ISSN 1070-3632, Russian Journal of General Chemistry, 2008, Vol. 78, No. 6, pp. 1139–1145. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © V.L. Stolyarova, S.I. Lopatin, S.M. Shugurov, 2008, published in Zhurnal Obshchei Khimii, 2008, Vol. 78, No. 6, pp. 912–918.

# Thermodynamic Properties of Melts of the System $CaO–B_2O_3$

**V. L. Stolyarova, S. I. Lopatin, and S. M. Shugurov**

*St. Petersburg State University, Universitetskii pr. 26, St. Petersburg, 198504 Russia*
*e-mail: svl@ipme.ru*

Received December 27, 2007

**Abstract**—Activities, chemical potentials, Gibbs energies, and also the corresponding excess values for CaO and $B_2O_3$ in the homogeneity region of melts of the $CaO–V_2O_3$ system at 1600 K were determined. These parameters were also calculated in terms of the generalized lattice theory of associated solutions. Considerable negative deviations from the ideal behavior are observed in the melts studied.

**DOI:** 10.1134/S1070363208060078

Information on the vaporization processes and thermodynamic properties of melts of the $CaO–B_2O_3$ system is necessary for optimizing compositions of multicomponent borosilicate glasses as matrices for dumping of radioactive waste in ecologically friendly technologies [1, 2].

The vaporization of the individual components of the $CaO–V_2O_3$ system has been repeatedly studied. The information on the vaporization processes and thermodynamic properties of calcium and boron oxides has been reviewed in [3]. Under neutral vaporization conditions boron oxide passes into vapor congruently without decomposition, and calcium oxide practically completely dissociates into atomic metal and oxygen. Individual oxides CaO and $B_2O_3$ much differ from each other in volatility. When vaporized from molybdenum or tungsten cells (weakly reductive vaporization conditions) boron oxide is not reduced, whereas the dissociation degree of calcium oxide increases. In this case, the temperature of CaO vaporization is reduced [4, 5]. Oxygen is bound in volatile molybdenum or tungsten oxides, which in turn form gaseous calcium molybdates or tungstates [5]. On joint vaporization of calcium and boron oxides $CaB_2O_4$ [6, 7] and $CaBO_2$ [7] associates are present in the vapor. Starting from the temperature of about 1500 K, boron oxide and calcium borate $CaB_2O_4$ are preferentially vaporized in the $CaO–B_2O_3$, system, and calcium oxide is accumulated in the condensed phase. As the condensed phase is enriched with the metal oxide and as the temperature increases, $CaBO_2$ and CaO molecules and atomic calcium and oxygen begin to pass in vapor. At temperatures higher than 2000 K, $CaBO_2$, CaO, BO, and monatomic calcium and oxygen are only present in the vapor.

Richardson [8] estimated the activities and chemical potentials of CaO and $B_2O_3$, and also Gibbs energies over a wide range of concentrations of the components of the condensed phase at 1527 K on the basis of the reference standard enthalpies of formation and entropies of the compounds formed in the system $CaO–B_2O_3$. In the homogeneous melt region, the system is characterized by negative deviations from the ideal behavior. In [9], the activities of CaO and $B_2O_3$ in the system $CaO–B_2O_3$ were determined by studying the equilibrium between slag and the metal formed on the reduction of calcium and boron oxides by carbon. The results obtained agree satisfactorily with the calculations in [8].

According to the phase diagram of the $CaO–B_2O_3$ system [10], a number of compounds, such as $3CaO \cdot B_2O_3$, $2CaO \cdot B_2O_3$, $CaO \cdot B_2O_3$, $2CaO \cdot 3B_2O_3$, and $CaO \cdot 2B_2O_3$, are formed in the condensed phase. The standard enthalpies of formation and the entropies of the above calcium borates are given in the handbook [11].

Thermodynamic properties of the systems $SrO–V_2O_3$ and $BaO–B_2O_3$ were studied in [12]. Melts in these systems are characterized by considerable negative deviations from the ideal behavior, caused by the presence of thermally stable compounds in the condensed phase.

The $CaBO_2^+$ and $B_2O_3^+$ ions were identified in the mass spectra of vapor over the $CaO–B_2O_3$ system in

**Table 1**. Activities, chemical potentials, and excess chemical potentials of CaO in melts of the system $CaO–B_2O_3$ at 1600 K (1), found by high-temperature mass spectrometry and (2) calculated on the basis of the vacancy variant of the generalized lattice theory of associated solutions

| $x$(CaO), mole fraction | $a$(CaO) | | $-\Delta\mu_{CaO}$, kJ mol$^{-1}$ | | $-\Delta\mu^E_{CaO}$, kJ mol$^{-1}$ | |
|---|---|---|---|---|---|---|
| | (1) | (2) | (1) | (2) | (1) | (2) |
| 0.67 | 0.32 | 0.15 | 15.2 | 25.1 | 9.8 | 19.8 |
| 0.60 | 0.11 | 0.08 | 29.4 | 33.6 | 22.6 | 26.8 |
| 0.50 | 0.02 | 0.03 | 52.0 | 45.8 | 42.8 | 36.6 |
| 0.40 | $1.2\times10^{-2}$ | $1.3\times10^{-2}$ | 58.8 | 57.8 | 46.6 | 45.6 |
| 0.30 | $4.0\times10^{-3}$ | $5.0\times10^{-3}$ | 73.4 | 70.3 | 57.4 | 54.3 |
| 0.20 | – | $1.6\times10^{-3}$ | – | 85.4 | – | 64.0 |
| 0.10 | – | $2.9\times10^{-4}$ | – | 108.0 | – | 77.7 |

the temperature range 1575–1650 K. The appearance energies of these ions are 11.7 and 13.9 eV, respectively. As the temperature was raised to 1700 K, the $Ca^+$ ion was observed in the vapor mass spectra. The procedure of the determination of molecular precursors of the above ions is considered in detail in [7, 13]. The values obtained in the present work coincided within error limits with the appearance energies of ions in the mass spectra of vapor over $CaB_2O_4$ [7], which points to the fact that the vapor over the studied samples at 1600 K comprises the $CaB_2O_4$ and $B_2O_3$ molecules.

The activities of the $CaO–B_2O_3$ melt components were determined at 1600 K. According to the phase diagram [10], the homogeneous melt region in this system at 1600 K lies in the concentration range from 27 up to 70 mol % of $B_2O_3$. In the temperature range 1580–1610 K, $B_2O_3^+$ ion peaks were reliably detected in the mass spectra of the vapor over samples containing from 30 up to 90 mol % of boron oxide, and the rate of preferential $B_2O_3$ vaporization was not very high, which allows us to assign thus obtained values of the boron oxide activity to the initial melt composition.

The activity of $B_2O_3$ was found by the method of comparing ionic currents according to Eq. (1), using individual boron oxide as standard, and by the Belton–Fruechan method [14] according to Eq. (2).

$$a(B_2O_3) = I(B_2O_3^+)/I^0(B_2O_3), \quad (1)$$

$$\ln\gamma(B_2O_3)[x(B_2O_3)]$$
$$= -\int_{x(B_2O_3)=1}^{x(B_2O_3)=x(B_2O_3^+)}[x(CaO)/x(B_2O_3)]d\{\ln[I(CaBO_3^+)/I(B_2O_3^+)] - \ln[x(CaO)/x(B_2O_3)]\}. \quad (2)$$

The activity of calcium oxide was calculated by the Gibbs–Duhem equation (3).

$$\ln\gamma(CaO)[x(CaO)] = -\int_{\ln\gamma^0(B_2O_3)}^{\ln\gamma(B_2O_3)}[x(B_2O_3)/x(CaO)]d\ln\gamma(B_2O_3). \quad (3)$$

Here $a_i$, $g_i$, and $x_i$ are activity, activity coefficient, and mole fraction of the $i$th melt component; $I_i$ and $I_i^0$, intensities of the ion currents produced by ionization of the $i$th molecular form in vapor of over the melt of a specified composition and pure oxide, in relative units. The chemical potentials ($\Delta\mu_i$) and excess chemical potentials of components ($\Delta\mu_i^E$), as well as the Gibbs energies ($\Delta G$) and excess Gibbs energies ($\Delta G^E$) in melts of the system $CaO–B_2O_3$ were calculated by Eqs. (4)–(7).

$$\Delta\mu_i = RT\ln a_i, \quad (4)$$

$$\Delta G = \Sigma_i x_i\cdot\Delta\mu_i, \quad (5)$$

$$\Delta\mu_i^E = RT\ln\gamma_i, \quad (6)$$

$$\Delta G^E = \Sigma x_i\cdot\Delta\mu_i^E. \quad (7)$$

The $B_2O_3$ activities calculated by Eqs. (1) and (2) have coincided with an accuracy of 3–5%; therefore, the activities of CaO were calculated using an averaged value of $\gamma(B_2O_3)$. The resulting values of thermodynamic functions in melts of the $CaO–B_2O_3$ system at 1600 K are given in Table 1. The dependences of activities, chemical potentials of calcium and boron oxides, and also $\Delta G$ and $\Delta G^E$ in melts of the $CaO–V_2O_3$ system at 1600 K are presented in Figs. 1–3, respectively. As follows from the resulting values of thermodynamic functions, negative deviations from the ideal behavior are observed in melts of the studied system, which is connected with the formation of stable chemical compounds in the condensed phase, according to the data on the phase equilibria in the system under study [10]. It is necessary to note that the maximal deviations of the values of Gibbs energy and, respectively, of the excess Gibbs energy from ideality are characteristic of $CaB_2O_4$. The extent of the deviation from ideality in

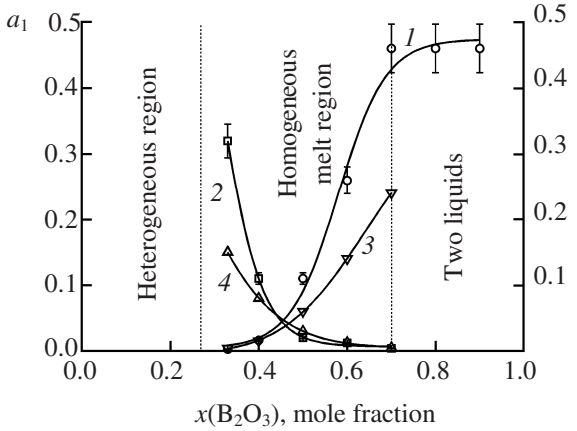


**Fig. 1**. Activities of the components of the $CaO–B_2O_3$ melt, determined by high-temperature mass spectrometry [(*1*) $a(B_2O_3)$; (*2*) $a$(CaO)] and calculated on the basis of the vacancy variant of the generalized lattice theory of associated solutions [(*3*) $a(B_2O_3)$; (*4*) $a$(CaO)] vs. melt composition.

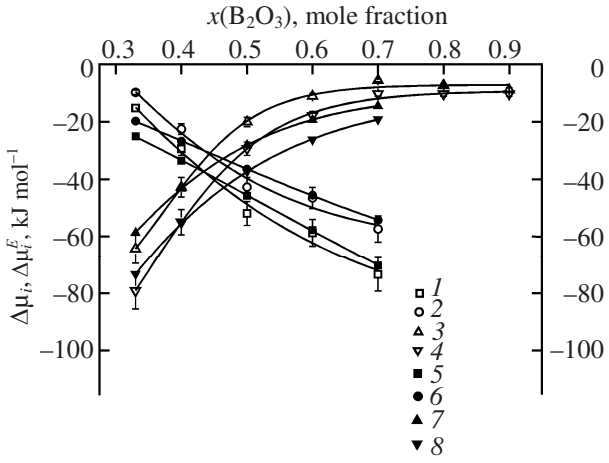


**Fig. 2**. Chemical potentials and excess chemical potentials, determined by high-temperature mass spectrometry [(*1*) $\Delta\mu(B_2O_3)$; (*2*) $\Delta\mu$(CaO); (*3*) $\Delta\mu^E(B_2O_3)$; (*4*) $\Delta\mu^E$(CaO)] and calculated on the basis of the vacancy variant of the generalized lattice theory of associated solutions [(*5*) $\Delta\mu(B_2O_3)$; (*6*) $\Delta\mu$(CaO); (*7*) $\Delta\mu^E(B_2O_3)$; (*8*) $\Delta\mu^E$(CaO)] vs. melt composition in the $CaO–B_2O_3$ system at 1600 K.

melts of the $MO–V_2O_3$ systems (MO = CaO, SrO, and BaO) increases on passing from calcium oxide to barium oxide, which is connected with increasing difference in the acid–base properties of the corresponding oxides [15]. A similar behavior takes place in binary silicate systems containing alkali-earth metal oxides as modifiers [16].

The thermodynamic characteristics of melts of the $CaO–B_2O_3$ system were calculated by the vacancy variant of the generalized lattice theory of associated solutions [17–19]. Taking into consideration the principal postulates of the generalized lattice theory of associated solutions and the vacancy variant of this approach, considered earlier in [20, 21], and also special structural features of melts of the $CaO–B_2O_3$ system, we obtained Eqs. (8) and (9) for the thermodynamic characteristics of this system.

$$\Delta\mu^E_{CaO} = RT\left(Q_{Ca–O}\ln\frac{X^{CaO}_{Ca–O–}}{x_{CaO}X^{1CaO}_{Ca–O–}} + Q_{Ca–}\ln\frac{X^{CaO}_{Ca–}}{x_{CaO}X^{1CaO}_{Ca–}} + r_{CaO}(1/2z-1)\ln\frac{r(B_2O_3)x(B_2O_3)}{r_{CaO}}\right) \quad (8)$$

$$\Delta\mu^E_{B_2O_3} = RT\left(Q_{B–O}\ln\frac{X^{B_2O_3}_{B–O–}}{x_{B_2O_3}X^{1B_2O}_{B–O–}} + Q_{B–}\ln\frac{X^{B_2O_3}_{B–}}{x_{B_2O_3}X^{1B}_{B–O–}} + r_{B_2O_3}(1/2z-1)\ln\frac{r_{CaO}x_{CaO}}{r_{B_2O}}\right) \quad (9)$$

Here $x$(CaO) and $x(B_2O_3)$ are the mole fractions of CaO and $B_2O_3$, respectively; $r$(CaO) and $r(B_2O_3)$, numbers of lattice sites occupied by the structural elements CaO and $B_2O_3$. Like earlier in [20], we accepted the following parameters of the model for the description of thermodynamic properties of glasses and melts of the $CaO–B_2O_3$: system $Q$(Ca–O–) = 1 is the number of CaO contact points corresponding to the Ca–O–[…] bonds in view of the second coordination sphere; $Q$(Ca–) = 2; number of CaO contact points having vacancies; $Q$(B–) = 1, number of $B_2O_3$ contact points corresponding to the B–[…] bonds; $Q$(B–O–) = 2, number of $B_2O_3$ contact points corresponding to the B–O–[…] bonds; $X^{CaO}_{Ca–O–}$, $X^{CaO}_{Ca–}$, $X^{B_2O_3}_{B–O–}$, and $X^{B_2O_3}_{B–}$, parameters found by solving the system of nonlinear equations (10) for the description of thermodynamic properties of the corresponding pure components.

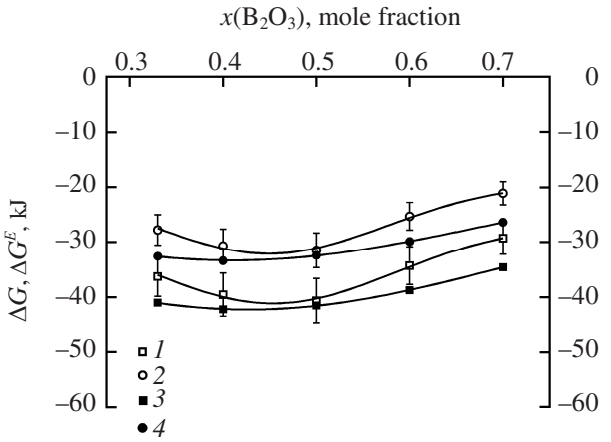


**Fig. 3**. Integral Gibbs energy and excess Gibbs energy, determined by high-temperature mass spectrometry [(*1*) $\Delta G$; (*2*) $\Delta G^E$)] and calculated on the basis of the vacancy variant of the generalized lattice theory of associated solutions [(*3*) $\Delta G$; (*4*) $\Delta G^E$)] vs. melt composition in the $CaO–B_2O_3$ system at 1600 K.

$$\left.\begin{aligned}
&X^{CaO}_{Ca-O-}(\eta_{Ca-O[-B]}X_B+\eta_{Ca-O-[Ca]}X^{CaO}_{Ca-}) = \frac{Q^{CaO}_{Ca-O-}}{2}x_{CaO}\\
&X^{CaO}_{Ca-}(\eta_{Ca-O[-B]}X^{B_2O_3}_{B-O-}+\eta_{Ca-O-[Ca]}X^{CaO}_{Ca-O-}) = \frac{Q^{CaO}_{Ca-O-}}{2}x_{CaO}\\
&X^{B_2O_3}_{B-O-}(\eta_{B-O-[Ca]}X^{CaO}_{Ca-}+\eta_{B-O-[B]}X^{B_2O_3}_{B-}) = \frac{Q^{B_2O_3}_{B-O-}}{2}x_{B_2O_3}\\
&X^{B_2O_3}_{B-O-}(\eta_{B-O-[Ca]}X^{CaO}_{Ca-O-}+\eta_{B-O-[B]}X^{B_2O_3}_{B-O-})\frac{Q^{B_2O_3}_{B}}{2}x_{B_2O_3}.
\end{aligned}\right\} \quad (10)$$

The coordination number of the lattice in melts of the $CaO–B_2O_3$ system is three, as follows from Eqs. (11) and (12).

$$q_{CaO}z = r_{CaO}z - 2r_{CaO} + 2, \quad (11)$$

$$q_{BO\ \ z} = r_{BO\ \ z} - 2r_{BO\ \ } + 2. \quad (12)$$

Here $q$(CaO) and $q(BO_{3/2})$ are total numbers of contact points of structural oxide fragments; r(CaO) and $r(BO_{3/2})$, numbers of lattice sites occupied by this fragment; and z, lattice coordination number.

Using the mole volumes for CaO of 16.6 $cm^3\ mol^{-1}$ and for $B_2O_3$ of 38.4 $cm^3\ mol^{-1}$, estimated with the data in [23], we calculated the numbers of lattice sites occupied by the structural elements CaO and $BO_{3/2}$ in melts of the $CaO–B_2O_3$ system. The calculated values are equal to unity for CaO and $BO_{3/2}$. Thus, we obtained the system of nonlinear equations (10) for the description of thermodynamic properties of melts of the $CaO–B_2O_3$ system.

As earlier in [20], in terms of the principal postulates of the generalized lattice theory of associated solutions [17–19], the most probable numbers of bonds in melts of the $CaO–B_2O_3$ system were found by Eqs. (13)–(15).

$$N_{B-O-[Ca]} = 2X^{CaO}_{Ca-O-}X^{B_2O_3}_{B-}\eta_{Ca-O-[B]}N, \quad (13)$$

$$N_{Ca-O-[Ca]} = X^{CaO}_{Ca-O}X^{CaO}_{Ca-O-}\eta_{Ca-O-[Ca]}N, \quad (14)$$

$$N_{B-O-[B]} = X^{B_2O_3}_{B-O-}X^{B_2O_3}_{B-}\eta_{B-O-[B]}N. \quad (15)$$

Here $N^{AB}_{\mu\nu}$ is the relative number of A–B bonds; $X^{CaO}_{Ca-O-}$, $X^{CaO}_{Ca-}$, $X^{B_2O_3}_{B-O-}$, and $X^{B_2O_3}_{B-}$, parameters found by solving system (10); and $N$, total number of molecules in the melt.

$$N = \sum_A N_A. \quad (16)$$

The activities of CaO [$a$(CaO)] and $B_2O_3$ [$a(B_2O_3)$] in melts of the $CaO–B_2O_3$ system as a function of the $B_2O_3$ mole fraction, calculated on the basis of the vacancy variant of the generalized lattice theory of associated solutions using Eqs. (8) and (9) are given in Fig. 1 and compared with the data obtained by the high-temperature mass spectrometry at 1600 K.

The dependences of the chemical potentials $\Delta\mu_i$ and excess chemical potentials $\Delta\mu_i^E$ of the components of melt of the $CaO–B_2O_3$ system on melt composition are given in Fig. 2. Figure 3 illustrates the fact that the integral Gibbs energy ($\Delta G$) and the excess Gibbs energy ($\Delta G^E$) in melts of the system $CaO–B_2O_3$ at 1600 K as functions of the mole fraction of $B_2O_3$, calculated on the basis of the vacancy variant of the generalized lattice theory of associated solutions and determined by mass spectrometry at 1600 K fairly fit each other.

The activities of the components and the Gibbs energy in melts of the $CaO–B_2O_3$ system, calculated on the basis of the vacancy variant of the generalized lattice theory of associated solutions satisfactory fit the experimental values obtained by high-temperature mass spectrometry (Tables 1–3) within no more 25% on the average, that agrees with the calculated relative error. This finding provide evidence for the correctness of the vacancy variant of the generalized lattice theory of associated solutions for the description of thermodynamic properties of melts of binary oxide systems formed by a modifier oxide (alkaline-earth oxide) and a glass-forming oxide ($B_2O_3$).

**Table 2**. Activities, chemical potentials, and excess chemical potentials of $B_2O_3$, Gibbs energies and excess Gibbs energies of melts of the $CaO–B_2O_3$ system at 1600 K (1) found by high-temperature mass spectrometry and (2) calculated on the basis of the vacancy variant of the generalized lattice theory of associated solutions

| $x$(CaO), mole fraction | $a(B_2O_3)$ | | $-\Delta\mu(B_2O_3)$, kJ mol$^{-1}$ | | $-\Delta\mu^E(B_2O_3)$, kJ mol$^{-1}$ | |
|---|---|---|---|---|---|---|
| | (1) | (2) | (1) | (2) | (1) | (2) |
| 0.67 | $2.6\times10^{-3}$ | $4.0\times10^{-3}$ | 79.2 | 73.4 | 64.4 | 58.7 |
| 0.60 | $1.6\times10^{-2}$ | $1.5\times10^{-2}$ | 55.0 | 55.5 | 42.8 | 43.3 |
| 0.50 | 0.11 | 0.06 | 29.4 | 37.4 | 20.1 | 28.2 |
| 0.40 | 0.26 | 0.14 | 17.9 | 26.2 | 11.1 | 19.4 |
| 0.30 | 0.46 | 0.24 | 10.3 | 19.2 | 5.6 | 14.5 |
| 0.20 | 0.46 | – | 10.3 | – | 7.4 | – |
| 0.10 | 0.46 | – | 10.3 | – | 8.9 | – |

**Table 3**. Gibbs energies and excess Gibbs energies of melts of the $CaO–B_2O_3$ system at 1600 K (1) found by high-temperature mass spectrometry and (2) calculated on the basis of the vacancy variant of the generalized lattice theory of associated solutions

| $x$(CaO), mole fraction | $-\Delta G$, kJ | | $-\Delta G^E$, kJ | |
|---|---|---|---|---|
| | (1) | (2) | (1) | (2) |
| 0.67 | 36.3 | 41.1 | 27.8 | 32.6 |
| 0.60 | 39.6 | 42.3 | 30.7 | 33.4 |
| 0.50 | 40.7 | 41.6 | 31.5 | 32.4 |
| 0.40 | 34.3 | 38.8 | 25.3 | 29.9 |
| 0.30 | 29.3 | 34.6 | 21.1 | 26.4 |

On the basis of the vacancy variant of the generalized lattice theory of associated solutions in view of the second coordination sphere, using Eqs. (13)–(15), we calculated the relative numbers of bonds of the following types (Figs. 4 and 5): Ca–O(–Ca), Ca–O(–B), B–O(–B), Ca–O(–V), and B–O(–V) formed in melts of the system $CaO–B_2O_3$ (V is a vacancy at 1600 K). It should be noted that the relative number of Ca–O(–Ca) bonds in the entire concentration range remains negligibly small (less than 0.03 rel. units). The relative number of B–O(–B) bonds increases in the considered concentration range of the $CaO–B_2O_3$ system as the mole fraction of $B_2O_3$ increases from 0.10 to 0.12 rel. units. The number of vacancies in the melt is much smaller than the number of Ca–O(–Ca) and B–O(–B) bonds in the entire concentration range.

The experimental Gibbs energies $\Delta G(T)$ for a melt corresponding to $CaB_2O_4$ and $2CaO \cdot B_2O_3$, reduced to 298 K, allow us to pass to standard enthalpies of

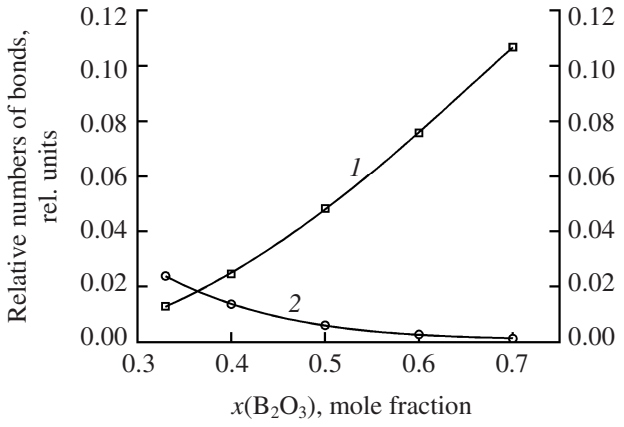


**Fig. 4**. Relative numbers of bonds formed in glasses and melts of the $CaO–B_2O_3$ system and calculated on the basis of the vacancy variant of the generalized lattice theory of associated solutions [(*1*) B–O(–B), (*2*) Ca–O(–Ca)] vs. melt composition at 1600 K.

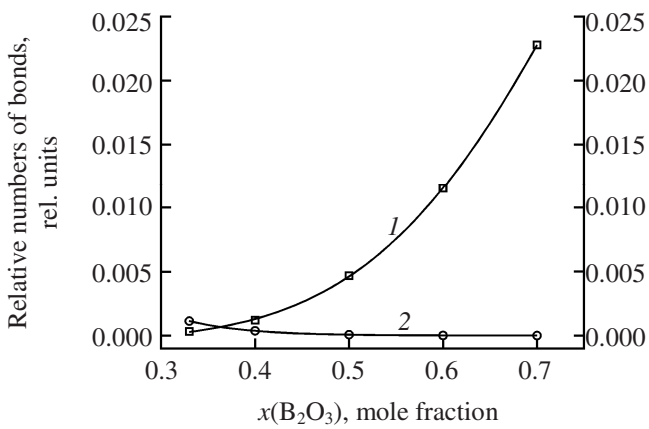


**Fig. 5**. Relative numbers of bonds formed in glasses and melts of the $CaO–B_2O_3$ system and calculated on the basis of the vacancy variant of the generalized lattice theory of associated solutions [(1) B–O(–V), (2) Ca–O(–V), where V is vacancy] vs. melt composition at 1600 K.

**Table 4**. Enthalpies of formation of calcium borates from the elements and constituent oxides

| Borate | $-\Delta_f H^0$ (298) kJ mol$^{-1}$ | $-\Delta_f H^0_{ox}$ (298) kJ mol$^{-1}$ | Reference |
|---|---|---|---|
| $CaB_2O_4$ (s) | 2022.1 | 112.5 | [11] |
| | 2031.1 | 123.1 | [24] |
| | 1960 | 54.1 | Our data + [24] |
| | 1937 | 28.1 | Our data + [26] |
| $2\,CaO{\cdot}B_2O_3$ (s) | 2726.3 | 182.6 | [11] |
| | 2735.4 | 191.5 | [24] |
| | 2710 | 166 | Our data + [24] |
| | 2708 | 164 | Our data + [26] |

formation of these compounds. The calculations were carried out using the reference data [11, 24, 25] and Landiya's method [26]. The calculated values together with the reference data for calcium metaborates are presented in Table 4.

Our value of the enthalpy of $Ca_2B_2O_5$ formation practically coincides with the reference data [11, 24], and the enthalpy of $CaB_2O_4$ formation is lower in absolute value by 60–70 kJ mol$^{-1}$ than the reference value. A number of reasons can be responsible for such a discrepancy, and the first of them is the uncertainty in our determined activities of the melt components. However, to increase the absolute value of $\Delta G(T)$ by 60–70 kJ mol$^{-1}$, the error in the determination of the $B_2O_3$ activity should exceed two orders of magnitude. The error in activity measurements by differential mass spectrometry with an individual component as standard is no more than 5%. Even under the most unfavorable measurement conditions, it is practically impossible to be even twofold mistaken. A certain error in the calculation of the formation enthalpies is introduced when experimental $\Delta G(T)$ values are reduced to the standard temperature (298 K). The $H^0(T)$–$H^0(298)$ and $S^0(T)$–$S^0(298)$ values were calculated by Landiya's method [26] using reference data [24]. The error of this method does not exceed 3%, when standard entropy and temperatures of melting and polymorphous transformations are known. The $\Delta G(T)$ values reduced to 298 K with the data of [24] and [26] proved almost equal to each other.

The second reason is the incorrectness of reference data. Such cases are not rare. For example, four values of $-\Delta_f H^0$(s, 298) for barium tungstate are given in the reference and original literature: 1633.8 [27], 1697.4 ± 4.2 [11], 1680.1 ± 10.5 [28], and 1630.8 [24] kJ mol$^{-1}$. Considerable disagreements in reference values of standard enthalpies of silicates of alkali-earth metals are noted in [29].

The use of molybdenum cells introduces a certain error in measurements. Though molybdenum does not reduce boron oxide, calcium oxide is partially reduced, and its volatility and, correspondingly, activity increase. However, it is unlikely that calcium oxide reduction can increase the CaO activity by two orders of magnitude.

In connection with the above-stated, not claiming for the ultimate absolute truth, we recommend to use the values of the enthalpies of formation of $CaB_2O_4$(s) and $Ca_2B_2O_5$(s) formation of –1960 and –2710 kJ mol$^{-1}$ at 298 K, respectively, as resulting from a sufficiently correct experiment.

## EXPERIMENTAL

This work was performed by high-temperature differential mass spectrometry on an MS-1301 mass-spectrometer at the ionizinf electron energy 25 eV. The block of double molybdenum one-temperature effusion chambers was heated by electron bombardment. The temperature was measured with an EOP-66 optical pyrometer with an accuracy of ±5° in the range of 1450–1650 K. The instrument was preliminarily calibrated by $CaF_2$ vapor pressure [25]. The systems studied were synthesized from analytical grade boric acid and pure grade calcium carbonate. The synthesis was performed in platinum crucibles at 1423–1773 K depending on composition. After the charge had welded, the temperature was raised to the operation level, and the melt was stirred with a quartz tube. Then the melt was poured out on a heated steel plate and cooled. The resulting blocks were annealed in a muffle furnace at 773–873 K for 30 min.

## ACKNOWLEDGMENTS

This work was financially supported by the Russian Foundation for Basic Research (project no. 07-03-00-238a).

## REFERENCES

1. Sobolev, I.A., Ozhovan, M.I., Shchervatova, T.D., and Batyukhina, O.G., *Stekla dlya radioaktivnykh otkhodov* (Glasses for Radioactive Wastes), Moscow: Energoatomizdat, 1999.

2. Ojovan, M.I. and Lee, W.E., *An Introduction to Nuclear Waste Immobilization*, Sheffield: Elsevier, 2005.
3. Kazenas, E.K. and Tsvetkov, Yu.V., *Ispareniye oksidov* (Vaporization of Oxides), Moscow: Nauka, 1997.
4. Hilpert, K. and Gerads, H., *High Temp. Sci.*, 1975, vol. 7, no. 1, p. 11.
5. Lopatin, S.I., Shugurov, S.M., and Semenov, G.A., *Zh. Obshch. Khim.*, 2003, vol. 73, no. 2, p. 187.
6. Stolyarova, V.L. and Seetharaman, S., *Vacuum*, 1998, vol. 49, no. 3, p. 161.
7. Lopatin, S.I., Semenov, G.A., Baranovskii, V.I., Shugurov, S.M., and Sizov, V.V., *Zh. Obshch. Khim.*, 2001, vol. 71, no. 9, p. 1422.
8. Richardson, F.D., *Physical Chemistry of Melts and Metallurgy*, London: Acad. Press, 1974, vol. 1, p. 136.
9. Dai, C., Zhang, X., and Shui, L., *Metallurg. Materials Trans. B.*, 1995, vol. 26B, no. 6, p. 651.
10. *Diagrammy sostoyaniya silikatnykh system. Spravochnik* (Phase Diagrams of Silicate Systems. Handbook), Toropov, N.A. and Barzakovskii, V.P., Leningrad: Nauka, 1969, vol. 1.
11. *Termodinamicheskie konstanty veshchestv* (Thermodynamic Constants of Substances), Glushko, V.P., Ed., Moscow: Izd. Akad Nauk SSSR, 1979, issue IX.
12. Lopatin, S.I., Stolyarova, V.L., Tyurnina, N.G., and Tyurnina, Z.G., *Zh. Obshch. Khim.*, 2006, vol. 76, no. 11, p. 1761.
13. Lopatin S.I., Semenov G.A., and Shugurov S.M., *Zh. Obshch. Khim.*, 2001, vol. 71, no. 1, p. 68.
14. Belton, G.R. and Fruechan, R.J., *J. Phys. Chem.*, 1967, vol. 71, no. 5, p. 1403.
15. Lopatin, S.I., *Doctoral (Chem.) Dissertation*, St. Petersburg, 2001.
16. Anfilogov, V.N., Bykov, V.N., and Osipov, A.A., *Silikatnye rasplavy* (Silicate Melts), Moscow: Nauka, 2005.
17. Barker, J.A., *J. Chem. Phys.*, 1954, vol. 22, no. 3, p. 375.
18. Barker, J.A., *J. Chem. Phys.*, 1952, vol. 10, no. 10, p. 1526.
19. Barker J., Brown I., and Smith F., *Disc. Faraday Soc.,* 1953, vol. 15, no. 1, p. 142.
20. Stolyarova, V.L., Ivanov, G.G., and Shul'ts, M.M., *Fiz. Khim. Stekla*, 1991, vol. 17, no.5, p. 689.
21. Plotnikov, E.N. and Stolyarova, V.L., *Fiz. Khim. Stekla,* 2006, vol. 32, no. 2, p. 251.
22. Stolyarova, V.L., Shornikov, S.I., Ivanov, G.G., and Shultz, M.M., *J. Electrochem. Soc.*, 1991, vol. 138, no. 12, p. 3710.
23. Mazurin, O.V., Strel'tsina, M.V., and Shvaiko-Shvaikovskaya, T.P., *Svoistva stekol i stekloobrazuyushchikh rasplavov. Trekhkomponentnye silikatnye sistemy* (Properties of Glasses and Glass-Forming Melts. Ternary Silicate Systems), Leningrad: Nauka, 1977, vol. III, part 1.
24. Barin, I., Knacke, O., and Kubaschewski, O., *Thermochemical Properties of Inorganic Substances*, Berlin: Springer–Verlag, 1973 (Suppl. 1977).
25. *Termodinamicheskie svoistva individual'nykh veshchestv: Spravochnik* (Thermodynamic Properties of Individual Substances: Handbook), Glushko, V.P., Ed., Moscow: Izd. Akad Nauk SSSR, 1978-1984, vols. 1-4.
26. Landiya, N.A., *Raschet vysokotemperaturnykh teploemkostei neorganicheskikh veshchestv po standartnoi entropii* (Calculation of High-Temperature Heat Capacities of Inorganic Substances by Standard Entropies), Tbilisi: Izd. Akad Nauk GrSSR, 1962.
27. Naumov, G.B., Ryzhenko, B.N., and Khodakovskii, I.L., *Spravochnik termodinamicheskikh velichin* (Handbook of Thermodynamic Values), Moscow: Atomizdat, 1971.
28. Levitski, V.A., Hekimov, Yu., and Gerassimov, Ja.I., *J. Chem. Thermodyn.*, 1979, vol. 11, no. 11, p. 1075.
29. Shul'ts, M.M., Borisova, N.V., and Kozhina, E.L., *Khimiya silikatov i oksidov* (Chemistry of Silicates and Oxides), Leningrad: Nauka, 1982, p. 3.