Advantages of the pO-index Method to Estimate the Acid-Base Properties of Oxide Materials

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The following parameters can be commonly used as the measure of acid-base properties of oxide materials: 1) the electronegativity of the elements formed oxides, 2) the formation enthalpy from oxides at 298K, 3) the activity of alkali oxide in melts, and, at last, 4) the most universal parameter that characterizes the basicity of oxide melts, pO. The methodical investigations carried out were focused on developing a method of normalizing the activity of oxygen ions in oxide melts, to get the universal index to be used to define their acid-base properties. In the oxide systems all the processes carry out with the participation of oxygen ions, O^{2-}, which is considered to be the carrier of the base properties of melt. As this takes place, pO **= -** $\lg a_{O^{2-}}$.

By the general theory of acid-base properties of oxide melts [1], at the dissociation of any oxygen-containing composition there takes place a breaking or an attachment of ½ mol of oxygen ions, O^{2-}, according to the following reaction:

$$M_nR_mO_k = M_nR_mO_{k-1} + \frac{1}{2}O^{2-}$$
$$K = \frac{a_{M_nR_mO_{k-1}} \cdot a_{O^{2-}}^{1/2}}{a_{M_nR_mO_k}} \qquad (1)$$

With such an approach one can estimate the acid-base properties of oxide melts and give predictions on the behaviour of materials at their cooperative uses.

The first challenge of this work was how the cation basicity influences the summary basicity of melt, by Li_2O-GeO_2, Na_2O-GeO_2, K_2O-GeO_2 systems. The other was devoted to the anion influence to the summary basicity of melt, by of Na_2O-B_2O_3, Na_2O-SiO_2, Na_2O-GeO_2 systems. Then the comparison of different approaches to the estimation of the acid-base properties of binary melts was made.

The pO values were determined by the available procedure on the basis of EMF method [2]. Figure 1 shows that the increase in the alkali oxide contents gives rise

to the increase in the basicity of melts of equimolar compositions. The basicity of melts increases (and pO, decreases) in the order: $pO_{Li2O}<pO_{Na2O}<pO_{K2O}$.

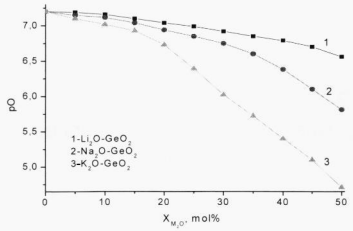

Figure 1. pO dependences, T=950°C.

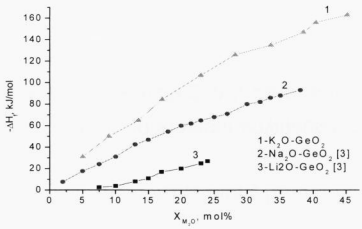

Figure 2. Formation enthalpy dependences.

Figure 2 shows that the increase in alkali oxide concentration gives rise to the energy effects: $\Delta H_{fLi2O}<\Delta H_{fNa2O}<\Delta H_{fK2O}$, that means the higher the melt basicity the higher exothermic nature of the interaction in: Li_2O-GeO_2<Na_2O-GeO_2<K_2O-GeO_2.
Figure 3 shows the concentration dependences of chemical potentials of alkali oxide in the alkali germinate systems. The greatest interaction is observed in the melts of K_2O-GeO_2 (the lowest values of μ_{M2O}). The lower the μ_{M2O} value, the more basic the melt is. The more interaction between the oxides of binary system the more difference in the acid-base properties of oxides, which form it. The order of the basicity change is analogous to the one determined by the pO method.
Table 1 shows the values of electronegativity of the elements. There are some scales of electronegativity, but for our purposes the crystal one gives the best fit [6].

Table 1. Electronegativity of some elements.

Element	Li	Na	K	B	Si	Ge	O
Value of Electronegativity	0.6	0.5	0.45	1.7	1.6	1.7	3.2

Having compared the concentration dependences of the formation enthalpies, the potentials of alkali oxides and pO, one can see that their relative positions coincide. So in the event that if the difference in the acid-base properties of the oxides formed the system is high, one can use any way of estimation of their acid-base properties: in terms of pO, by the chemical potential of oxide, or by the formation enthalpy from oxides. However, it should be realized that such a comparison is quite qualitative.

The concentration dependences of pO for Na_2O-B_2O_3, Na_2O-SiO_2 and Na_2O-GeO_2 systems are given in figure 4. The general run of the curves is analogous to the one of Li_2O-B_2O_3, Li_2O-SiO_2, Li_2O-GeO_2 systems [10], but the concentration dependence of pO could be divided into some regions.

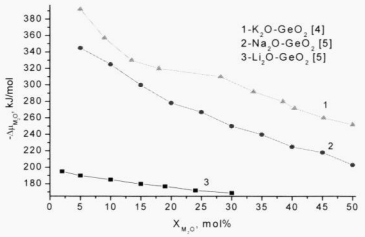

Figure 3. Chemical potentials of alkali oxides for germanate systems.

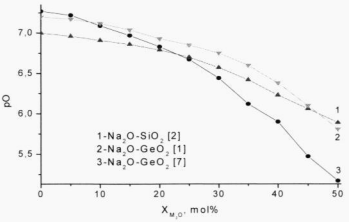

Figure 4. pO dependences, T=950°C.

Region I: 0-8 mol% Na_2O. The position of curves is determined generally by the basicity of glass forming oxides. The basicity of the glass forming oxides, SiO_2, GeO_2 and B_2O_3, decreases from silica to boron oxide [11]. The structure chemical groupings with the higher coordination number of the element of glass forming oxide begin forming. These are: 4 for boron [12] and 6 for germanium [13].

Region II: ≈8 mol% Na_2O, the "equibasic" point for Na_2O-B_2O_3 and Na_2O-GeO_2. The dissociation constants of structure chemical groupings of these melts are equal, it says about the quantitative closeness of their "dissociation" state. The acid-base properties of these two melts are equal.

Region III: 8-22.5 mol% Na_2O. pO are arranged as: Na_2O-GeO_2<Na_2O-B_2O_3<Na_2O-SiO_2. The structure chemical groupings containing four-coordinated boron cease to influence remarkably to the basicity of sodium boron melts.

Region IV: ≈22.5 mol% Na_2O, the "equibasic" point for Na_2O-B_2O_3 and Na_2O-SiO_2.

Region V: 22-47.5 mol% Na_2O. The basicities are arranged as: Na_2O-GeO_2<Na_2O-SiO_2<Na_2O-B_2O_3.

Region VI: ≈47.5 mol% Na_2O, the "equibasic" point for Na_2O-GeO_2 and Na_2O-SiO_2.

Region VII: >47.5 mol% Na_2O. pO are arranged as: Na_2O-SiO_2<Na_2O-GeO_2<Na_2O-B_2O_3. pO is determined by their dissociation with breaking of ionised oxygen.

Figures 5 and 6 show that the increase in alkali oxide increases the energy effects, but the order of the curve positions is the same.

So the comparison of acid-base properties determined in different terms showed that the pO-index is considered to be the most universal.

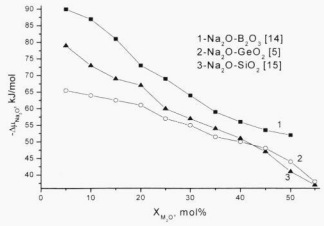

Figure 5. Concentration dependences of chemical potentials.

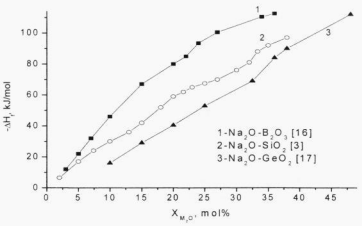

Figure 6. Formation enthalpy dependences.

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