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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 formatio of the BiO^- and BiO_2^- ions by the ion–molecule equilibrium method

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ABSTRACT. The Knudsen effusion method with m spectroscopic detection of negative ions has been used to meas equilibrium constants involving BiO^- and BiO_2^- ions. The enthal of formation $\Delta_f H^\circ_0(BiO^-) = -33 \pm 7$ kJ mol^{-1} and $\Delta_f H^\circ_0(BiO_2^-$ -187 ± 10 kJ mol^{-1} and the electron affinities $EA(BiO)$ = 156 14 kJ mol^{-1} and $EA(BiO_2)$ = 311 ± 27 kJ mol^{-1} have b determined.

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

Experimental

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

Equilibrium constants involving the BiO_2^- ion. We have studie evaporation of Bi_2O_3 with small additions of Cr_2O_3 and K_2C The role of the additives was to increase the concentratio electrons in the Bi_2O_3 vapour, thus favouring the formatio measurable concentrations of BiO^- and BiO_2^- (the problem has discussed[1] 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 $Bi_2O_3-Cr_2O_3-K_2CrO_4$ system at 1182 K.

Experiment	Bi_2O_3, mol%	Cr_2O_3, mol%	$I(CrO_3^-)$	$I(CrO_4^-)$	$I(Cr_2O_6^-)$	$I(BiO_2^-)$	$I(BiO^-)$
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 ^{52}Cr isotope are quoted in the case of ions containing chromium.

The enthalpy of formation of the BiO_2^- ion was determined by measuring the equilibrium constant of the reaction

$$Bi_2O_3(s,l)+4CrO_3^- = 2BiO_2^- + Cr_2O_3(s) + 2CrO_4^- , \quad (1)$$

which can be written

$$K^\circ(1)=\frac{p^2(BiO_2^-)\,p^2(CrO_4^-)}{p^4(CrO_3^-)}\,\frac{a(Cr_2O_3)}{a(Bi_2O_3)} .$$

The activity of Bi_2O_3 (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 CrO_3^-, CrO_4^-, and $Cr_2O_6^-$ ions

$$a(Cr_2O_3)=\frac{p^2(Cr_2O_6^-)\,p(CrO_3^-)}{p^3(CrO_4^-)}\,\frac{1}{K^\circ(2)},$$

where $K^\circ(2)$ is the equilibrium constant of the reaction

$$Cr_2O_3(s)+3CrO_4^- = 2Cr_2O_6^- + CrO_3^- . \quad (2)$$

As reported,[4] $\ln K^\circ(2) = 9734/T + 3.28$.

Replacing the partial pressures by the measured ion currents,[5] using the above equation for the activity of Cr_2O_3, gives the following formula for the equilibrium constant of reaction (1):

$$\ln K^\circ(1)=\ln\frac{I^2(BiO_2^-)\,I^2(Cr_2O_6^-)}{I^5(CrO_3^-)\,I(CrO_4^-)}-\ln K^\circ(2)+2.98.$$

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

$$Bi_2O_3(s)+6CrO_3^- = 2BiO^- + Cr_2O_3(s) + 4CrO_4^- . \quad (3)$$

The activity of Cr_2O_3 was determined as in the case of BiO_2^-. Similarly, the equilibrium constant of the reaction (3) can be written in terms of the measured ion currents as

$$\ln K^\circ(3)=\ln\frac{I^2(BiO^-)\,I(CrO_4^-)\,I^2(Cr_2O_6^-)}{I^7(CrO_3^-)}-\ln K^\circ(2)+3.15.$$

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	$-\ln K^\circ(1)$	s_i	n_i	$\Delta_r H_0^\circ(1)$, kJ mol^{-1}	T, K	$-\ln K^\circ(1)$	s_i	n_i	$\Delta_r H_0^\circ(1)$, 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	22.87	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	$-\ln K^\circ(3)$	s_i	n_i	$\Delta_r H_0^\circ(3)$, 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 BiO_2^-. 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 + O_2 system by the matrix isolation method, and showed that the BiO_2 molecule has a nonlinear structure with C_{2v} symmetry and a bond angle $\angle OBiO = 112 \pm 10^\circ$. The frequencies of the symmetric (ν_1 = 499 cm^{-1}) and of the antisymmetric vibrations (ν_3 = 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 found[9] to be ν_2 = 231 cm^{-1}. The molecular constants of the BiO_2^- negative ion were assumed to be equal to the corresponding values for the BiO_2 molecule ($I_AI_BI_C$ = 1.06 × 10^{-114} g^3 cm^6) except for the degeneracy of the electronic ground state (g_0 = 1). The error of Φ°_{1000} was estimated to be ±6.3 J mol^{-1} K^{-1}.

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

T, K	Φ°	$H^\circ_T-H^\circ_0$	Φ°	$H^\circ_T-H^\circ_0$
	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} was estimated to be approximately ±0.5 J mol^{-1} 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 α-Bi_2O_3, the high-temperature δ-Bi_2O_3, and the two metastable β and γ-Bi_2O_3 phases. It has been shown that upon being heated the monoclinic α-Bi_2O_3 is converted into the cubic δ-Bi_2O_3 at 1003 ± 2 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 α–δ transition was taken to be 33.05 kJ mol^{-1} (as reported[24]). 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 ± 0.8 kJ mol^{-1} was used in the present work.

The specific heat of Bi_2O_3 has been studied experimentally at 11–50 K [27] and at 60–298 K.[26] In order to obtain self-consistent results, data from low-temperature calorimetry[22,23] (11–300 K) and high-temperature handbook data[28] (400–800) 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 Bi2O3 (see Table 5). The error of the reduced Gibbs free en of Bi_2O_3 at 1000 K is estimated to be ±4 J mol^{-1} K^{-1}.

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

T, K	$H^\circ_T-H^\circ_0$ kJ mol^{-1}	C_p	S°_T	Φ°_T
		J mol^{-1} K^{-1}		
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 f Glushko's tabulations[30] and recalculated for 0 K by using functions calculated here. The resulting value (−573.5 ± kJ mol^{-1}) agrees well with the calculation by Gorbunov et al.[27]

Enthalpies of formation of the BiO^- and BiO_2^- ions. enthalpies of the reactions, calculated by the third law thermodynamics, were $\Delta_r H^\circ_0(1)$ = 178 ± 24 (±2) kJ mol^{-1} $\Delta_r H^\circ_0(2)$ = 262 ± 34 (±4) kJ mol^{-1}. The reduced Gibbs energies for Bi_2O_3, BiO^-, and BiO_2^- were calculated by the wri those for Cr_2O_3 and CrO_3^- were taken from standard tabulatio and those for CrO_4^- were taken from our previous paper.[31] errors were calculated by allowing for the reproducibility e (shown in brackets) and for the error of the chosen thermodyn functions.

The enthalpies of formation of BiO^- and BiO_2^- were calcu by using the enthalpies of formation $\Delta_r H^\circ_0(Cr_2O_3)$ = −1134.8 ± kJ mol^{-1},[32] $\Delta_r H^\circ_0(CrO_3^-)$ = −669 ± 9 kJ mol^{-1}, $\Delta_r H^\circ_0(CrO_4^-)$ = −781 ± 11 kJ mol^{-1}.[31] The result $\Delta_r H^\circ_0(BiO_2^-)$ = −187 ± 10 kJ mol^{-1} and $\Delta_f H^\circ_0(BiO^-)$ = −33 kJ mol^{-1}.

In the calculation of the errors of the enthalpies formation of BiO^- and BiO_2^- we allowed for the m correlation of the thermodynamic parameters of the stan ions: Cov{$\Delta_f H^\circ_0(CrO_3^-)$, $\Delta_f H^\circ_0(CrO_4^-)$} = 58 (kJ mol Cov{$\Delta_f H^\circ_0(CrO_3^-)$, $\Phi^\circ(CrO_3^-)$} = 20 kJ·J mol^{-1}

$Cov\{\Delta_f H^\circ_0(CrO_4^-)\} = 43$ kJ·J mol^{-2} K^{-1} (using the formula already published[2]). The covariances were obtained during the solution of the overdetermined system of equations.[31]

The enthalpy of formation $\Delta_f H^\circ_0(BiO, g) = 123 \pm 13$ kJ mol^{-1} was used by Pedley and Marshall.[10] Minaeva[33] calculated the enthalpy of formation $\Delta_f H^\circ_0(BiO_2, g) = 124 \pm 25$ kJ mol^{-1}. By using these values we obtained the electron affinities $EA(BiO) = 156 \pm 14$ kJ mol^{-1} and $EA(BiO_2) = 311 \pm 27$ 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 $CuSiO_3 \cdot H_2O$ at 6–322 K

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ABSTRACT. The specific heat of copper silicate $CuSiO_3 \cdot H_2O$ 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 $T_c = 14.5$ 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 $CuSiO_3 \cdot H_2O$ (dioptase) 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 $a_0 = 14.61$ Å and $c_0 = 7.8$ Å. Belov[1] has reported a detailed study of dioptase, which showed that the six-membered $[Si_6O_{18}]$ rings form columns parallel to the c axis in conjunction with six-membered ice-like $(H_2O)_6$ 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 $[Si_6O_{18}]$ rings, expanded to a six-coordination by two oxygen atoms from water molecules (Fig. 1). It