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Thermodynamic Properties of Silicate Glasses and Melts: III.[1] System Rb_2O–B_2O_3–SiO_2

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Abstract — The composition of vapor over the system Rb_2O–B_2O_3–SiO_2 and the activities of RbBO in melts of this system at 1000 K were determined. The sign of deviations of the $RbBO_2$ and Rb_2SiO_3 activities from ideality changes in the melts under study.
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Borosilicate glasses are matrices for immobilization of radioactive waste; therefore, the study of vaporization and thermodynamic properties of components of glasses and melts of R_2O–B_2O_3–SiO_2 systems (R is an alkali metal) is of significant interest [2]. To prevent evaporation of the most volatile components from the glasses, it is necessary to select the component ratios in the condensed phase that ensure the minimal thermodynamic activities and activity coefficients of volatile components. The most volatile components of the above-indicated glasses are alkali metal oxides [3]. It is known that, if the R_2O/B_2O_3 molar ratio is less than or equally to unity, alkali metal ions are completely associated with borate anions [4, 5]. Therefore RBO_2, $(RBO_2)_2$, and in some cases also $(RBO_2)_3$ molecules are present in the vapor over alkaline borosilicate glasses [6–12], as well as over R_2O–B_2O_3 systems (R is an alkali metal) [13–15].

The partial pressures of molecular species in the vapor over the $RbBO_2$–SiO_2 system, the activities and activity coefficients of components, and also the Gibbs energies of mixing in melts at 1000 K were determined in [11] in a wide range of compositions of the condensed phase. Negative deviations from the ideal behavior were found in the system under study.

The activities of components in the condensed phase of the system Rb_2O–B_2O_3 containing from 50 to 92 mol% B_2O_3 were determined in [15]. The composition of vapor over this system was shown to depend on the composition of the condensed phase and temperature in the range 950–1350 K: in the range 950–1220 K, $RbBO_2$ and $(RbBO_2)_2$ molecules were present in vapor, and at temperatures higher than 1300 K, $RbBO_2$, $(RbBO_2)_2$, B_2O_3 molecules and rubidium atoms. The activities of $RbBO_2$ and B_2O_3 and the calculated thermodynamic functions of the systems $RbBO_2$–B_2O_3 and Rb_2O–B_2O_3 are indicative of significant negative deviations from the ideal behavior of the melt.

In this study we determined the composition of vapor and $RbBO_2$ activities in melts of the Rb_2O–B_2O_3–SiO_2 system at 1000 K. The synthesis of the samples was described in [12]. The compositions of the samples under study are presented in Table 1. In the mass spectra of vapor over melts of the system, recorded in the range 930–1050 K, the Rb^+, $RbBO_2^+$, and $Rb_2BO_2^+$ peaks were detected. The $RbBO_2^+/Rb^+$ ion current ratio in the mass spectra of the vapor over the samples depends on the concentration ratio of the oxides Rb_2O/B_2O_3 in the melt. When the molar ratio Rb_2O/B_2O_3 was less than or equal to unity, the $RbBO_2^+/Rb^+$ peak intensity ratio was constant and equal to 0.05–0.06, and the appearance potential of Rb^+ ions was 9.8 eV. When the temperature was increased to approximately 1300 K, the ion current of $B_2O_3^+$ with the appearance potential of 14.0 eV was detected in the mass spectra. The $Rb_2BO_2^+/RbBO_2^+$ ratio was within the range 0.63–0.09 and depended on temperature. The appearance potentials of $RbBO_2^+$ and $Rb_2BO_2^+$ are 8.9 and 10.5 eV, respectively. When the molar ratio Rb_2O/B_2O_3 was higher than unity, the peak of the Rb^+ ion with the appearance potential of 4.2 eV became noticeable at approximately 750 K, and the $RbBO_2^+/Rb^+$ ion current ratio at 1000 K was 0.01–0.02. The nature of ions and the technique of interpreting the mass spectra of the vapor over alkali

[1] For communication II, see [1].

Content of oxides in samples of the Rb_2O–B_2O_3–SiO_2 system, assumed compositions of melts, and $RbBO_2$ activities at 1000 K

Sample no.	Content of components, mol %			Assumed composition of melt, mol %				$a(RbBO_2)$
	Rb_2O	B_2O_3	SiO_2	$RbBO_2$	B_2O_3	SiO_2	Rb_2SiO_3	
1	5.0	19.0	76.0	10.0	71.0	19.0	–	0.03
2	20.0	64.0	16.0	40.0	44.0	16.0	–	0.05
3	33.3	53.0	13.7	66.6	19.7	13.8	–	0.47
4	50.0	40.0	10.0	88.9	–	–	11.1	0.96
5	5.0	57.0	38.0	10.0	52.0	38.0	–	0.04
6	20.0	48.0	32.0	40.0	28.0	32.0	–	0.10
7	33.3	26.7	40.0	66.6	6.7	26.7	–	0.69
8	50.0	30.0	20.0	75.0	–	–	25.0	0.86
9	5.0	37.5	57.5	10.0	32.5	57.5	–	0.04
10	20.0	32.0	48.0	40.0	12.0	48.0	–	0.06
11	33.3	26.7	40.0	57.1	–	35.8	7.1	0.68
12	50.0	20.0	30.0	57.1	–	–	42.9	0.78
13	5.0	19.0	76.0	10.0	14.0	76.0	–	0.03
14	20.0	16.0	64.0	33.3	–	62.5	4.2	0.11
15	33.3	13.7	53.0	31.4	–	24.4	41.5	0.71
16	50.0	10.0	40.0	33.0	–	–	67.0	0.75
17	5.0	47.5	47.5	10.0	42.5	47.5	–	0.03
18	16.7	16.7	66.6	33.4	–	66.6	–	0.04
19	50.0	–	–	–	–	–	100.0	0.00

metal metaborates was described in detail elsewhere [16, 17].

The intensities of the Rb^+, $RbBO_2^+$, and $Rb_2BO_2^+$ ion currents gradually decreased in the course of isothermal heating. The maximal temperature of heating the block of effusion cells with the samples was 1550 K. Silicon dioxide cannot be evaporated at this temperature; therefore, after measuring the $RbBO_2$ activity and partially evaporating the sample, the effusion cell was moved to a high-temperature evaporator allowing the cell with the sample to be heated to 2500 K, to completely remove the sample residue. Silicon oxide started to pass into vapor as SiO and oxygen at approximately 1700 K.

The mass spectra measured, their dependence on temperature and evaporation duration, the ratio of ion current intensities, the appearance potential of ions, and the character of the ionization efficiency curves indicate that the vapor over the melts of the Rb_2O–B_2O_3–SiO_2 system in the range 930–1040 K consists of monomeric $RbBO_2$ molecules and insignificant amount of $(RbBO_2)_2$ dimers. Furthermore, atomic rubidium is present in the vapor over melts with Rb_2O/B_2O_3 ratios greater than unity. As the melt and hence the vapor phase are depleted of rubidium metaborate and the temperature is increased to 1350–1370 K, in some cases B_2O_3 molecules start to pass into vapor, as demonstrated by detection of $B_2O_3^+$ ions with the appearance potential equal to the ionization potential of boron oxide [18].

The activities of $RbBO_2$ in melts of the system Rb_2O–B_2O_3–SiO_2 at 1000 K were determined by Eqs. (1) and (2) [12, 15]. The results obtained are presented in the table.

$$a(RbBO_2) = \frac{I_m}{I_m^0}, \quad (1)$$

$$a(RbBO_2) = \frac{I_d/I_m}{I_d^0/I_m^0}. \quad (2)$$

Here $a(RbBO_2)$ is the activity of rubidium metaborate in the melt, I_d and I_m are the intensities of ion currents of the dimer and monomer, respectively, in the mass spectrum of vapor over the melt of the system of the specified composition, and I_d^0 and I_m^0 are intensities of the ion currents of the dimer and monomer in the mass spectrum of vapor over pure rubidium metaborate. The activities of $RbBO_2$ calculated by Eqs. (1) and (2) coincided with each other within the limits of the measurement error, and in the table we give the averaged values.

From the data of [19, 20] we can conclude that the acid properties of B_2O_3 are stronger than those of

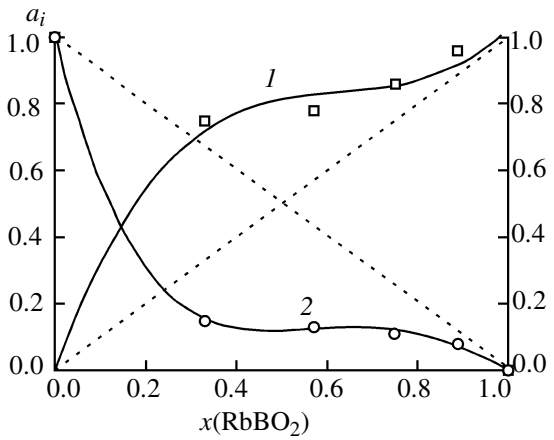

Fig. 1. Concentration dependence of activities of (*1*) $RbBO_2$ and (*2*) Rb_2SiO_3 in the system $RbBO_2$–Rb_2SiO_3 at 1000 K.

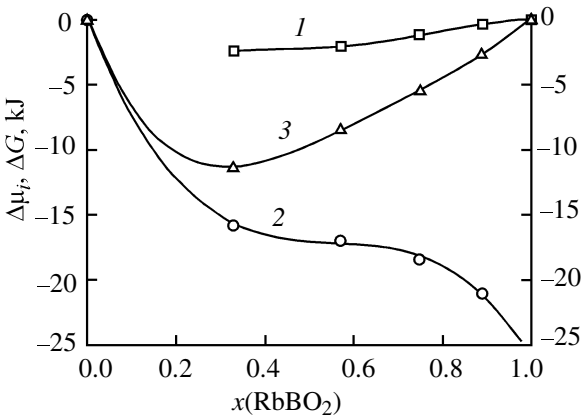

Fig. 2. Dependence of the chemical potentials (*1*) $\Delta\mu(RbBO_2)$ and (*2*) $\Delta\mu(Rb_2SiO_3)$ and (*3*) of the integral Gibbs energy on the melt composition in the system $RbBO_2$–Rb_2SiO_3 at 1000 K.

SiO_2; therefore, the modifier oxide Rb_2O in the condensed phase is primarily bound to give rubidium borate. If the Rb_2O/B_2O_3 ratio is higher than unity, the borate forms an equimolar amount of rubidium oxide, and excess rubidium oxide is bound to give a silicate. The above assumptions are proved by the qualitative and quantitative coincidence of the mass spectra of the vapor over samples 1–3, 5–7, 9, 10, 13, 17, 18, and pure rubidium metaborate at 1000 K, an increase in the $Rb^+/RbBO_2^+$ ion current ratio in the mass spectra of vapor over samples 4, 8, 11, 12, and 14–16, and the absence of $B_2O_3^+$ peak from the mass spectra of vapor over samples 4, 8, 12, and 16 at the temperature increased to 1350 K. The assumed compositions of the melts are presented in the table. The presence of atomic rubidium in vapor over samples 4, 8, 11, 12, and 14–16 is caused with the thermal dissociation of rubidium silicate according to Eq. (3), which is confirmed by the experiments on evaporation of pure rubidium silicate.

$$k\mathrm{Rb_2O}\cdot m\mathrm{SiO_2(l)}$$

$$\longrightarrow [k-n]\mathrm{Rb(gas)} + \mathrm{O_2(gas)} + n\mathrm{Rb_2O}\cdot m\mathrm{SiO_2(l)}. \quad (3)$$

Measuring the temperature dependence of the Rb^+ ion current in the mass spectrum of vapor over rubidium silicate allowed us to obtain Eq. (4) for the vapor pressure of atomic rubidium over rubidium silicate in the range 745–908 K. The partial pressures of Rb(gas) over rubidium silicate were determined by comparing the ion currents using silver as an external pressure reference [21].

$$\log p\,(\mathrm{Pa}) = -(8176\pm253)/T + (7.4\pm0.1). \quad (4)$$

A part of the ternary system Rb_2O–B_2O_3–SiO_2, namely, samples 4, 8, 12, and 16, can be considered as a pseudobinary mixture $RbBO_2$–Rb_2SiO_3. The activities of $RbBO_2$ in samples of the $RbBO_2$–Rb_2SiO_3 system were determined experimentally using Eq. (1) and pure rubidium metaborate as an activity reference. The activity coefficients of Rb_2SiO_3 were calculated by integrating the Gibbs–Duhem equation in form (5), and the Rb_2SiO_3 activities were calculated by Eq. (6).

$$\ln\gamma(\mathrm{Rb_2SiO_3}) = -\int_{\ln\gamma^0(\mathrm{RbBO_2})}^{\ln\gamma(\mathrm{RbBO_2})} \frac{x(\mathrm{RbBO_2})}{x(\mathrm{Rb_2SiO_3})}\,d\ln\gamma(\mathrm{RbBO_2}), \quad (5)$$

$$a_i = \gamma_i x_i. \quad (6)$$

The chemical potentials of components, Gibbs energies, and the corresponding excess quantities for glasses and melts of the $RbBO_2$–Rb_2SiO_3 system were calculated by Eqs. (7)–(10).

$$\Delta\mu_i = RT\ln a_i, \quad (7)$$

$$\Delta G = \Sigma x_i\mu_i, \quad (8)$$

$$\Delta\mu_i^E = RT\ln a_i - RT\ln x_i, \quad (9)$$

$$\Delta G^E = \Sigma x_i\Delta\mu_i^E. \quad (10)$$

In Eqs. (5)–(10), a_i, γ_i, and $\Delta\mu_i$ are the activity, activity coefficient, and chemical potential of *i*th component, respectively; x_i, mole fraction of *i*th component; ΔG, integral Gibbs energy; and $\Delta\mu_i^E$ and ΔG^E, the corresponding excess quantities for glasses and melts of the $RbBO_2$–Rb_2SiO_3 system at 1000 K.

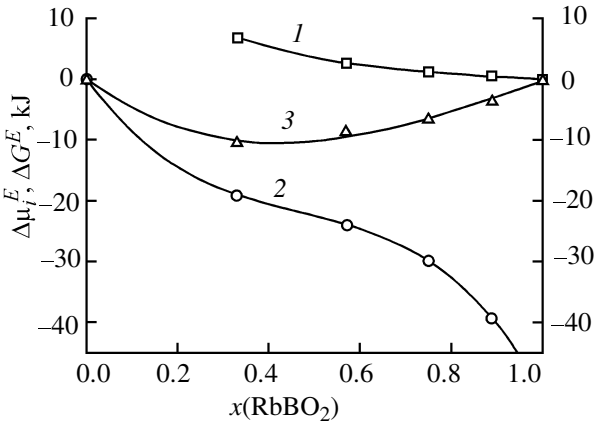

Fig. 3. Dependence of excess chemical potentials (*1*) $\Delta\mu^E(RbBO_2)$ and (*2*) $\Delta\mu^E(Rb_2SiO_3)$ and (*3*) of excess Gibbs energy on the melt composition in the system $RbBO_2$–Rb_2SiO_3 at 1000 K.

The dependences of the thermodynamic functions of melts of the $RbBO_2$–Rb_2SiO_3 system on the composition of the melt, calculated by Eqs. (1) and (6)–(10), are presented in Figs. 1–3.

As follows from the thermodynamic functions given in the table and in Figs. 1–3, at 1000 K the $RbBO_2$ and Rb_2SiO_3 activities deviate from the ideal behavior. When the composition of the melt corresponds to the ternary system $RbBO_2$–B_2O_3–SiO_2, the deviation of the $RbBO_2$ activity from ideality is negative. The replacement of B_2O_3 by Rb_2SiO_3 results in a decrease in the negative deviation proportional to the concentration of rubidium silicate in the melt. In melts and glasses of the $RbBO_2$–Rb_2SiO_3 system, the deviation of the $RbBO_2$ activity from ideality is positive, and that of rubidium silicate, negative. The results of this study agree well with the data obtained in [11, 12, 22] for the $RbBO_2$–SiO_2, Rb_2O–B_2O_3, Cs_2O–B_2O_3 and Cs_2O–B_2O_3–SiO_2 systems.

EXPERIMENTAL

The study of vaporization of the Rb_2O–B_2O_3–SiO_2 system and the determination of the $RbBO_2$ activity were made by high-temperature mass spectrometry on an MS-1301 mass spectrometer at the ionizing electron energy of 25 V. Samples were evaporated from a double one-temperature molybdenum cell. The technique of measurement and determination of thermodynamic properties of components of melts has been described in detail in [12].

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