

MASS-SPECTROMETRIC DETERMINATION OF THE ENTHALPY OF FORMATION  
AND ELECTRON AFFINITY OF  $\text{BO}_2$

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The effusion method of Knudsen with mass-spectral analysis is employed to investigate the gas phase of the systems  $\text{Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ ,  $\text{PbO-B}_2\text{O}_3$ , and  $\text{ZnO-B}_2\text{O}_3$ . The enthalpy of formation of gaseous  $\text{BO}_2^-$  is determined using the method of ion-molecular equilibria. The electron affinity of the  $\text{BO}_2$  molecule  $\text{EA}(\text{BO}_2) = 4.33$  eV.

In the JANAF handbook [1] the value  $\Delta H_{f,0}^\circ = -284.5$  kJ/mole was chosen for the enthalpy of formation of  $\text{BO}_2$  (gas) from analysis of the published data obtained up to 1971, and in the handbook [2], where published data up to 1977 are examined, the value  $\Delta H_{f,0}^\circ = -325 \pm 20$  kJ/mole was adopted. In [3] the equilibria in the gas phase above liquid boron oxide were studied by the mass-spectrometric method:



The enthalpies of the reactions (1) and (2), calculated based on the third law of thermodynamics, lead to two values for the enthalpies of formation of  $\text{BO}_2$  (gas):  $-312.5 \pm 15.5$  and  $-308.4 \pm 9$  kJ/mole. As one can see, the recommendations of [1, 2] significantly differ from one another and from the data of [3]. According to [1, 2], the heats of formation of the anion  $\text{BO}_2^-$  differ by 12.6 kJ/mole.

In this work we studied the saturated vapor of the systems  $\text{Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ ,  $\text{PbO-B}_2\text{O}_3$ , and  $\text{ZnO-B}_2\text{O}_3$ . These systems were chosen because of the fact that the dissociation of bismuth, lead, and zinc oxides is accompanied by liberation of oxygen. As a result the evaporation of boron oxide proceeds in an oxygen atmosphere, and under these conditions  $\text{BO}_2$  molecules can be easily identified at temperatures of 1200-1400°K. Such conditions make it possible to carry out precision measurements of the equilibrium constant of the gas-phase reaction



To determine the heats of formation of  $\text{BO}_2^-$  we studied the anionic exchange reaction with the participation of  $\text{BO}_2^-$  and  $\text{AlF}_4^-$ .

Experimental Procedure. Enthalpy of Formation of  $\text{BO}_2$  (gas). Measurements of  $K_p$  for the reaction (3) were performed by the mass-spectrometric method, representing a combination of Knudsen's effusion method for determining the vapor pressure and a mass-spectrometer, which enables analysis of the composition of the gas phase of the systems of interest. The measurements were performed on an MI-1201 apparatus, reequipped for high-temperature studies, with an ionizing voltage of 50-70 V. A mobile diaphragm, by moving which it was possible to separate the molecular beam from the background of the device, was placed between the opening in the effusion chamber and the region of ionization. Platinum effusion chambers with the evaporation to effusion area ratio  $R = 400\text{-}1500$  were employed in the experiments. The effusion chamber was heated by radiation with the help of a molybdenum wire coil. The temperature was measured with Pt/Pt-10% Rh thermocouples, calibrated to the melting point of KCl. The ions were identified from their mass numbers and the isotropic distribution. To determine the equilibrium constant of the reaction (3) it is necessary to measure the oxygen partial pressures in the system as well as the pressures of  $\text{B}_2\text{O}_3$  and  $\text{BO}_2$ .

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TABLE 1. Relative Mass Spectra of Saturated Vapors of the Systems Studied and of Pure B<sub>2</sub>O<sub>3</sub>

System	T, K	I(M <sup>+</sup> )	I(O <sub>2</sub> <sup>+</sup> )	I(MO <sup>+</sup> )	I(M <sub>2</sub> O <sub>3</sub> <sup>+</sup> )	I(MBO <sub>2</sub> <sup>+</sup> )	I(B <sub>2</sub> O <sub>3</sub> <sup>+</sup> )	I(B <sub>3</sub> O <sub>4</sub> <sup>+</sup> )	I(BO <sub>2</sub> )	I(BO <sup>+</sup> )
Bi <sub>2</sub> O <sub>3</sub> - B <sub>2</sub> O <sub>3</sub>	1285	35 700	12 000	-	-	550	100	6.9	34.9	18.6
	1427	17 160	1 800	-	-	412	100	7.8	17.6	14.7
PbO - B <sub>2</sub> O <sub>3</sub>	1305	4 000	610	1330	12.5	97	100	4.4	14.0	3.5
	1391	1 760	88.4	730	1.8	88	100	4.7	9.1	2.5
ZnO - B <sub>2</sub> O <sub>3</sub>	1292	274	44.2	-	-	-	100	6.5	4.0	7.0
	1400	411	230	-	-	-	100	5.2	5.8	3.8
B <sub>2</sub> O <sub>3</sub>	1435	-	-	-	-	-	100	4.6	1.5	4.0

Measurement of B<sub>2</sub>O<sub>3</sub> and BO<sub>2</sub> Pressures. The mass spectrum of the system studied contains the BO<sub>2</sub><sup>+</sup> ion, which has two molecular precursors - the molecules BO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub>. Therefore, the first problem is to separate the total magnitude of the ionic current I(BO<sub>2</sub><sup>+</sup>) into components formed from the molecules BO<sub>2</sub> - I(BO<sub>2</sub><sup>+</sup>, BO<sub>2</sub>) - and B<sub>2</sub>O<sub>3</sub> - I(BO<sub>2</sub><sup>+</sup>, B<sub>2</sub>O<sub>3</sub>). This problem is solved by the simplest method, namely, by comparing the mass-spectra of the system and of pure boron oxide, measured under identical conditions. This was achieved as follows. A weighed quantity of the system studied was placed into the effusion chamber. The evaporation was performed at the temperature T and at the same time the mass spectrum was recorded with constant energy of the ionizing electrons. The experiment continued until virtually pure boron oxide remained in the cell, which made it possible to record the mass spectrum above pure boron oxide. Table 1 shows the mass spectra of the saturated vapor of the systems and for pure boron oxide. Comparison of the mass spectra makes it possible to calculate the ionic current of BO<sub>2</sub> molecules from the equation

$$I(\text{BO}_2^+, \text{BO}_2) = I(\text{BO}_2^+) - bI(\text{B}_2\text{O}_3^+),$$

where  $b = I(\text{BO}_2^+, \text{B}_2\text{O}_3)/I(\text{B}_2\text{O}_3^+)$ . As one can see, the saturated vapor of the systems contains significant quantities of bismuth, lead, and zinc metaborates. The possibility of the formation of BO<sub>2</sub><sup>+</sup> ions with dissociative association of metaborates has not been excluded, but it is difficult to make a quantitative determination of these ions. However, because their content in the mass spectrum of metaborates of alkali metals is insignificant,  $I(\text{BO}_2^+)/I(\text{MBO}_2^+) \approx 0.01-0.001$ , the contribution of these ions to the total BO<sub>2</sub><sup>+</sup> ion current was neglected.

To check that the BO<sub>2</sub><sup>+</sup> ion in the vapors above pure boron oxide was formed primarily from B<sub>2</sub>O<sub>3</sub> molecules, the differences in the potentials at which BO<sub>2</sub><sup>+</sup> and B<sub>2</sub>O<sub>3</sub><sup>+</sup> ions appear in the vapors above the mixture and above pure boron oxide were measured. The value 0.3 eV was obtained in the first case and 5 eV in the second case. The result shows convincingly that the vapor above pure boron oxide consists virtually completely (more than 95%) of B<sub>2</sub>O<sub>3</sub> molecules, while the ion BO<sub>2</sub><sup>+</sup> is formed by dissociative ionization of B<sub>2</sub>O<sub>3</sub>. At the same time in the vapors of the system where the oxygen pressure is comparatively high the content of BO<sub>2</sub> molecules is comparable to that of B<sub>2</sub>O<sub>3</sub> molecules.

In order to transfer from the measured ionic currents to the partial pressures it is necessary to find the coefficient of sensitivity k in the equation

$$P = \frac{k}{\sigma_j} I_{ij} T.$$

In this work the apparatus was calibrated in the course of the experiment by measuring the equilibrium constants of the gas-phase and heterogeneous reactions, whose numerical values have been published in the literature. The following were employed.

1. The saturated vapor pressure of boron trioxide [2]. The sensitivity constant was calculated in those cases when at the end of the evaporation the mass spectrum of the saturated vapor of pure B<sub>2</sub>O<sub>3</sub> was recorded.

2. In the experiments with the participation of bismuth trioxide the calibration was performed based on the numerical value of the equilibrium constants of the reaction  $2\text{Bi} = \text{Bi}_2$  [4] and the measured ratio of the ionic currents  $I(\text{Bi}^+)/I(\text{Bi}_2^+)$ .

TABLE 2. Equilibrium Constants and Standard Enthalpies of the Reaction  $B_2O_3 + 1/2 O_2 = 2BO_2$

System	n	T, K	$K_p \cdot 10^*$	$\Delta H_s^0$ , kJ/mole
Bi <sub>2</sub> O <sub>3</sub> - B <sub>2</sub> O <sub>3</sub>	1	1285	2,47	233,0
	2	1293	2,68	233,6
	3	1302	2,96	234,2
	...	...	...	...
	13	1369	1,25	254,8
	14	1360	1,50	252,7
	15	1427	5,11	251,0
		Mean value		246,5±6,2 kJ/mole <sup>†</sup>
PbO - B <sub>2</sub> O <sub>3</sub>	1	1296	1,10	243,3
	2	1305	2,70	236,1
	3	1314	0,72	252,2
	...	...	...	...
	14	1330	1,50	247,2
	15	1356	1,10	255,1
	16	1369	2,50	248,1
		Mean value		250,0±3,9 kJ/mole
ZnO - B <sub>2</sub> O <sub>3</sub>	1	1350	1,70	249,6
	2	1360	1,30	254,7
	3	1384	1,90	254,6
	...	...	...	...
	22	1400	2,30	255,4
	23	1422	3,40	254,7
	24	1484	9,20	254,1
		Mean value		253,6±1,9 kJ/mole

\* $K_p$  is a dimensionless quantity, scaled to the standard state 1 atm =  $1.013 \cdot 10^5$  Pa.  
<sup>†</sup>The error equals  $\sigma_{0,95}/\sqrt{n}$ .

3. In the experiments with the participation of lead oxide the experimentally obtained values of  $I(PbO^+)$  and the ratio  $I(PbO^+)/I(Pb_2O_2^+)$  were used for calibration. The ratio made it possible to calculate the activity of the oxide  $a_{PbO}$  in the system, and the value of  $I(PbO^+)$  made it possible to calculate the sensitivity coefficient  $k$ . At the same time the partial pressure of the monomer  $p_{PbO}$  in the system was calculated using the equation  $p_{PbO} = a_{PbO} p_{PbO}^0$ . The value of  $p_{PbO}^0$  was taken from [2]. In all the calculations the following values of the ionization cross sections were employed:  $\sigma_{B_2O_3} = 4.35 \text{ \AA}^2$ ,  $\sigma_{BO_2} = 3.25 \text{ \AA}^2$  [3],  $\sigma_{O_2} = 1.8 \sigma_0 = 2.3 \text{ \AA}^2$  [5],  $\sigma_{Bi} = 8.12 \text{ \AA}^2$ ,  $\sigma_{PbO} = 9.12 \text{ \AA}^2$  [6].

Measurement of the Oxygen Pressure. The oxygen pressure in the systems was determined by two independent methods.

1. The total  $O_2^+$  signal and the signal after the molecular beam was covered were measured. As a result of the covering, the signal in different experiments equaled 50-80% of the total signal, and this part of the signal served in later calculations as a measure of the oxygen pressure.

2. The oxygen pressure was calculated from the condition of conservation of the stoichiometry of the oxide, i.e., it was assumed that in the course of evaporation the system is not enriched with dissociation products. For example, the oxygen pressure in the system  $Bi_2O_3-B_2O_3$  was calculated using the formula

$$p_{O_2} = \frac{3}{4} p_{Bi} \sqrt{M_{O_2}/M_{Bi}}$$

which follows from the condition that the evaporation of  $Bi_2O_3$  be congruent under conditions of molecular efflux, i.e., from the condition  $\rho_{Bi}/\rho_{O_2} = 4/3$ , where  $\rho = p/(2\pi MkT)^{1/2}$  is given in molecules/(cm<sup>2</sup>·sec).

The oxygen partial pressures, calculated from the condition of congruent evaporation and determined based on the overlapping part of the signal  $I(O_2^+)$ , differed by less than 50% at relatively low temperatures (up to 1300°K for all systems). At higher temperatures the values differed by a factor of three. For this reason the values of the oxygen partial

TABLE 3. Equilibrium Constants and Enthalpies of the Reactions (4)

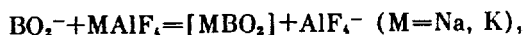
System	T, K	ln K <sub>p</sub>	s <sub>i</sub> <sup>*</sup>	n <sub>i</sub> <sup>†</sup>	-ΔH <sub>0</sub> <sup>‡</sup> , kJ/mole
NaBO <sub>2</sub> - NaAlF <sub>4</sub>	951	23,08	0,17	2	356,7
	961	22,52	0,05	2	355,9
	970	21,38	0,44	2	354,0
	986	21,42	0,29	6	355,9
	993	21,10	0,04	2	355,8
	1013	19,69	-	2	350,9
	1020	18,99	-	1	347,3
	1029	19,36	-	1	353,5
	1068	17,55	-	1	350,5
KBO <sub>2</sub> - KAlF <sub>4</sub>	1026	16,48	0,19	3	ΔH <sub>0</sub> <sup>°</sup> = -355 ± 13 ‡ 330,7
	1035	15,94	0,18	2	321,9
					ΔH <sub>0</sub> <sup>°</sup> = -330 ± 16 ‡

\*S<sub>i</sub> is the standard deviation of a separate measurement.  
 †n<sub>i</sub> is the number of measurements at a given temperature.  
 ‡The total error, including the error in determining the thermodynamic functions of the participants in the reaction, is shown.

pressures calculated from the condition of congruent evaporation were employed in all calculations of the equilibrium constants.

Table 2 shows the equilibrium constants and the standard enthalpies of the reaction (3), calculated from the third law of thermodynamics. Combined analysis of all experimental data for the three systems gives the value ΔH<sub>0</sub><sup>°</sup> (3) = 250.0 ± 2.2 kJ/mole. Here the arithmetic mean value of the enthalpy of the reaction is presented with a 95% probability of reproducibility. The value of the enthalpy of the reaction (3) corresponds to the standard enthalpy of formation ΔH<sub>f,0</sub><sup>°</sup> [BO<sub>2</sub> (gas)] = -292.1 ± 8.4 kJ/mole. The thermodynamic functions of the participants in the reaction (3) and the enthalpy of formation ΔH<sub>f,0</sub><sup>°</sup> (B<sub>2</sub>O<sub>3</sub>), required for the calculations, were taken from [2].

Enthalpy of Formation of the BO<sub>2</sub><sup>-</sup> Ion. The enthalpy of formation of BO<sub>2</sub><sup>-</sup> was determined by the method of ion-molecular equilibria. The equilibrium constants of the ion-exchange reactions



$$K_p = \frac{p_{\text{AlF}_4^-} \cdot a_{\text{MBO}_2}}{p_{\text{BO}_2^-} \cdot p_{\text{MAlF}_4}}$$

were studied.

The brackets indicate that the metaborate of the alkali metal in the condensed phase is included in the equilibrium. The method for carrying out the experiments is described in detail in [7]. The system MBO<sub>2</sub>-MAlF<sub>4</sub> (5 mole %) was placed into the effusion chamber. The ratios of the partial pressures of the ions were calculated from the measured ionic currents of AlF<sub>4</sub><sup>-</sup> and BO<sub>2</sub><sup>-</sup>. The partial pressure of MAlF<sub>4</sub> was determined through the measured intensities of the ionic currents of MAl<sub>2</sub>F<sub>8</sub><sup>-</sup> and AlF<sub>4</sub><sup>-</sup> using the equilibrium constant of the reaction



The numerical value of the equilibrium constant of the reaction (5) is taken from [8].

The activities of MBO<sub>2</sub> were determined from the values of the ratios of the ionic currents of MB<sub>2</sub>O<sub>4</sub><sup>-</sup> and BO<sub>2</sub><sup>-</sup> and the equilibrium constant of the reaction



The values of K<sub>p</sub> for (6) were calculated from the results of experiments with pure sodium and potassium metaborates, log K<sub>p</sub> (6) = -12,800/T + 10.9 for NaBO<sub>2</sub>, log K<sub>p</sub> (6) = -14,100/T + 12.2 for KBO<sub>2</sub>.

The enthalpy of the reaction (4) was calculated using the third law of thermodynamics (Table 3). The required thermodynamic functions of the participants of the reaction were taken from [2]. The enthalpies of formation of the gas-phase compounds  $\text{AlF}_4^-$ ,  $\text{NaAlF}_4$ ,  $\text{KAlF}_4$  and solid sodium and potassium metaborates [2] were used to calculate the enthalpy of formation of  $\text{BO}_2^-$ . In the system  $\text{NaBO}_2\text{-NaAlF}_4$ ,  $\Delta H_0^\circ(4) = -355 \pm 13$  kJ/mole, which gives  $\Delta H_{f,0}^\circ(\text{BO}_2^-) = -718 \pm 17$  kJ/mole. In the system  $\text{KBO}_2\text{-KAlF}_4$ ,  $\Delta H_0^\circ(4) = -330 \pm 16$  kJ/mole, which gives the value  $\Delta H_{f,0}^\circ(\text{BO}_2^-) = -699 \pm 22$  kJ/mole. The mean value  $\Delta H_{f,0}^\circ(\text{BO}_2^-) = -709 \pm 16$  kJ/mole is recommended. The electron affinity  $\text{EA}(\text{BO}_2) = 417 \pm 18$  kJ/mole.

All experimental results on the determination of the enthalpy of formation of gaseous  $\text{BO}_2^-$  are presented in the handbook [2]. Our data agree satisfactorily with the data of [10], but differ significantly from the results of [12], which were the main results used in [2].

In [3] a somewhat lower value was obtained for  $\Delta H_{f,0}^\circ[\text{BO}_2(\text{gas})]$  than that in this work, but no inconsistencies are observed. In this work the results of the investigation of the equilibrium (3) in the three oxide systems were actually obtained independently of one another, and the good agreement between the values found and the small error in the reproducibility indicate that the enthalpy of formation of  $\Delta H_{f,0}^\circ(\text{BO}_2)$  is determined with adequate accuracy.

The situation is more complicated in the case of the determination of the heats of formation of the gaseous anion  $\text{BO}_2^-$ . The enthalpy of formation adopted in [2]  $\Delta H_{f,0}^\circ(\text{BO}_2^-) = -685 \pm 25$  kJ/mole is the average of the values  $-663 \pm 20$  and  $-703 \pm 25$  kJ/mole, obtained by the mass-spectrometric method [13] and in the study of the ion-molecular reactions in flames [14]. The data from these studies differ with one another and from our results. The disagreements are in all probability caused by the methodical characteristics of each method used to carry out the investigation.

On the whole the results of this work lead to lower values of the heat of formation of  $\text{BO}_2$  and higher values for  $\text{BO}_2^-$ . There is a larger disagreement with the published data for the electron affinity. In this work  $\text{EA}(\text{BO}_2) = 4.33$  eV, while in [2]  $\text{EA}(\text{BO}_2) = 3.73$  eV.

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