-chemical groupings of the potassium germanate system one can see that the influence of the sixcoordinated germanium on the basicity of melt is less detectable than for the sodium germanate and lithium germanate. The basicity of potassium germanate melt containing more than 25-30 mol. % of alkali oxide changes sharply.

6. CONCLUSIONS

The development of acid-base notions in apply to the oxide melts allowed to state the unified acid-base conception. This conception suggests that in the melt the dissociation processes with the detachment of O^{2-} ions take place. This conception describes adequately the change in acid-base characteristics of oxide systems with the composition change and can be used for a great number of oxide melts. This unified acid-base conception for the oxide melts describes quite well the change in acid-base characteristics of oxide melts in pO terms. Along with it there is not any serious contradictions with such ways of estimation of the acid-base properties of oxide melts as electronegativity, formation enthalpy and activity of alkali oxide. The theory is enough universal. However it is restricted by the structure chemical views about the dissociation pro-

cesses of structural groupings akin to the crystals with the same chemical compositions. Also it does not touch the polymerisation processes of these groupings with the formation of electroneutral or charged associates. That gives the way to the further development of the acid-base conception in apply to the melts of oxide systems.

The creation of the monitoring method of oxide melts is principally important. The EMF method is the base to determine and normalize the pO indexes. It can be used within the wide range of temperatures and for the systems of different chemical nature. This method has shown the significance and reliability of the obtained results. The solution of this problem was achieved by the close selection and investigation of physico-chemical properties of the first standard and the set of second ones with the methods of EMF, calorimetry of solution, quantitative X-ray analysis, differential scanning and chemical analysis. The scientific groundworks for the investigation method and normalization of pO have opened prospects to investigate a great number of oxide systems including not only the oxides of boron, germanium, tungsten and molybdenum, but oxides of tantalum, niobium and titanium as well. The efficiency of the method is shown in the present paper by the example of the melts of M_2O-GeO_2 systems (M=Li, Na, K).

The physico-chemical aspects of the method development and the normalization of pO -scale in oxide melts have been worked up quite well to go over to the next stage, which is the state procedure of pO normalizing and measuring. This stage is connected not only with the solution of chemical problems, but with some engineering decisions on evolution of the technologically applied electrode pair as well.

The field of application stretches over the glass manufacturing, ferrous and nonferrous metallurgy and also, withing certain limits, the cement production. Using the pO monitoring in oxide melts will allow to do a technological breaking through which can be compared only with the effect of pH -scale creation for the aqueous solutions.

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