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Thermodynamic Properties of the System $MgO–B_2O_3$ Melts

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Abstract—Vaporization processes of melts of the system $MgO–B_2O_3$ at 1640 K were studied by high-temperature mass spectrometry, and thermodynamic properties (activity, chemical potentials of MgO and B_2O_3, and also the corresponding excess values) were determined. Considerable negative deviations from the ideal behavior in the melts of the studied system are observed. The termodynamic properties of the system $MgO–B_2O_3$ can be calculated within the framework of the lattice theory of associated solutions.

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Magnesium and boron oxides play the major role in manufacturing special-purpose glasses [1]. The addition of magnesium oxide to glasses reduces their melting point and propensity to crystallization and raises surface tension and a linear expansion coefficient. Boron oxide is widely applied to the production of various glasses, such as chemically and thermally resistant, medical, optical, and glasses for electricalproducts, glasses for chemical laboratories and for protection against X rays, and also for atomic technique.

Thermodynamic properties of melts of the systems $CaO–B_2O_3$, $SrO–B_2O_3$, and $BaO–B_2O_3$ have been studied earlier by the method of high-temperature mass spectrometry [2, 3]. Melts of these systems are characterized by significant negative deviations from the ideal behavior, which are probably caused by the presence of thermally stable compounds in a condensed phase. Thermodynamic properties of the system $MgO–B_2O_3$ were not studied earlier. According to the phase diagram of the system $MgO–B_2O_3$ [4], in a condensed phase there are three thermally stable compounds: $3MgO·B_2O_3$, $2MgO·B_2O_3$, and $MgO·B_2O_3$. First two compounds melt congruently at 1638 and 1613 K, respectively, and $MgO·B_2O_3$ dissociates into $2MgO·B_2O_3$ and a liquid in the temperature range of 988–1415 K. At a mole ratio $[MgO]:[B_2O_3] = 1$ the region of homogeneous melt lies above 1415 K.

According to the data systematized in [5], volatilities of individual MgO and B_2O_3 oxides considerably differ. Under neutral vaporization conditions boron oxide starting from ~1300 K is vaporized congruently without decomposition. When vaporized from a molybdenum or tungsten cell (weakly reducing vaporization conditions) boron oxide is not reduced to lower oxides. Magnesium oxide starts to pass in vapor at temperatures above 1800 K, practically completely dissociating into monoatomic metal and oxygen. The content of MgO in vapor does not exceed 2% of the monoatomic magnesium concentration. Under weakly reducing vaporization conditions the degree of magnesium oxide dissociation increases, and the temperature of its passing in vapor decreases [6]. Oxygen is bound into volatile molybdenum and tungsten oxides, which, in turn, form gaseous magnesium molybdates or tungstates [6].

The vaporization products in the system $MgO–B_2O_3$ (94 mol % of magnesium oxide) were investigated by high-temperature mass spectrometry in [7]. In this region of the phase diagram a liquid and individual magnesium oxide [4] coexist. In the mass spectra of the vapor the ions Mg^+, $B_2O_3^+$, $MgBO_2^+$, and $MgB_2O_4^+$ were identified. Measured appearance energies of the ions are 7.6, 14.0, 8.4, and 12.0 eV, respectively. It is probable that all the ions are products of the direct ionization of corresponding molecules [4]. The curve of the effectiveness of $MgBO_2^+$ ionization contains a break assigned to the dissociative MgB_2O_4 ionization (1).

$$MgB_2O_4 + e^- = MgBO_2^+ + BO_2 + 2e^-. \quad (1)$$

Measuring of equilibrium constants of reactions (2) and (3) has allowed us the calculation of the standard

enthalpies of formation of gaseous MgB_2O_4 and $MgBO_2$ (at 0 K: –1305.4±16.7 and –502±12.6 kJ mol^{-1}, respectively).

$$MgO(cr.) + B_2O_3(gas) = MgB_2O_4(gas), \quad (2)$$

$$1/2\ MgO(cr.) + 1/2\ B_2O_3(gas) + 1/2\ Mg(gas) = MgBO_2(gas). \quad (3)$$

Activities of the melt components in the system $MgO–B_2O_3$ were determined at 1640 K. At higher temperatures the preferential evaporation of boron oxide and magnesium borate MgB_2O_4 from melts of this system was observed, whereas the condensed phase became enriched with magnesium oxide. According to the phase diagram [4], the homogeneous melt region in the system $MgO–B_2O_3$ at 1640–1700 K lies in the concentration range from 25 up to 50 mol % of B_2O_3. As well as in the case of studying vapor formation and thermodynamic properties of the systems $CaO–B_2O_3$ [2], $SrO–B_2O_3$, and $BaO–B_2O_3$ [3], in the determination of thermodynamic activity of boron oxide we used pure boron oxide as the standard, which was loaded into one of cells of a twinned single-temperature effusion chamber. Compositions of the studied melts are given in the table.

In the mass spectra of vapor above samples of the system $MgO–B_2O_3$, starting from ~1370 K, the ions $B_2O_3^+$ were observed. The intensity of the $B_2O_3^+$ ionic current increased with temperature, and ionic currents of $MgBO_2^+$ and $MgB_2O_4^+$ were detected in the vapor mass spectrum starting from 1590 K. In the 1400–1600 K range we were able to measure only the appearance energy of the $B_2O_3^+$ ion (14.0 eV). The ionic currents of $MgBO_2^+$ and $MgB_2O_4^+$ were so small that we could not measure their appearance energies at 1590 K. As temperature was increased further, the ratio of $MgBO_2^+$ and $MgB_2O_4^+$ ionic currents gradually varied in the direction of the relative rise of the $MgBO_2^+$ intensity. At a temperature above 1800 K peaks of the ions Mg^+, BO^+, and BO_2^+ with appearance energies equal to the ionization energies of the corresponding molecules [8] appeared in the mass spectra of vapor above the system $MgO–B_2O_3$ melts. We were able to estimate the energies of appearance of the ions $MgBO_2^+$ and $MgB_2O_4^+$ at these temperatures accurate to ±0.7 eV: $MgBO_2^+$ 8.1 and $MgB_2O_4^+$ 11.7 eV.

An examination of the mass spectra of vapor above samples of the system $MgO–B_2O_3$ has shown that $B_2O_3^+$ ions represent a product of the direct ionization of B_2O_3 molecules, as the appearance energy of the ion $B_2O_3^+$ (14 eV) corresponds to the ionization energy of boron oxide [8]. The nature of MBO_2^+ ions (M = Ca, Sr, Ba) was considered in detail in [9–11], where it was shown that at ~1500 K this ion is a product of the dissociative ionization of molecules [see scheme (1)].

At higher temperatures and in the case when the condensed phase composition approaches that of a pure oxide of alkaline-earth metal, MBO_2^+ ions are formed not only by the dissociative ionization of MB_2O_4 molecules, but also as a result of the direct ionization of MBO_2 molecules [Eq. (4)].

$$MBO_2 + e^- = MBO_2^+ + 2e^-. \quad (4)$$

It is evidenced by the inflection of the ionization effectiveness curves and by a significant decrease in the appearance energy of the ion MBO_2^+. At tempera-

Activities, chemical potentials, excess chemical potential of MgO and B_2O_3, Gibbs energies, and excess Gibbs energies in melts of the system $MgO–B_2O_3$ at 1640 K found in the present work by the method of high-temperature mass spectrometry and calculated on the basis of generalized lattice theory of associated solutions

x(MgO), mole fraction	a_i, exp.		$-\Delta\mu_i$, kJ mol^{-1}, exp.		$-\Delta\mu_i^E$, kJ mol^{-1}				$-\Delta G_i$, kJ mol^{-1}, exp.	$-\Delta G_i^E$, kJ mol^{-1}	
					MgO		B_2O_3				
	MgO	B_2O_3	MgO	B_2O_3	experiment	calculation	experiment	calculation		experiment	calculation
0.50	0.10	0.104	31.0	30.9	21.5	23.7	21.4	19.1	30.9	21.5	21.4
0.60	0.21	0.044	21.2	42.6	14.3	13.6	29.9	30.8	29.6	20.4	20.5
0.667	0.29	0.026	17.1	49.8	11.6	8.5	34.6	39.6	27.9	19.2	18.6
0.70	0.31	0.022	16.0	52.0	11.2	6.5	35.6	43.2	26.8	18.5	17.5
0.75	0.40	0.006	12.6	70.7	8.7	4.1	43.5	49.1	25.1	17.4	15.4

tures above 2000 K the vapor contains only MBO_2 molecules with low appearance energies. The examination of the mass spectra of vapor above samples of the $MgO–B_2O_3$ system suggests that at 1590 K, in addition to B_2O_3, the vapor contains MgB_2O_4 molecules forming the $MgBO_2^+$ and $MgB_2O_4^+$ ions on ionization. On further vaporization (as the composition of the condensed phase approaches MgO) the ratio of $MgBO_2^+$ and $MgB_2O_4^+$ ionic currents varies. It is caused by the appearance of $MgBO_2$ molecules in the vapor. It is rather difficult to separate ionic currents of $MgBO_2^+$ of various origin (MgB_2O_4 and $MgBO_2$). In practice we acted as follows: the ratio of intensities of $MgBO_2^+$ and $MgB_2O_4^+$ ionic currents recorded at 1590 K was assigned to the individual mass spectrum of the MgB_2O_4 molecule and further we took it into account when separating components of the $MgBO_2^+$ ionic current. At temperatures above 1800 K the vapor above melts of the system $MgO–B_2O_3$ contains also the BO and BO_2 molecules and monoatomic magnesium. Magnesium oxide was detected in the vapor above the melts under study at temperatures above 2100 K.

We have determined the activity of B_2O_3 in the melts of the system $MgO–B_2O_3$ using pure boron oxide as the activity standard. Unfortunately, it is impossible to act similarly for the determination of the magnesium oxide activity, as the pure magnesium oxide starts to pass in vapor at higher temperatures. It would be possible to apply the Belton–Fruechan method [12] for the determination of activities of the condensed phase components, however for this purpose it is necessary to measure intensities of the $B_2O_3^+$, $MgBO_2^+$, and $MgB_2O_4^+$ ionic currents with a high degree of accuracy. As to the ionic current of $B_2O_3^+$, its value is sufficiently high and can be measured correctly with an insignificant error. Ionic currents of $MgBO_2^+$ and $MgB_2O_4^+$ are rather low at ~1600 K and therefore they are measured with a high relative error, which affects the reliability of the results obtained. At higher temperatures the intensities of $MgBO_2^+$ and $MgB_2O_4^+$ ionic currents are measured much more precisely, but in this case the condensed phase is fast depleted of volatile boron oxide. In this connection the activity of magnesium oxide in the samples under study at 1640 K was calculated by the Gibbs–Duhem equation (5).

$$\log \frac{a(\mathrm{MgO})}{x(\mathrm{MgO})} = -\int_{x(\mathrm{B_2O_3})=0}^{x(\mathrm{B_2O_3})=a(\mathrm{B_2O_3})} \frac{x(\mathrm{B_2O_3})}{x(\mathrm{MgO})}\, d\log \frac{a(\mathrm{B_2O_3})}{x(\mathrm{B_2O_3})}, \quad (5)$$

where a_i is the activity and x_i is the concentration of an oxide in melt. The results of the determination of the activities of components in the melts of the system $MgO–B_2O_3$ at 1640 K are given in the table. Dependences on the mole fraction of magnesium oxide of the activities of the melt components and of Gibbs energy and excess Gibbs energy changes in the melts of the system $MgO–B_2O_3$ at 1640 K are presented in Figs. 1 and 2, respectively.

Negative deviations from the ideal behavior are observed in the system $MgO–B_2O_3$ in the homogeneous melt region. The melt with the ratio [MgO]: $[B_2O_3]$ = 1:1 corresponding to the compound MgB_2O_4 shows the greatest deviation.

For comparison the dependences of integral Gibbs energies on the mole fractions of an alkaline-earth metal oxide in melts of the systems $MO–B_2O_3$ (M = Mg, Ca, Sr, Ba) are given in Fig. 3. Maximal deviations of Gibbs energy values from ideality in all cases are observed for melts with compositions corresponding to MB_2O_4 compounds. The degree of deviations from ideality in the melts of $MO–B_2O_3$ systems and hence the thermal stability increase with increasing difference in acid–base properties of MO and B_2O_3. A similar behavior was observed in binary silicate systems where oxides of alkaline-earth metals acted as modifying oxides [13].

To describe thermodynamic properties of melts of oxide systems we can apply the methods of generalized lattice theory of associated solutions (GLTAS) [14, 15]. The above-given experimental

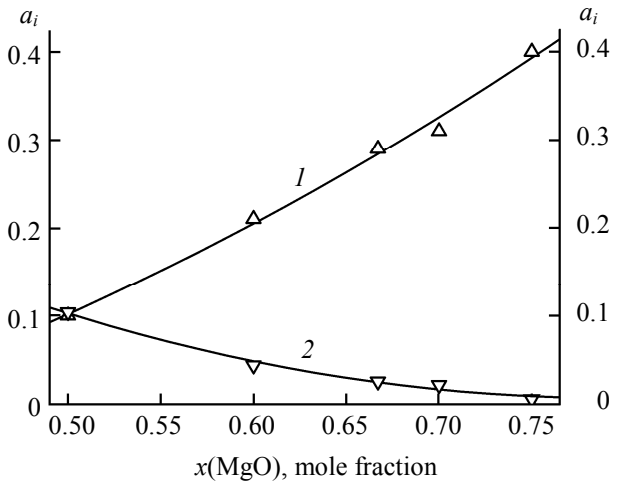

Fig. 1. Dependences of activities of components on the melt composition in the system $MgO–B_2O_3$ at 1640 K. (*1*) MgO and (*2*) B_2O_3.

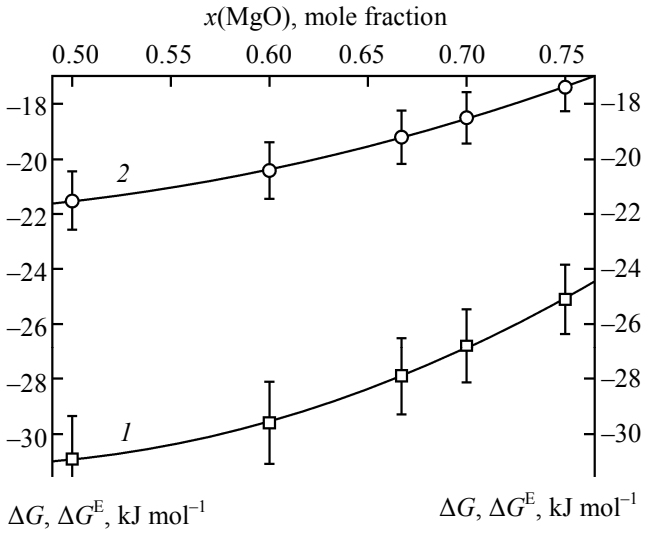

Fig. 2. Dependences of (*1*) integral Gibbs energy and (*2*) excess Gibbs energy on the melt composition in the system $MgO–B_2O_3$ at 1640 K.

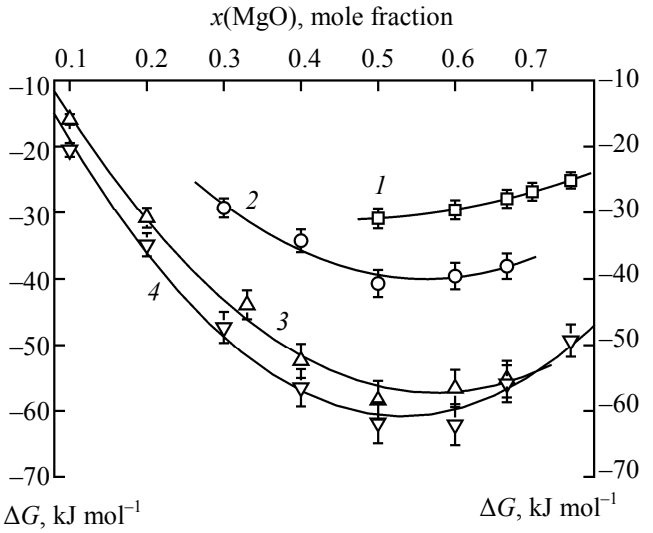

Fig. 3. Dependences of integral Gibbs energy on the melt composition in $M–B_2O_3$ systems [M: (*1*) Mg, (*2*) Ca, (*3*) Sr, and (*4*) Ba].

data, in particular the excess chemical potentials of components (see the table), allow the estimation of energies of intermolecular interaction and to calculate relative numbers of various bonds between structural elements in melts of the system $MgO–B_2O_3$. For this purpose we used the version of Barker's theory [16, 17] with temperature-dependent energy parameters, which had been considered in detail in [18].

To carry out the calculation, it is necessary to select a certain model reflecting as near as possible the real structure of the melt, namely, structural elements ("molecules") of the melt and of the corresponding space lattice. Parameters of the model have been chosen in view of available data on borate glasses [19] and crystalline magnesium pyroborate [20].

We took MgO and B_2O_3 as structural elements, the lattice coordination number z was taken to be 3, the numbers r of the lattice sites occupied by structural elements [r(MgO) = 1 and $r(B_2O)$ = 2] corresponded to the values of molar volumes of pure oxides. The chosen values of z and r are connected [16] with the number c of contact points of a molecule by the relation $c = (z - 2)r + 2$, from which it follows that three contact points should be chosen on the MgO surface and four points, on the B_2O_3 surface. According to the common formalism, they are divided into classes of equivalent points: two contact points of the MgO structural elements are assigned to the Mg atom (they are designated further by the index Mg–) and one point, to the oxygen atom (Mg–O–); two contact points of the B_2O_3 structural elements are assigned to boron atoms (B–) and two points, to oxygen atoms (B–O–). The chosen parameters are explained in the Fig. 4.

A pair of contact points of molecules a and b from classes i and k are characterized by the intermolecular interaction, to which a free energy U_{ik}^{ab} of interchange corresponds. It determines the energy parameter of the theory $\eta_{ik} = \exp(-U_{ik}^{ab}/RT)$. All further results of the theory are based on the solutions of a set of equations connecting energy parameters η_{ik}, concentrations of components x, numbers of contact points of each class Q, and unknowns X_i^a corresponding to the coefficients defining a fraction of contact sections of the ith class of structural elements a taking part in the specified interaction mode. Thus, for the system $MgO–B_2O_3$ the set of Eqs. (6) can be formulated.

$$X_{Mg–O–}(X_{Mg–O–} + \eta_{B–O–[Mg]}X_{Mg–} + X_{B–O–} + \eta_{B–O–[B]}X_{B–}) = 1/2Q_{Mg–O}x_{MgO},$$

$$X_{Mg–}(\eta_{Mg–O–[Mg]}X_{Mg–O–} + X_{Mg–} + \eta_{Mg–O–[B]}X_{B–O–} + X_{B–}) = 1/2Q_{Mg–}x_{MgO},$$

$$X_{B–O–}(X_{Mg–O–} + \eta_{B–O–[Mg]}X_{Mg–} + X_{B–O–} + \eta_{B–O–[B]}X_{B–}) = 1/2Q_{B–O–}x_{B_2O_3},$$

$$X_{B–}(\eta_{B–O–[Mg]}X_{Mg–O–} + X_{Mg–} + \eta_{B–O–[B]}X_{B–O–} + X_{B–}) = 1/2Q_{B–}x_{B_2O_3}. \quad (6)$$

Subscripts designate classes of contact points described by the corresponding values, atoms of the second coordination sphere for bonds defining values

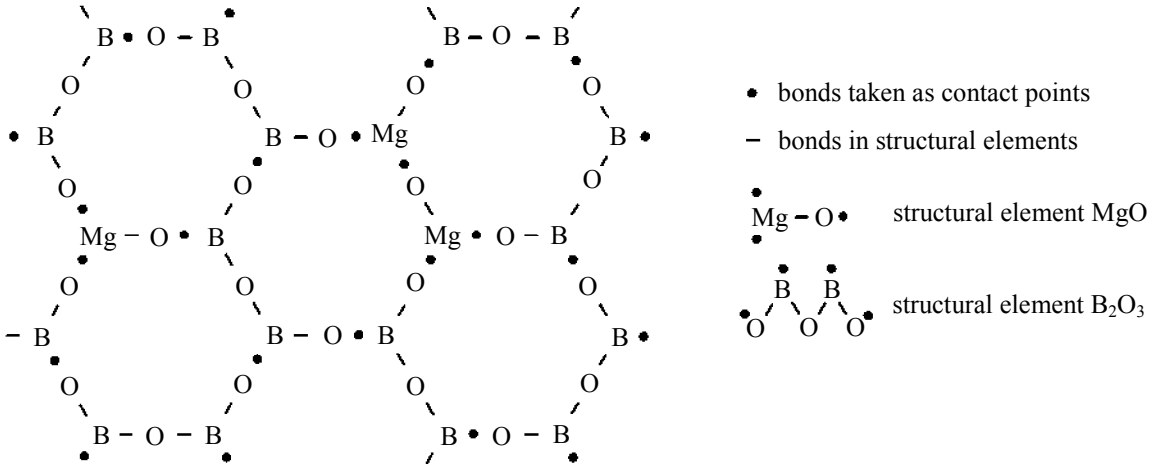

Fig. 4. Structural elements and contact points of the model lattice of melts of the MgO–B_2O_3 system used in calculations based on GLTAS.

of the specified energy parameters are shown in brackets. It is seen from the equations that four various energy parameters only for the bonds with bridging oxygen atoms are introduced in the calculations (Fig. 4), whereas the energies of remaining bonds are taken to be zero, and the corresponding η are equal to 1. The substitution of solutions into formulas (7), (8) yields values of excess chemical potential of components of the system with a specified composition [here x_{MgO} and $x_{B–O–}$ are concentration of components; $X_{Mg–O–}$, $X_{Mg–}$, $X_{B–O–}$, and $X_{B–}$ a solution of the set of Eq. (6) for the data x_{MgO} and x_{B_2O}; $X^0_{Mg–O–}$, X^0_{Mg} a solution of system (6) at $x_{MgO} = 1$; $X^0_{B–O–}$ and $X^0_{B–}$ a solution at $x_{B_2O} = 1$].

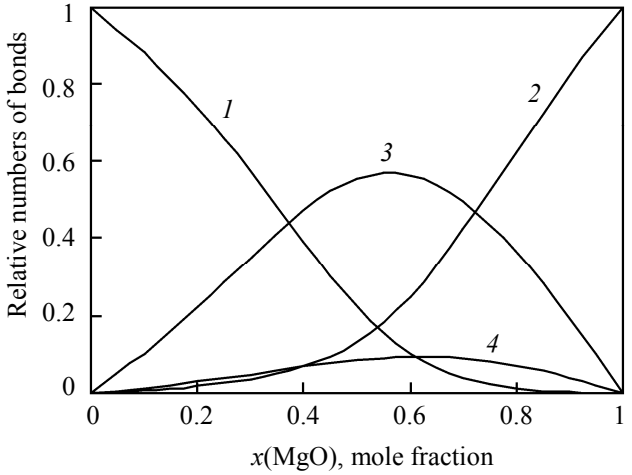

Fig. 5. Relative numbers of various bonds formed in melts of the MgO–B_2O_3 system at 1640 K: (*1*) B–O–[B], (*2*) Mg–O–[Mg], (*3*) B–O–[Mg], and (*4*) Mg–O–[B].

$$\Delta\mu^E_{MgO} = RT(Q_{B–O–}\ln(X_{Mg–O–}/x_{MgO}/X^0_{Mg–O–}) Q_{Mg–}\ln(X_{Mg–}/x_{MgO}/X^0_{Mg–}) + r_{MgO}(z/2-1)\ln[(r_{MgO}x_{MgO} + r_{B_2O_3}x_{B_2O_3})/r_{MgO}], \quad (7)$$

$$\Delta\mu^E_{B_2O_3} = RT(Q_{B–O–}\ln(X_{B–O–}/x_{B_2O_3}/X^0_{B–O–}) Q\ln(X_{B–}/x_{B_2O_3}/X^0_{B–}) + r_{B_2O_3}(z/2-1)\ln[(r_{MgO}x_{MgO} + r_{B_2O_3}x_{B_2O_3})/r_{B_2O_3}]. \quad (8)$$

Energies of intermolecular interaction in melt of the investigated system were taken to be unknown, therefore η_{ik} values were determined by successive approximations, i.e. by substitution of trial values of these parameters in the set of equations (6), calculation of excess chemical potential by formulas (7) and (8), and comparison of resulting dependences $\Delta\mu^E(x)$ with experimental dependences (see the table). The results of this adjustment are given in the table. The values of excess Gibbs energies were calculated by formula (9) (see the table).

$$\Delta G^E = x_{MgO}\Delta\mu^E_{MgO} + x_{B_2O_3}\Delta\mu^E_{B_2O_3}. \quad (9)$$

As there are no rigorous criteria for the adjustment of parameters, the approximation of experimental data by solving Eqs. (6)–(8) involves a certain ambiguity. A satisfactory correspondence of the experimental and theoretical values of excess chemical potential and Gibbs energies in melts of the MgO–B_2O_3 system proves correctness of the determination of energy parameters η_{ik}.

The estimate of the amount of various bonds forming in the melts under study is also of interest for the detection of the connection between the found values of thermodynamic properties and the structure of the MgO–B_2O_3 system melts. Within the limits of

GLTAS [18] the most probable number of bonds N_{ik} corresponding to a pair of contact points from classes i and k can be calculated by using expression (10), where N is a total number of molecules in the system.

$$N_{ik} = 2\,X_i\eta_{ik}X_kN. \quad (10)$$

It is possible to find expressions for relative numbers n of various bonds in melts of the $MgO–B_2O_3$ system from this equation. Being limited only by those pairs of contact points for which energy parameters are not equal to unity and having designated the total number of such pairs as ΣN_{ik}, we shall obtain expressions (11)–(14).

$$n_{Mg–O–[Mg]} = 2\,X_{Mg–O–}X_{Mg–}\eta_{Mg–O–[Mg]}N/\Sigma N_{ik}, \quad (11)$$

$$n_{Mg–O–[B]} = 2\,X_{Mg–O–}X_{B–}\eta_{Mg–O–[B]}N/\Sigma N_{ik}, \quad (12)$$

$$n_{B–O–[Mg]} = 2\,X_{B–O–}X_{Mg–}\eta_{B–O–[Mg]}N/\Sigma N_{ik}, \quad (13)$$

$$n_{B–O–[B]} = 2\,X_{B–O–}X_{B–}\eta_{B–O–[B]}N/\Sigma N_{ik}. \quad (14)$$

Here

$$\Sigma N_{ik} = 2\,N(X_{Mg–O–}X_{Mg–}\eta_{Mg–O–[Mg]} + X_{Mg–O–[B]} + X_{B–O–}X_{Mg–}\eta_{B–O–[Mg]} + X_{B–O–}X_{B–}\eta_{B–O–[B]}).$$

Concentration dependences of relative numbers of various bonds in melts of the $MgO–B_2O_3$ system are given in Fig. 5. It is obvious that the number of contact points of the structural element MgO only slightly corresponds to the structure of pure MgO, therefore at a high content of magnesium oxide Eq. (11) cannot adequately express the number of bonds in the melt.

EXPERIMENTAL

The work was fulfilled by the method of high-temperature mass spectrometry on an MS-1301 mass spectrometer at the energy of ionizing electrons of 25 V. Samples under study were vaporized from a twinned single-temperature molybdenum effusion cell heated by electron bombing. Temperature was measured by an EOP-66 optical pyrometer accurate to ±5 K in the temperature range of 1600–1750 K. The apparatus was preliminarily graduated by the CaF_2 vapor pressure [21]. To obtain samples of the system $MgO–B_2O_3$ under study, analytical-grade boric acid and special purity-grade magnesium carbonate were chosen as initial reagents. To prepare samples, we applied the standard procedure of multistage solid-phase synthesis with intermediate grindings.

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