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THERMODYNAMIC INVESTIGATIONS IN THE Bi–O SYSTEM*

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Abstract

With the use of various calculation methods, unknown thermodynamic properties (TP) of Bi_2O_5 and BiO_2, as well as the temperature dependencies of reduced Gibbs energy (TDRGE) were determined. With the help of thermodynamic simulation (TS) methods at 300–1500 K, common $P=10^5$ Pa the thermal decompositions of condensed Bi_2O_5, BiO_2, Bi_2O_3 and BiO have been investigated in initial atmosphere of O_2 and Ar. Every condensed substance was presented as the individual phase.

It was found that Bi_xO_y oxides have temperature stability fields and also districts of possible mixture formation. During equilibrium heating of Bi_xO_y oxides the various types of phase transformations were observed. The characteristics of some transformations were estimated.

Keywords: decomposition, mixture, oxide, phase transformation, standard enthalpy of formation, thermodynamic simulation

Introduction

According to [1–4] in the Bi–O system condensed oxides BiO, Bi_2O_3, BiO_2 and Bi_2O_5 can exist. The thermodynamic properties (TP) and temperature dependencies of the reduced Gibbs energy (TDRGE) for BiO and Bi_2O_3 are known, and introduced into the databases IVTANTERMO and ASTRA.BAS [5]. For others oxides the known TP are presented in Table 1. It is clear, that those TP are not enough for calculation of the TDRGE of Bi_2O_5 and BiO_2.

The lack of and TDRGE for the above mentioned oxides does not permit reliable thermodynamic investigations into the systems containing bismuth and oxygen (high temperature superconductors, phases with ‘fast ionic transport’ [6, 7] and so on). As a rule, in published works (for example [6–10]) only the properties of condensed Bi_2O_3 are taken into account. According to above mentioned references, this oxide is the most stable in the Bi–O system. The data about temperature dependencies of partial pressures of gaseous components over Bi_2O_3 are known and summarized in [11]. But

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[*] Dedicated to Prof. Šesták in recognition of his outstanding activity in thermal analysis

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Table 1 Thermochemical properties and thermodynamic functions (TDRGE) for Bi_2O_3 and BiO_2

Oxide	ΔH^{o}_{298},/ kJ mol^{-1}	S^{0}_{298},/ J K^{-1} mol^{-1}	$H^{o}_{298}-H^{o}_{0}$/ J mol^{-1}	$T_{decomposition}$/ K	a^*	b^*	c^*	C_p at $T>T_{tr}$/ J K^{-1} mol^{-1}
Bi_2O_5	–185[13] –728.1	139.3±10.8	23230	423[3]	161.16	15.978	45.979	142.22
BiO_2	–335.2	74.3±7.7	11784	573[3] 538[2] 578[1]	69.07	13.432	3.700	75.60

	T /K	Coefficients q_i in equation $\Phi^*(T)=q_1+q_2\lg x+q_3x^{-2}+q_4x^{-1}+q_5x+q_6x^2+q_7x^3$						
		q_1	q_2	q_3	q_4	q_5	q_6	q_7
Bi_2O_5	298–423	121.548	38.5001	–0.00549424	0.977894	19.085	0	0
	423–6000	116.468	33.986	0	0.493134	0	0	0
BiO_2	298–573	57.7669	16.5001	–0.0004427	0.254093	16.00	0	0
	573–6000	62.6359	18.0601	0	0.275511	0	0	0

$^*a$, b, c are coefficients of equation: $C_p=a+b\cdot10^{-3}T-c\cdot10^5T^{-2}$/J K^{-1} mol^{-1}

$\Phi^*(T)$ in cal K^{-1} mol^{-1} for Bi_2O_5 and BiO_2 ($x=10^{-4}\cdot T$/K) we did not find in the available literature the full data about the thermal and thermodynamic stability of condensed Bi_2O_3. For others oxides those characteristics evidently are unknown too.

Therefore the goals of this work were:

- the determination of the unknown TP and TDRGE for condensed Bi_2O_5 and BiO_2; introduction of those data into the database ASTRA.OWN [12] for application in computer modeling;
- a study of temperature and composition dependencies of condensed BiO, Bi_2O_3, BiO_2 and Bi_2O_5 thermal decomposition.

Methods and procedures

Different calculation methods and procedures (for example [12]) were used for determination of the unknown TP of Bi_2O_5 and BiO_2. The essence of the main methods are given below, together with the calculation results.

Thermal decomposition of condensed Bi_xO_y was studied with the use of thermodynamic simulation (TS) methodology, which was described in detail in [5, 14, 15]. In the system 'Bi_xO_y+O_2(Ar)' we take into account the thermodynamic functions of condensed Bi, BiO, Bi_2O_3, gaseous Bi, Bi_2, Bi_3, Bi_4, BiO, Bi_4O_6, O_2, O and Ar [5], condensed Bi_2O_5, and BiO_2 (this work). Every condensed substance was present as an individual phase. The study was carried out from 300 to 1500 K with the steps of 10 to 100 K in initial O_2 or Ar atmosphere, common $P=10^5$ Pa with the application of program ASTRA.4 [5].

Determination of the TP and TDRGE for Bi_2O_5 and BiO_2

Bi_2O_5

The S^0_{298} values were calculated:

– from the empirical relation [16]:

$$\log S^0_{298} \approx 0.875 + 0.725 \log n \tag{1}$$

where S^0_{298} is in [cal mol^{-1} K^{-1}]; n is the number of atoms in the molecule;

– from the equation [17]

$$S^0_{298} \approx A \log M + B \tag{2}$$

where M is molecular mass of compound, A and B are empirical constants in the row of similar compounds (values of S^0_{298} for As_2O_5 and Sb_2O_5 were taken from [18]).

The average value of S^0_{298} equal to 139.4±10.8 J mol^{-1} K^{-1} we have taken as reliable.

The value of increment $H^0_{298}-H^0_0$ was calculated with the use of equation [19]

$$H^0_{298}-H^0_0 \approx 204\bar{S}^0_{298}\exp-\frac{\bar{S}^0_{298}}{23.5},\ \text{cal g-atom}^{-1} \tag{3}$$

where, $\bar{S}^0_{298}=S^0_{298}/n$ and n is the number of atoms in the molecule.

For determination of the dependence $C_p(T)$, first we calculated the $C^0_{p\,298}$ value. For it we used:

– the equation [12]:

$$C^{\;0}_{p\,298}\approx A\log M+B \tag{4}$$

where M, A and B are the same as in Eq. (2). (Values of $C^0_{p\,298}$ for As_2O_5 and Sb_2O_5 were taken from [18, 20]);

– calculation procedures based on the equations:

$$\begin{aligned} C^0_{p\,298}(Bi_2O_5)&\approx C^0_{p\,298}(Bi_2O_3)+2C^0_{p\,298}(O)\\ C^0_{p\,298}(Bi_2O_5)&\approx 2C^0_{p\,298}(BiO)+3C^0_{p\,298}(O)\end{aligned} \tag{5}$$

where $C^0_{p\,298}$ (Bi_2O_3) and $C^0_{p\,298}$ (BiO) were taken from the database ASTRA.BAS [5] and

$$C_p(T)(O)\approx 20.04+4.07\cdot 10^{-3}T-9.42\cdot 10^5T^{-2} \tag{6}$$

in J mol^{-1} K^{-1} were taken according to Dr. H. Yokokawa (private communication);

– with the use of the empirical equation [16]

$$C_p(T)\approx(7n+2)-(1.16n-1)\cdot 10^{-3}T^{-1}+(1.333n-66)\cdot 10^3T^{-2}, \tag{7}$$

in cal mol^{-1} K^{-1}, where n is the number of atoms in the molecule.

The average value $C^{\;0}_{p\,298}(Bi_2O_5)=114.2\pm 5.6$ J mol^{-1} K^{-1} was taken as reliable and used for calculation of $C_p(T)$ using the method, described in [21]. In result we found:

$$C_p(Bi_2O_3)\approx 161.161+15.978\cdot 10^{-3}T-45.979\cdot 10^5T^{-2},\ \text{J mol}^{-1}\ \text{K}^{-1} \tag{8}$$

According to [3], the Bi_2O_5 decomposition finished at 423 K; the change of enthalpy at this temperature was taken as equal to 0.

BiO_2

For the estimation of S^0_{298} values we used: – the Latimere method [12]; – Eq. (1); – comparison of $S^0_{298}(MO_2)$ (M = Hf, Sb, Pb, W) on row, period and diagonal of the Periodic System (a variant of the Birkengaime method [12]); – the additive method:

$$\begin{aligned} S^0_{298}(BiO_2)&\approx S^0_{298}(Bi_2O_3)-S^0_{298}(BiO),\\ S^0_{298}(BiO_2)&\approx S^0_{298}(Bi_2O_5)+S^0_{298}(Bi_2O_3))/4\end{aligned} \tag{9}$$

The values of S^0_{298} for Bi_2O_3 and BiO were taken from the database ASTRA.BAS [5], S^0_{298} (Bi_2O_5) was taken from this work, and the average=74.3±7.7 J mol^{-1} K^{-1} was taken as reliable.

The value of $H^0_{298}-H^0_0$ was calculated with the use of Eq. (3).

The values of $C^0_{p\,298}$ and the function $C_p(T)$ have been determined with the help of procedures described above for Bi_2O_5, and are equal to:

$$C^0_{p_{298}}(\mathrm{BiO_2})\approx 68.9\pm 4.1 \text{ and}$$
$$C_p(\mathrm{BiO_2})\approx 69.07+13.432\cdot 10^{-3}\cdot T-3.7\cdot 10^5\cdot T^{-2},\ \mathrm{J\,mol^{-1}K^{-1}} \tag{10}$$

The decomposition temperature of BiO_2 is 573 K according to [3]; the change of enthalpy at this temperature was taken as equal to 0.

For the determination of standard enthalpies of formation (ΔH^0_{298}, SEF) of Bi_2O_5 and BiO_2, various methods and estimations have been used.

First, we used the approximate ratios

$$\frac{T_{\mathrm{ph.tr}}(\mathrm{Sb_2O_5})}{T_{\mathrm{ph.tr}}(\mathrm{Bi_2O_5})}\approx\frac{\mathrm{SEF(Sb_2O_5)}}{\mathrm{SEF(Bi_2O_5)}},\ \frac{T_{\mathrm{ph.tr}}(\mathrm{SbO_2})}{T_{\mathrm{ph.tr}}(\mathrm{BiO_2})}\approx\frac{\mathrm{SEF(SbO_2)}}{\mathrm{SEF(BiO_2)}}, \tag{11}$$

using known data for Sb_2O_5 and SbO_2 taken from [4, 18, 20], and the estimated SEF values of Bi_2O_5 and BiO_2 were equal to –566.4 and –13.4 kJ mol^{-1}, respectively.

Then we used the universal linear approximation rules (ULAR) [22] (Fig. 1), and determined SEF values of Bi_2O_5 and BiO_2 equal to –615.3 and –307.2 kJ mol^{-1}, respectively. These values were calculated from linear regression equations, constructed with the use of known SEF for Bi_2O_3 and BiO [5]:

left side:

$$H^0_{\mathrm{at}}(j)\approx -307.5X(\mathrm{Bi}),\ \mathrm{kJ\ g\text{-}atom^{-1}} \tag{12}$$

right side:

$$H^0_{\mathrm{at}}(j)\approx 205(X(\mathrm{Bi})-1),\ \mathrm{kJ\ g\text{-}atom^{-1}} \tag{13}$$

In the last stage, we used the agreement procedure (AP) [23] on the supposition that only the SEF values for BiO and Bi_2O_3 are correct [5].

The SEF values for Bi_2O_5 and BiO_2 oxides were determined to be equal –728.1 and –335.2 kJ mol^{-1}, respectively.

The agreement procedure [23] allows correction of known, and determination of unknown, SEF values of related inorganic substances by use of the following function:

$$\Psi(j)=\frac{H^0_{\mathrm{at}}(j)}{\varphi_j},\ \mathrm{kJ\ g\text{-}atom^{-1}\ sort^{-1}} \tag{14}$$

where we named $\Psi(j)$ as the ‘sort standard enthalpy of formation’ (SSEF), for the j-th relative compound (in our case Bi_xO_y);

$$H^0_{\mathrm{at}}(j)=\frac{\Delta H^0_{298}(j)}{n_j},\ \mathrm{kJ\ g\text{-}atom^{-1}} \tag{15}$$

where n_j is the number of atoms in a molecule of the compounds;

$$\varphi_j = \left(\frac{x}{y}\right)_j \tag{16}$$

where we named φ_j as the 'sort' of the *j*-th related compound (in our case for Bi_2O_5 φ=2/5=0.4; for BiO_2 φ=1/2=0.5, and so on).

It was found that, for related compounds in definite systems, if the values of SEF were determined correctly, then in the coordinates '$\lg\Psi_j - \varphi_j$' we must observe linear dependencies

$$\lg\Psi_j \approx A + b\varphi_j \tag{17}$$

In our case

$$\lg\Psi_j = 2.6784 - 0.6584\varphi_j\text{, kJ g-atom}^{-1}\text{ sort}^{-1} \tag{18}$$

and calculations of SEF for Bi_2O_5 and BiO_2 were made with the use of Eq. (18). Note, that application of the ULAR to analysis of reference data gave an average divergence between calculated and reference data of not more than ±7.5% [22]; whereas for application of the AP, divergence was not more than ±2.5% [23].

The results of the various calculations and estimations of SEF values for Bi_xO_y oxides are presented in Table 2. It is seen from Table 2 and Fig. 1, that if we take the SEF for Bi_2O_3 and BiO [5] as reliable, then the value of the SEF for Bi_2O_5 estimated in this work [13] is not correct. We thus take as reliable the SEF for Bi_2O_5 and BiO_2 calculated with the use of the AP.

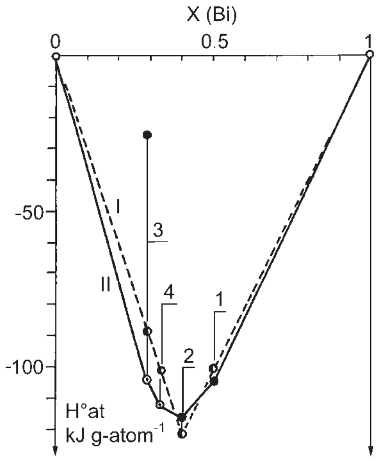

Fig. 1 The results of the use of universal linear approximation rules – ULAR [22] (curve 1) and AP [23] (curve 2) for the determination of H^0_{at} for Bi_2O_5 and BiO_2; 1–4 – H^0_{at} for BiO, Bi_2O_3, Bi_2O_5 and BiO_2; • – 1 and 2 – H^0_{at} for BiO and Bi_2O_3 according to [5]; • – 3 – for Bi_2O_5 according to [13]; o – H^0_{at} for Bi_xO_y according to the ULAR; o – H^0_{at} for Bi_xO_y according to the AP

Table 2 Known data and results of the estimation and calculation of SEF for bismuth oxides

Oxide	ΔH^0_{298}/kJ mol^{-1} known data	ΔH^0_{at}/kJ g-atom^{-1} known data	estimation on Eq. (11)	on ULAR, Eqs (12), (13)	on AP Eq. (18)	ΔH^0_{298}/kJ mol^{-1} taken as reliable
BiO	–209.4*	–104.7*	–	–102.5	–104.7	–209.4
Bi_2O_3	–578.3*	–115.7*	–	–123.0	–115.7	–578.3
Bi_2O_5	–185**	–26.43**	–80.9	–87.9	–104.7	–728.1
BiO_2	–	–	–71.1	–102.4	–111.7	–335.2

* – according to [5];
** – according to [13]

Table 3 Mole fraction of Bi_2O_3

A – in mixtures of BiO_2+Bi_2O_3 (initial system BiO_2+Ar)									
T/K	400	500	600	700	800	820	840	860	880
$X(Bi_2O_3)$	$1.284\cdot10^{-12}$	$6.536\cdot10^{-8}$	$8.143\cdot10^{-5}$	$1.247\cdot10^{-2}$	$5.806\cdot10^{-2}$	$1.196\cdot10^{-1}$	$2.60\cdot10^{-1}$	$6.74\cdot10^{-1}$	1.0
B – in mixtures of Bi+Bi_2O_3 (initial system BiO+Ar, 300 –1220 K)									
T/K	600	700	800	900	1000	1100	1200	1220	
$X(Bi_2O_3)$	$1.962\cdot10^{-15}$	$2.815\cdot10^{-12}$	$7.58\cdot10^{-10}$	$6.198\cdot10^{-8}$	$2.256\cdot10^{-6}$	$7.64\cdot10^{-5}$	$1.995\cdot10^{-3}$	$3.35\cdot10^{-3}$	
C – in mixtures of Bi+Bi_2O_3 (initial system BiO+Ar, 1240–1500 K)									
T/K	1240	1260	1280	1300	1320	1340	1400	1500	
$X(Bi_2O_3)$	0.5035	0.5047	0.5060	0.5080	0.5105	0.5140	0.5287	0.5970	

All the properties for Bi_2O_5 and BiO_2 that are taken as reliable are presented in Table 1. They were used for the determination of the TDRGE values for those oxides with the help of the subprogram TERMOS [5]. The numerical coefficients of the approximating polynomials of the TDRGE are given in the second part of Table 1.

The thermal decompositions of BiO, Bi_2O_3, BiO_2 and Bi_2O_5

Some results of investigations are presented in Figs 2 to 5 and in Tables 3 to 5.

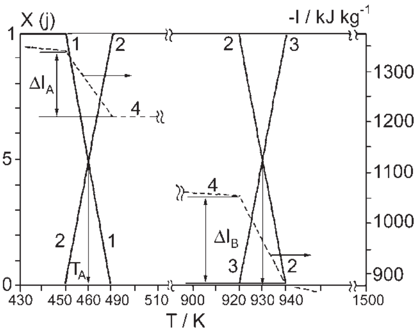

Fig. 2 The systems Bi_xO_y+O_2; Changes of compositions and energetic characteristics in the interval 450–1500 K; 1–3 – $X(Bi_2O_5)$, $X(BiO_2)$ and $X(Bi_2O_3)$; 4 – changes of systems enthalpies ($I=f(T)$); T_A and T_B, ΔI_A and ΔI_B are the temperatures of the transformations in Eqs (19) and (20), and the changes of system enthalpies near T_A and T_B, respectively

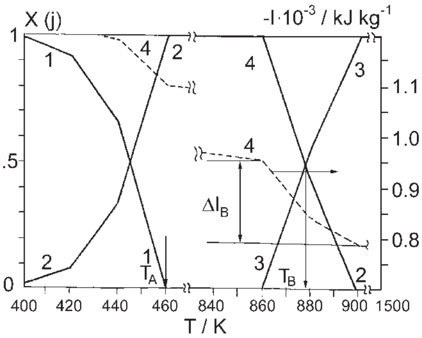

Fig. 3 The system Bi_2O_5+Ar; Changes of compositions and energetic characteristics in the interval 400–1500 K; 1–3 – $X(Bi_2O_5)$, $X(BiO_2)$ and $X(Bi_2O_3)$; 4 – $I=f(T)$; $T_A \cong 460$ K is the temperature at the end of phase BiO_2 formation; $T_B \cong 880$ K – the same for the Bi_2O_3 phase

The equilibrium heating of Bi_xO_y in O_2 (Fig. 2, Table 4)

In surplus oxygen (the initial content of O_2 in every system was equal to 14 mass%) oxides BiO, Bi_2O_3 and BiO_2 are transformed into Bi_2O_5 by 300 K. This phase existed

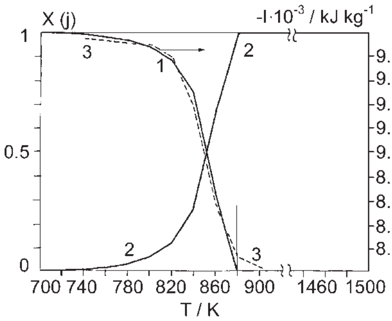

Fig. 4 The system BiO_2+Ar; Changes of compositions and energetic characteristics in the interval 700–1500 K; 1 and 2 – $X(BiO_2)$ and $X(Bi_2O_3)$; 3 – $I=f(T)$; $T_A \cong 880$ K is the temperature at the end of phase Bi_2O_3 formation

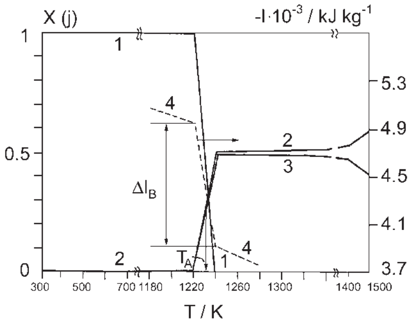

Fig. 5 The system BiO+Ar; Changes of compositions and energetic characteristics in the interval 300–1500 K; 1–3 – X(BiO), $X(Bi_2O_3)$ and X(Bi); 4–$I=f(T)$; $T_A \cong 1230$ K and ΔI_A are the temperature of phase transformation and the change of system enthalpy nearly T_A

up to 480 K. Between 480 and 930 K the phase BiO_2 and at T>930 K the phase Bi_2O_3 were observed.

The sequence of phase composition changes of the oxides can be connected with the transformations:

$$Bi_2O_5 \rightarrow 2BiO_2(cd)+0.5O_2,\ 480\ K \tag{19}$$

$$2BiO_2 \rightarrow Bi_2O_3(cd)+0.5O_2,\ 930\ K \tag{20}$$

The equilibrium heating of Bi_xO_y in Ar (Fig. 3 to 5, Tables 3 and 4)

Every bismuth oxide under these conditions (initial content of Ar was equal to 14 mass%) has its own type of decomposition.

Bi_2O_5+Ar (Fig. 3, Table 4)

In the interval 300 to 460 K the condensed phases Bi_2O_5 and BiO_2 can coexist. The mole fraction of BiO_2 in the mixture, – $X(BiO_2)$, – with rise of temperature increase to:

T/K	300	400	420	440	460
$X(BiO_2)$	$9.984\cdot10^{-7}$	$1.392\cdot10^{-2}$	$7.757\cdot10^{-2}$	$3.427\cdot10^{-1}$	1.0

Between 460 and 880 K the lone condensed phase in system is BiO_2, and at T>880 K it is Bi_2O_3. Consequently, in contrast with the Bi_2O_5+O_2 system, an initial phase of Bi_2O_5 in Ar can exist only with a mixture of phase BiO_2; the temperature range of existence for the individual phase BiO_2 moves to the low temperature side. These differences are natural results of the atmosphere change and are easily explained.

BiO_2 + Ar (Fig. 4, Tables 3A and 4)

The phases BiO_2 and Bi_2O_3 can coexist at 300–880 K, and a rise of temperature is accompanied by an increasing $X(BiO_2)$ in a mixture of phases (Table 3A). At T>880 K sesquioxide of bismuth is the lone condensed phase in the system.

BiO+Ar (Fig. 5, Tables 3B,C and 4)

Between 300 and 1230 K, a rise of temperature in a mixture of BiO + Bi_2O_3 resulted in an increase of $X(BiO_2)$ from ~$1\cdot10^{-18}$ (300 K) to ~$3.35\cdot10^{-3}$ (1230 K) (Table 3B). A possible reason for it is disproportion of part of the 'mother' phase

$$3BiO(cd) \rightarrow Bi_2O_3(cd) + Bi(g) \tag{21}$$

Between 1240 and 500 K, the coexisting phases Bi_2O_3 and Bi were observed as a result of the possible transformation:

$$3BiO(cd) \rightarrow Bi_2O_3(cd) + Bi(cd) \tag{22}$$

at about 1230 K (Table 3C). A decrease of the metallic bismuth content in the mixture Bi_2O_3+Bi with rise of temperature can be explained by bismuth evaporation.

Bi_2O_3+Ar

Over all temperature intervals this oxide is practically the lone condensed phase. Only between 300 and 500 K we observed the existence of BiO_2, ($X(BiO_2)$ in the mixture Bi_2O_3+BiO_2 being equal to ~$3.3\cdot10^{-6}$).

In Table 4, the composition and temperature intervals of existence of the phases are summarized, and the T and ΔH values of some of the phase transformations are given. The last mentioned characteristics were determined according to the methods described in [14, 15]. Let us remember that in the temperature range of a phase transformation, the full enthalpy of system (ΔI) changes by a leap (ΔI, Fig. 2 to 5). Because we can calculate numerically by computer experiments not only the function $I=f(T)$, but also the molar content of every condensed phase (and gaseous component

Table 4 Temperature ranges of existence of oxides and characteristics of some phase transformations during equilibrium heating of bismuth oxides

		$Bi_xO_y + O_2$		
300–480 K	480 K	480–930 K	930 K	930–1500 K
Bi_2O_5	$Bi_2O_5 \rightarrow 2BiO_2 + 0.5O_2$ $\Delta H \approx 66.5$ kJ mol^{-1} Bi_2O_5 $\Delta H \approx 32.9$ kJ mol^{-1} BiO_2	BiO_2	$2BiO_2 \rightarrow Bi_2O_3 + 0.5O_2$ $\Delta H \approx 45.9$ kJ mol^{-1} BiO_2 $\Delta H \approx 91.8$ kJ mol^{-1} Bi_2O_3	Bi_2O_3
		$Bi_2O_5 + Ar$		
360–460 K	460–880 K	880 K	880–1500 K	
Mixture Bi_2O_5+BiO_2	BiO_2	$2BiO_2 \rightarrow Bi_2O_3 + 0.5O_2$ $\Delta H \approx 48$ kJ mol^{-1} BiO_2 $\Delta H \approx 96$ kJ mol^{-1} Bi_2O_3	Bi_2O_3	–
		$Bi_2O_3 + Ar$		
300–500 K	500–1500 K			
Mixture Bi_2O_3+BiO_2 $X(BiO_2) \approx 6 \cdot 10^{-7}$	Bi_2O_3	–	–	–
		$BiO_2 + Ar$		
300–880 K	880–1500 K			
Mixture Bi_2O_3+BiO_2	Bi_2O_3	–	–	–
		BiO + Ar		
300–1230 K	1230 K			
Mixture BiO+Bi_2O_3	$3BiO \rightarrow Bi_2O_3 + 0.5Bi$ $\Delta H \approx 25.7$ kJ mol^{-1} BiO $\Delta H \approx 38.4$ kJ mol^{-1} mixture Bi+Bi_2O_3	–	–	–

also) at every temperature, we can determine ΔH for the phase transformation from the equation

$$\Delta H \approx \frac{\Delta I}{m_T}, \text{ kJ mol}^{-1} \qquad (23)$$

where m_T is the number of moles of the j-th substance below the phase transformation temperature, or the number of moles of phase transformation products at the temperature of its completion.

Discussion

Before interpreting these results, we must note a few important initial conditions and assumptions that we used.

(i). We take as reliable the TP and TDRGE for condensed BiO and Bi_2O_3 from the data base ASTRA.BAS [5]. With the application of the SEF of BiO and Bi_2O_3, and assuming that in the Bi–O system can exist the thermodynamically stable phases Bi_2O_5 and BiO_2, we calculated, with the use of AP [23], the most important properties, – SEF, – for those oxides. Consequently, if the SEF for BiO and Bi_2O_3 [5] are not correct, we have used only agreed values of the SEF for Bi_xO_y oxides. An independent analysis with the use of a 'rough' approximation (Eq. (11)) and the ULAR [22] (Fig. 1) gives us the definite assurance, that the SEF values of Bi_xO_y oxides are determined more-or-less correctly. But, for 'full' assurance, it is necessary to measure the SEF for Bi_xO_y oxides in precise experiments, as well as the other thermochemical properties.

(ii). For the study of the Bi_xO_y thermal decomposition, we used the assumption that every condensed compound can be present as an individual phase. This assumption was made for the determination of the principal behaviours of the bismuth oxide and, of course, is only a preliminary and 'ideal' point of view on the objects of this investigation.

The following speculations must be reasonable if we take into account the above mentioned notes.

Under the chosen conditions of computer experiments we can conclude, that, in the Bi–O (Ar) systems between 300 and 1500 K, the individual oxides Bi_2O_5, BiO_2, Bi_2O_3, BiO as well as the mixtures Bi_2O_5+BiO_2, Bi_2O_3+BiO_2, BiO+ Bi_2O_3 and Bi_2O_3+ Bi, can exist.

In atmospheres with surplus O_2, all initial oxides would be oxidized at 300 K up to the 'highest' oxide Bi_2O_5, and with increasing temperature, the degree of bismuth oxidation changes from $+5 \rightarrow +4 \rightarrow +3$.

In an inert gaseous atmosphere, there is also a common tendency of lowering of the average degree of the bismuth oxidation with increasing temperature, but it is accompanied by formation of oxide and oxide–bismuth mixtures over definite temperature intervals.

Under the chosen conditions, the oxide Bi_2O_3 is most stable, but not the oxide BiO, as would be expected if the results of thermal decomposition investigations of many oxides of less-common metals [4, 5, 11, 14, 15] are taken into account. But at the same time, the results of our study agree with well known experimental facts (see for examples [1–4, 9–11], that the oxide Bi_2O_3 is the most stable oxide in the Bi–O system.

The values of the partial pressures of O_2, Bi and Bi_4O_6 calculated during the TS of thermal decomposition of Bi_2O_3(cd) in inert atmosphere agree satisfactorily with experimental data [11] (Table 5).

Table 5 Comparison of calculated partial components pressures over Bi_2O_3 with experimental data [11] (in MPa)

T/K	$P(O_2)$		P(Bi)		$P(Bi_4O)$	
	calc.	[11]	calc.	[11]	calc.	[11]
900	$4.27\cdot10^{-9}$	$4.59\cdot10^{-10}$	$1.47\cdot10^{-11}$	$6.10\cdot10^{-10}$	$8.10\cdot10^{-11}$	$8.97\cdot10^{-11}$
1000	$8.71\cdot10^{-9}$	$1.55\cdot10^{-8}$	$5.71\cdot10^{-9}$	$2.04\cdot10^{-8}$	$5.20\cdot10^{-9}$	$5.26\cdot10^{-9}$

This work is probably the first investigation of the thermal stability of bismuth oxides over a wide temperature interval and under different gas atmospheres. Therefore we cannot compare the results with known data. According to the review in [11] only the partial pressures of some components over Bi_2O_3(cd) were measured at about 900 to 1200 K. However, the results of our study are only a first numerical estimation, as according to [11] in the gas phase over condensed Bi_2O_3 together with Bi÷Bi_4, BiO and Bi_4O_6 (their thermodynamic functions taken into account at the TS) also volatile $(BiO)_n$, where n=2÷4, Bi_2O_3, Bi_4O_5, Bi_3O_2 and Bi_3O can exist. For these substances the thermodynamic functions have not yet been determined.

The majority of these data are new. In our opinion, the most interesting of them is the possibility of formation and coexistence of bismuth oxides with different degrees of oxidation at the same temperature. This observation we interpreted as the mixtures of phases, but we can also interpret it as the formation and existence of phases of changing composition, i.e. solid (or liquid) solutions in which molten and crystalline oxide phases can coexist. But these problems can be solved in special investigations, where we must find (or determine) all temperature boundaries 'solidus–liquidus' and use definite solution models.

Conclusions

With the help of various calculation methods, the unknown TP and TDRGE of Bi_2O_5 and BiO_2 have been determined. The thermal decompositions of BiO, Bi_2O_3, Bi_2O_5 and BiO_2 have been studied from 300 to 1500 K in initial O_2 and Ar atmospheres. The compositions of the condensed phases and the consequences and characteristics of some phase transformations were determined.

The results of this investigation agree with known information, about Bi_2O_3 behaviour at equilibrium heating. It was found that in the Bi–O(Ar) systems can coexist not only individual oxides, but also bismuth oxides, with different degrees of oxidation.

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