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Received 18th November 1991

Translated from *Zhurnal Fizicheskoi Khimii* **66** 3160-3165 (1992)

U.D.C. 541

Determination of the enthalpy of formation of the BiO^- and BiO_2^- ions by the ion-molecule equilibrium method

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ABSTRACT. The Knudsen effusion method with spectroscopic detection of negative ions has been used to measure equilibrium constants involving BiO^- and BiO_2^- ions. The enthalpy of formation $\Delta_f H_0^\circ(\text{BiO}^-) = -33 \pm 7 \text{ kJ mol}^{-1}$ and $\Delta_f H_0^\circ(\text{BiO}_2^-) = -187 \pm 10 \text{ kJ mol}^{-1}$ and the electron affinities $EA(\text{BiO}) = 156 \pm 14 \text{ kJ mol}^{-1}$ and $EA(\text{BiO}_2) = 311 \pm 27 \text{ kJ mol}^{-1}$ have been determined.

This work is a continuation of our systematic study of the thermodynamic properties of negative ions containing oxygen. The energetics of negative ions must be known in order to model the capture of electrons by electronegative additives in a low-temperature plasma.³ Furthermore, the presence of negative ions in the vapour of inorganic compounds allows the thermodynamic activity of oxygen to be determined in high-temperature systems.⁴ The results obtained can be used to develop a method of determining the activity of Bi_2O_3 .

Experimental

The measurements were made with an MX-1303 mass spectrometer (200 mmHg, 60 °C), modified for studies of the ion-molecule equilibrium.^{5,6} The temperature was measured with a Pt-Pt/Rh (10%) thermocouple, and held constant to within ± 1 K by a VRT-3 temperature regulator. The precision of the temperature measurement was ± 4 K. The ion currents were measured with a VEU-6 channel secondary electron multiplier.

Equilibrium constants involving the BiO_2^- ion. We have studied the evaporation of Bi_2O_3 with small additions of Cr_2O_3 and K_2CO_3 . The role of the additives was to increase the concentration of electrons in the Bi_2O_3 vapour, thus favouring the formation of measurable concentrations of BiO^- and BiO_2^- (the problem has

discussed¹ in the case of CoO). The additives also produced negative ions containing chromium, which were used as standards. The negative ions detected under these conditions are listed in Table 1.

Table 1. Mass spectra of the negative ions in the Bi₂O₃-Cr₂O₃-K₂CrO₄ system at 1182 K.

Experiment	Bi ₂ O ₃ , mol%	Cr ₂ O ₃ , mol%	I(CrO ₃ ⁻)	I(CrO ₄ ⁻)	I(Cr ₂ O ₆ ⁻)	I(BiO ₂ ⁻)	I(BiO ⁻)
1	91.4	3.3	100	0.4	2.6	0.3	0.02
2	91.1	3.5	100	0.5	3.7	0.18	0.02

Notes. The ion currents (*I*, relative intensity) were measured with an electron multiplier. The ion current for the ⁵²Cr isotope are quoted in the case of ions containing chromium.

Similarly, the equilibrium constant of the reaction (3) can be written in terms of the measured ion currents as

$$\ln K^\circ(3) = \ln \frac{I^2(\text{BiO}^-) I(\text{CrO}_4^-) I^2(\text{Cr}_2\text{O}_6^-)}{I^2(\text{CrO}_3^-)} - \ln K^\circ(2) + 3.15.$$

The experimental data needed for calculating the equilibrium constant of the reaction (3) are given in Table 3.

Table 2. Experimental data for the reaction (1).

T, K	-ln K°(1)	s _i	n _i	Δ _r H ₀ °(1), kJ mol ⁻¹	T, K	-ln K°(1)	s _i	n _i	Δ _r H ₀ °(1), kJ mol ⁻¹
Expt. 1					Expt. 2				
1070	24.33	0.53	2	179.8	1089	23.72	0.73	4	176.6
1089	23.33	0.26	4	173.0	1108	23.90	0.59	10	180.4
1108	23.35	0.43	5	175.3	1127	23.46	0.56	10	178.4
1127	23.09	0.15	4	174.9	1145	23.44	0.61	12	180.2
1145	23.24	0.54	6	178.3	1164	22.92	0.61	5	177.2
1182	22.36	0.36	4	173.6	1182	22.67	0.63	2	178.6

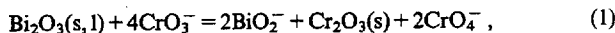
Symbols: s_i are the standard deviations of an individual determination from the mean;⁷ n_i is the number of measurements at the given temperature.

Table 3. Experimental data for the reaction (3).

T, K	-ln K°(3)	s _i	n _i	Δ _r H ₀ °(3), kJ mol ⁻¹
experiment 1				
1145	39.98	-	1	269.9
1182	38.16	0.53	4	258.6
experiment 2				
1108	38.64	0.19	3	250.8
1127	39.44	0.82	10	261.6
1145	39.65	0.56	9	266.7
1164	38.88	0.37	5	262.6
1182	37.91	0.42	2	256.2

Thermodynamic functions of BiO⁻ and BiO₂⁻. The thermodynamic functions were calculated by statistical thermodynamics from the chosen molecular constants (Table 4). Konnov et al.⁸ studied the IR spectra of the Bi + O₂ system by the matrix isolation method, and showed that the BiO₂ molecule has a nonlinear structure with C_{2v} symmetry and a bond angle ∠OBiO = 112 ± 10°. The frequencies of the symmetric (ν₁ = 499 cm⁻¹) and of the antisymmetric vibrations (ν₃ = 751 cm⁻¹) were determined experimentally. The Bi-O interatomic distance was taken to be 1.98 Å. The frequency of the bending vibrations has been found⁹ to be ν₂ = 231 cm⁻¹. The molecular constants of the BiO₂⁻ negative ion were assumed to be

The enthalpy of formation of the BiO₂⁻ ion was determined by measuring the equilibrium constant of the reaction



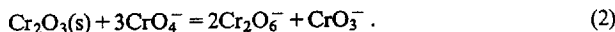
which can be written

$$K^\circ(1) = \frac{p^2(\text{BiO}_2^-) p^2(\text{CrO}_4^-) a(\text{Cr}_2\text{O}_3)}{p^4(\text{CrO}_3^-) a(\text{Bi}_2\text{O}_3)}$$

The activity of Bi₂O₃ (the main component of the system, >90%) was taken to be unity. The activity of chromium oxide was determined from the ratio of the partial pressures of the CrO₃⁻, CrO₄⁻, and Cr₂O₆⁻ ions

$$a(\text{Cr}_2\text{O}_3) = \frac{p^2(\text{Cr}_2\text{O}_6^-) p(\text{CrO}_3^-)}{p^3(\text{CrO}_4^-)} \frac{1}{K^\circ(2)}$$

where K°(2) is the equilibrium constant of the reaction



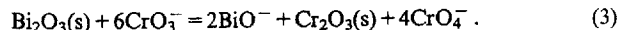
As reported,⁴ ln K°(2) = 9734/T + 3.28.

Replacing the partial pressures by the measured ion currents,⁵ using the above equation for the activity of Cr₂O₃, gives the following formula for the equilibrium constant of reaction (1):

$$\ln K^\circ(1) = \ln \frac{I^2(\text{BiO}_2^-) I^2(\text{Cr}_2\text{O}_6^-)}{I^2(\text{CrO}_3^-) I(\text{CrO}_4^-)} - \ln K^\circ(2) + 2.98.$$

Experimental data needed to determine the equilibrium constant of reaction (1) are given in Table 2.

Equilibrium constants involving the BiO⁻ ion. The enthalpy of formation of the BiO⁻ ion was determined by measuring the equilibrium constant of the reaction



The activity of Cr₂O₃ was determined as in the case of BiO₂⁻.

equal to the corresponding values for the BiO_2 molecule ($I_A I_B I_C = 1.06 \times 10^{-114} \text{ g}^3 \text{ cm}^6$) except for the degeneracy of the electronic ground state ($g_0 = 1$). The error of Φ_{1000}^0 was estimated to be $\pm 6.3 \text{ J mol}^{-1} \text{ K}^{-1}$.

Table 4. Thermodynamic functions of the BiO^- and BiO_2^- ions (Φ^0 in $\text{J mol}^{-1} \text{ K}^{-1}$, H^0 in kJ mol^{-1}).

T, K	Φ^0	$\bar{H}_T^0 - H_0^0$	Φ^0		$H_T^0 - H_0^0$
			BiO^-	BiO_2^-	
298	210.1	9.0	242.3	12.1	
400	219.1	12.4	254.6	17.3	
600	232.0	19.5	272.9	28.1	
800	241.4	26.8	286.6	39.2	
1000	249.0	34.1	297.8	50.6	
1200	255.2	41.6	307.1	62.0	
1400	260.6	49.1	315.1	73.5	
1600	265.3	56.7	322.2	85.0	
1800	269.5	64.3	328.5	96.6	
2000	273.3	72.1	334.1	108.2	

The thermodynamic functions of the BiO molecule are given in a recent review.¹⁰ The molecular constants of the BiO^- ion are assumed to be the same as for the BiO molecule, except for the degeneracy of the electronic ground state ($g_0 = 1$). The error of Φ_{1000}^0 was estimated to be approximately $\pm 0.5 \text{ J mol}^{-1} \text{ K}^{-1}$.

Thermodynamic functions and enthalpy of formation of Bi_2O_3 . The polymorphism and the thermodynamic properties of bismuth oxide have been studied extensively.¹¹⁻²⁵ X-Ray structural studies at various temperatures have identified four crystalline forms of bismuth oxide: the low-temperature $\alpha\text{-Bi}_2\text{O}_3$, the high-temperature $\delta\text{-Bi}_2\text{O}_3$, and the two metastable β and $\gamma\text{-Bi}_2\text{O}_3$ phases. It has been shown that upon being heated the monoclinic $\alpha\text{-Bi}_2\text{O}_3$ is converted into the cubic $\delta\text{-Bi}_2\text{O}_3$ at $1003 \pm 2 \text{ K}$, and that the latter phase is stable up to the melting point of the bismuth oxide (1098 K).²⁶

Hysteresis phenomena are observed on cooling, and the polymorphic transformations depend on the gas medium, the temperature to which the bismuth oxide has been heated, the hold time at that temperature, the cooling rate, and the impurity content of the sample.

The enthalpy of the solid-state $\alpha\text{-}\delta$ transition was taken to be $33.05 \text{ kJ mol}^{-1}$ (as reported²⁴). The enthalpies of melting determined electrochemically and calorimetrically are markedly different (58.8 ¹⁸ and 10.9 kJ mol^{-1} ²² respectively). Since the calorimetric measurements appear to be the more reliable a heat of melting of $10.9 \pm 0.8 \text{ kJ mol}^{-1}$ was used in the present work.

The specific heat of Bi_2O_3 has been studied experimentally at $11\text{--}50 \text{ K}$ ²⁷ and at $60\text{--}298 \text{ K}$.²⁶ In order to obtain self-consistent results, data from low-temperature calorimetry^{22,23} ($11\text{--}300 \text{ K}$) and high-temperature handbook data²⁸ ($400\text{--}800$) were jointly processed by using Reshetnikov's function.²⁹

From the chosen specific heat, enthalpies, and temperatures of phase transitions we calculated the thermodynamic functions of Bi_2O_3 (see Table 5). The error of the reduced Gibbs free energy of Bi_2O_3 at 1000 K is estimated to be $\pm 4 \text{ J mol}^{-1} \text{ K}^{-1}$.

Table 5. Thermodynamic functions of Bi_2O_3 (cr., l.).

T, K	$H_T^0 - H_0^0$ kJ mol^{-1}	C_p	S_T^0	Φ_T^0
100	3.2	65.3	55.4	22.9
200	11.5	95.5	111.5	53.9
298.15	21.6	109.4	152.4	79.9
300	21.8	109.6	153.1	80.3
400	33.2	117.7	189.9	102.8
500	42.3	123.0	212.8	122.2
600	57.8	126.7	235.5	139.2
700	70.6	129.4	255.3	154.4
800	83.7	131.4	272.7	168.1
900	96.9	133.1	288.3	180.6
1000	110.2	134.4	302.4	192.1
1003	110.7	144.6	302.8	192.4
1003	143.8	144.6	335.8	192.4
1098	157.4	144.6	348.8	205.5
1098	168.3	150.9	348.8	205.5
1100	168.6	150.9	359.0	205.8
1200	183.9	150.9	372.2	218.9
1300	199.2	150.9	384.3	231.0
1400	214.5	150.9	395.4	242.2
1500	229.9	150.9	405.9	252.6

The enthalpy of formation of Bi_2O_3 at 298 K was taken from Glushko's tabulations³⁰ and recalculated for 0 K by using functions calculated here. The resulting value ($-573.5 \pm \text{kJ mol}^{-1}$) agrees well with the calculation by Gorbunov et al.²⁷

Enthalpies of formation of the BiO^- and BiO_2^- ions. The enthalpies of the reactions, calculated by the third law thermodynamics, were $\Delta_f H_0^0(1) = 178 \pm 24$ (± 2) kJ mol^{-1} , $\Delta_f H_0^0(2) = 262 \pm 34$ (± 4) kJ mol^{-1} . The reduced Gibbs energies for Bi_2O_3 , BiO^- , and BiO_2^- were calculated by the method of Glushko et al.³¹ and those for Cr_2O_3 and CrO_3 were taken from standard tabulations and those for CrO_4 were taken from our previous paper.³¹ The errors were calculated by allowing for the reproducibility errors (shown in brackets) and for the error of the chosen thermodynamic functions.

The enthalpies of formation of BiO^- and BiO_2^- were calculated by using the enthalpies of formation $\Delta_f H_0^0(\text{Cr}_2\text{O}_3) = -1134.8 \pm \text{kJ mol}^{-1}$,³² $\Delta_f H_0^0(\text{CrO}_3) = -669 \pm 9 \text{ kJ mol}^{-1}$, $\Delta_f H_0^0(\text{CrO}_4) = -781 \pm 11 \text{ kJ mol}^{-1}$.³¹ The results are $\Delta_f H_0^0(\text{BiO}_2^-) = -187 \pm 10 \text{ kJ mol}^{-1}$ and $\Delta_f H_0^0(\text{BiO}^-) = -33 \text{ kJ mol}^{-1}$.

In the calculation of the errors of the enthalpies of formation of BiO^- and BiO_2^- we allowed for the mutual correlation of the thermodynamic parameters of the standard ions: $\text{Cov}\{\Delta_f H_0^0(\text{CrO}_3), \Delta_f H_0^0(\text{CrO}_4)\} = 58$ (kJ mol^{-1}), $\text{Cov}\{\Delta_f H_0^0(\text{CrO}_3), \Phi^0(\text{CrO}_3)\} = 20$ (kJ mol^{-1}).

$\text{Cov}\{\Delta_f H_0^\circ(\text{CrO}_4^-)\} = 43 \text{ kJ} \cdot \text{J mol}^{-2} \cdot \text{K}^{-1}$ (using the formula already published²). The covariances were obtained during the solution of the overdetermined system of equations.³¹

The enthalpy of formation $\Delta_f H_0^\circ(\text{BiO}, \text{g}) = 123 \pm 13 \text{ kJ mol}^{-1}$ was used by Pedley and Marshall.¹⁰ Minaeva³³ calculated the enthalpy of formation $\Delta_f H_0^\circ(\text{BiO}_2, \text{g}) = 124 \pm 25 \text{ kJ mol}^{-1}$. By using these values we obtained the electron affinities $EA(\text{BiO}) = 156 \pm 14 \text{ kJ mol}^{-1}$ and $EA(\text{BiO}_2) = 311 \pm 27 \text{ kJ mol}^{-1}$.

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Received 27th January 1992

Translated from *Zhurnal Neorganicheskoi Khimii* **66** 3166—3170 (1992)

U.D.C. 541.11:549.1

Specific heat and thermodynamic functions of copper silicate $\text{CuSiO}_3 \cdot \text{H}_2\text{O}$ at 6—322 K

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ABSTRACT. The specific heat of copper silicate $\text{CuSiO}_3 \cdot \text{H}_2\text{O}$ has been measured by the adiabatic method at 6—322 K. The thermodynamic functions (entropy, enthalpy change, reduced Gibbs free energy) have been calculated for the whole temperature range. A phase transition with $T_c = 14.5 \text{ K}$ has been observed. The specific heat and the magnetic susceptibility of the sample have been studied in detail near the phase transition.

This paper describes a new stage of our continuing experimental study of the fundamental thermodynamic properties of copper minerals, aimed at providing information urgently needed for the construction of phase diagrams, for studies of mineral, rock, and ore formation processes, and in the solution of basic scientific problems underlying technological processes.

Copper silicate $\text{CuSiO}_3 \cdot \text{H}_2\text{O}$ (diopside) has a structure composed of six-membered silicon—oxygen rings, and belongs to the zeolite group; it has a trigonal symmetry, with elementary cell parameters $a_0 = 14.61 \text{ \AA}$ and $c_0 = 7.8 \text{ \AA}$. Belov¹ has reported a detailed study of diopside, which showed that the six-membered $[\text{Si}_6\text{O}_{18}]$ rings form columns parallel to the c axis in conjunction with six-membered ice-like $(\text{H}_2\text{O})_6$ rings, and are interconnected by Cu^{2+} ion. The latter ions have a four-fold coordination with respect to the end oxygen atoms of three different $[\text{Si}_6\text{O}_{18}]$ rings, expanded to a six-coordination by two oxygen atoms from water molecules (Fig. 1). It