

A mass spectrometric and quantum chemical study of the vapourisation of lead monoxide in a flow of gaseous arsenic and antimony trioxides†

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Mass spectrometric studies of the vapours over solid lead oxide in a flow of gaseous arsenic and antimony trioxides were conducted. The following ions of the ternary oxides were detected: $\text{Pb}_3\text{As}_2\text{O}_6^+$, $\text{Pb}_3\text{AsO}_4^+$, $\text{PbAs}_2\text{O}_4^+$, PbAsO_2^+ , $\text{PbSb}_2\text{O}_4^+$, and PbSbO_2^+ . The origin of these species produced by the ionisation and/or fragmentation of ternary gaseous oxides is discussed. The PbAs_2O_4 species was undoubtedly identified by the determination of the appearance energy. Presumably, the $\text{Pb}_3\text{As}_2\text{O}_6$ and PbSb_2O_4 species also existed in the gas phase. Thermodynamic data for the ternary oxides were obtained experimentally by means of a mass spectrometric Knudsen-cell method and were confirmed by quantum chemical calculations.

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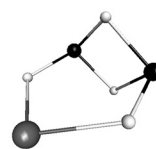
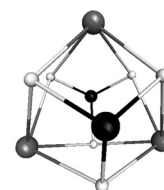
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1. Introduction

Previously, we reported the following gaseous ternary oxides built from a transition metal and a main group metal or metalloid: $\text{Sb}_2\text{Mo}_3\text{O}_{12}$, $\text{Sb}_2\text{M}_2\text{O}_9$, Sb_4MO_9 , Sb_2MO_6 (where $M = \text{Mo}$ or W), $\text{Mo}_3\text{TeO}_{11}$, Mo_2TeO_8 , MoTe_2O_7 and MoTeO_{15} .^{1,2} We continue our investigation of gaseous ternary oxides with a system consisting of a volatile metalloid oxide X_2O_3 (where $X = \text{As}$ or Sb) and the PbO metal oxide, which has a lower volatility. Several studies of the vapourisation of the pure oxides of PbO ,^{3–5} As_2O_3 ^{6,7} and Sb_2O_3 ^{8,9} using mass spectrometric methods have been reported by several authors. In the gas phase over solid lead monoxide at a temperature of approximately 1000 K, PbO , Pb_2O_2 and Pb_4O_4 were found to be the main compounds. Very low concentrations of Pb_3O_3 , Pb_5O_5 and Pb_6O_6 were also detected.^{3–5} Mass spectrometric studies of the vapourisation of As_2O_3 have shown that the gas phase of the As-O system is highly complex.⁶ Besides gaseous As_4O_6 and AsO species, which were previously known to exist in the gas phase, other stable species including As_4O_5 , As_4O_4 , As_4O_3 , As_3O_4 , As_2O_3 and AsO_2 were detected in the gas phase.⁶ The studies of the Sb-O system showed incongruent evaporation of Sb_2O_3 trioxide and revealed errors in previous studies on the congruent evaporation of Sb_2O_3 .^{8,9} Analogous to the As-O system, the gas phase over antimony trioxide primarily consisted of Sb_4O_6 molecules. The formation and thermodynamic stability of antimony monoxide SbO have been previously

investigated by mass spectrometry.¹⁰ The authors observed the formation of SbO species by the oxidation of atomic Sb at temperatures of approximately 1880 K.

There are several gaseous ternary oxides such as SnPO_2 , SnPO_3 ¹¹ and GePO_3 ,¹² which are related to the lead-arsenic and lead-antimony oxides, which have been detected using mass spectrometry. To the best of our knowledge, no other experimental and quantum chemical studies of gaseous ternary molecular oxides of groups 14 and 15 elements have been reported. Two relative solid compounds PbAs_2O_4 and $\text{Pb}_2\text{As}_2\text{O}_5$ were reported and their structures were investigated elsewhere.¹³ In the present work, with the help of mass spectrometry and quantum chemical calculations, we discuss the formation and stability of ternary oxides over two gaseous mixtures, $\text{PbO-As}_2\text{O}_3$ and $\text{PbO-Sb}_2\text{O}_3$. The structures of the gaseous ternary oxides PbAs_2O_4 , $\text{Pb}_3\text{As}_2\text{O}_6$ and PbSb_2O_4 are also reported and discussed.

 PbAs_2O_4 PbSb_2O_4  $\text{Pb}_3\text{As}_2\text{O}_6$

2. Results and discussion

2.1. Mass spectrometric study

The As_2O_3 , Sb_2O_3 and PbO oxides have very different volatilities. The melting points of the oxides are 585 K, 929 K and

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1161 K, respectively, and the equations describing the partial pressures as a function of temperature are as follows:

$$\text{for As}_2\text{O}_3 \lg(p/\text{atm}) = -(6067 \pm 125)/T + (9.905 \pm 0.319) \quad (367\text{--}429 \text{ K}) \quad (1)$$

$$\text{for Sb}_2\text{O}_3 \lg(p/\text{atm}) = -(10\,066 \pm 203)/T + (9.390 \pm 0.297) \quad (627\text{--}723 \text{ K}) \quad (2)$$

$$\text{for PbO } \lg(p/\text{bar}) = -32\,032/T + 1915 \quad (850\text{--}1100 \text{ K}) \quad (3)$$

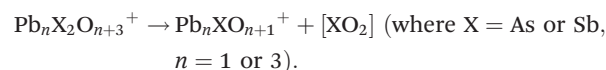
$$\text{or } \lg(p/\text{bar}) = -13\,345/T + 11.9 \quad (900\text{--}1150 \text{ K}) \quad (4)$$

Therefore, a double Knudsen cell was used in the mass spectrometric experiment. In the first experiment, solid As_2O_3 was continuously evaporated at 423 K and flowed through the solid PbO at 900 K. Analogously, in the second experiment, Sb_2O_3 was evaporated at 673 K and flowed through the solid PbO at 1110 K. The reaction products leaving the Knudsen cell were analysed by mass spectrometry.

The relative intensities of the ions in the mass spectra are presented in Table 1. Additionally, mass spectrometric measurements of the vaporisation of pure oxides were conducted for comparison, and those results are also presented in Table 1. The highest relative intensities were observed for the X_4O_6^+ ions, and the second highest relative intensities

belonged to the X_3O_4^+ ions in the mass spectra of the ternary oxides as well as the pure arsenic and antimony trioxides. The Pb_4O_4^+ , Pb_2O_2^+ and PbO^+ ions were detected in the mass spectrometric experiment with antimony oxide ($\text{PbO}\text{--}\text{Sb}_2\text{O}_3$ system), in which PbO was heated to 1110 K. In the experiment with arsenic oxide ($\text{PbO}\text{--}\text{As}_2\text{O}_3$ system), the partial pressure of PbO at 900 K was too low ($\sim 10^{-8}$ bar) for the detection of the PbO^+ signal in the mass spectra. Three parent ions of ternary oxides were detected: $\text{Pb}_3\text{As}_2\text{O}_6^+$ (M^+), $\text{PbAs}_2\text{O}_4^+$ (M^+) and $\text{PbSb}_2\text{O}_4^+$ (M^+) (where M^+ is the parent ion), which indicated the existence of gaseous $\text{Pb}_3\text{As}_2\text{O}_6$, PbAs_2O_4 and PbSb_2O_4 . The $\text{Pb}_2\text{As}_2\text{O}_5^+$ ion was not detected. The appearance energy was obtained only for the $\text{PbAs}_2\text{O}_4^+$ ion because the intensities of the $\text{Pb}_3\text{As}_2\text{O}_6^+$ and $\text{PbSb}_2\text{O}_4^+$ ions were too small. Extrapolation of the linear portion of the ionisation efficiency curves to an intensity of zero gave the following value for the appearance energy: $\text{AE}(\text{PbAs}_2\text{O}_4^+) = 9.7 \pm 0.5$ eV.

The following species, which can have two formation sources, were also observed: $\text{Pb}_3\text{AsO}_4^+$, PbAsO_2^+ and PbSbO_2^+ . The first way in which these ions could have been formed was by the splitting of $[\text{AsO}_2]$ from the $\text{Pb}_3\text{As}_2\text{O}_6^+$ and $\text{PbAs}_2\text{O}_4^+$ parent ions and the splitting of $[\text{SbO}_2]$ from $\text{PbSb}_2\text{O}_4^+$, *i.e.*, by the fragmentation process



Under the designation $[\text{XO}_2]$, neutral species were united to give a total of one X atom and two O atoms: XO_2 , $\text{XO} + \text{O}$, $\text{X} + \text{O}_2$ and $\text{X} + 2\text{O}$.

The second way in which the $\text{Pb}_3\text{AsO}_4^+$, PbAsO_2^+ and PbSbO_2^+ ions could have been formed was as products of the ionisation of molecules with X^{2+} . As mentioned above, gaseous AsO species, where the oxidation state of As is 2+, are thermodynamically stable. Brittain *et al.*⁶ have shown that AsO^+ formed primarily by the ionisation of $\text{AsO}(\text{g})$ in unsaturated vapour over $\text{As}_2\text{O}_3(\text{s})$ at 1160 K. In our experiment, the relative intensities of AsO^+ and PbAsO_2^+ in the mass spectra of the $\text{As}_2\text{O}_3\text{--PbO}$ gaseous mixture were quite high. The appearance energies for these two ions were determined to be $\text{AE}(\text{PbAsO}_2^+) = 10.0 \pm 0.5$ eV and $\text{AE}(\text{AsO}^+) = 15.7 \pm 0.5$ eV. The quantum chemical calculated ionisation energies for the individual molecules are $\text{IE}(\text{PbAsO}_2) = 6.74$ eV and $\text{IE}(\text{AsO}) = 8.48$ eV, and the experimental value of Brittain *et al.*⁶ was $\text{AE}(\text{AsO}^+) = 9.0 \pm 0.3$ eV. Thus, under the conditions of our experiment, AsO^+ and PbAsO_2^+ ions were the fragmented species but were not the parent ions as was originally believed. The intensities of the $\text{Pb}_3\text{AsO}_4^+$ and PbSbO_2^+ ions were too small to determine their appearance energies, but presumably, these ions were also fragments.

The dependence of the recorded ion currents on the partial pressure of the particular ion is described by the following equation:

$$p_i = c \frac{\sum I_i T}{\sigma_i S} \quad (5)$$

Table 1 Relative intensities of ionic species over $\text{PbO}\text{--}\text{X}_2\text{O}_3$ systems and the pure oxides X_2O_3 (X = As or Sb) and PbO at 70 eV

Ion	Relative intensity				PbO 1002 K
	$\text{X}_2\text{O}_3\text{--PbO}$		X_2O_3		
	X = As 900 K	X = Sb 1100 K	X = As 423 K	X = Sb 673 K	
Pb_4O_4^+ (M^+)	—	6.0	—	—	100
$\text{Pb}_3\text{X}_2\text{O}_6^+$ (M^+)	3.6	—	—	—	—
Pb_3XO_4^+	2.8	—	—	—	—
Pb_3O_3^+ (M^+)	—	—	—	—	10.5
Pb_3O_2^+	—	—	—	—	6.0
Pb_2O_2^+	—	2.9	—	—	59.7
Pb_2O^+	—	—	—	—	15.1
PbX_2O_4^+ (M^+)	37.5	7.9	—	—	—
PbXO_2^+	37.3	1.6	—	—	—
X_4O_6^+ (M^+)	100	100	100	100	—
X_4O_5^+	0.8	—	0.7	0.6	—
X_4^+	22.7	—	0.8	—	—
X_3O_4^+	74.8	20.3	66.2	24.2	—
X_3^+	1.8	—	1.6	—	—
PbO^+ (M^+)	—	2.7	—	—	44.2
Pb^+	18.7	11.6	—	—	45.1
X_2O_3^+	1.6	—	0.7	0.3	—
X_2O_2^+	5.7	—	0.7	2.7	—
X_2^+	14.0	—	4.4	—	—
XO^+	37.5	0.7	14.1	5.1	—
X^+	3.9	0.1	0.5	0.1	—

Table 2 Molecules and their ions in the gas phase of the PbO–As₂O₃ system

Molecule	Attributed ions	Partial pressure, <i>p</i> (bar) (900 K)
As ₄ O ₆	As ₄ O ₆ ⁺ , As ₄ O ₅ ⁺ , As ₄ ⁺ , As ₃ O ₄ ⁺ , As ₃ ⁺	3.1 × 10 ⁻⁵
PbAs ₂ O ₄	PbAs ₂ O ₄ ⁺ , PbAsO ₂ ⁺	2.5 × 10 ⁻⁵
Pb ₃ As ₂ O ₆	Pb ₃ As ₂ O ₆ ⁺ , Pb ₃ AsO ₄ ⁺	2.1 × 10 ⁻⁶

Table 3 Molecules and their ions in the gas phase of the PbO–Sb₂O₃ system

Molecule	Attributed ions	Partial pressure, <i>p</i> (bar) (1100 K)
PbO	PbO ⁺	1.0 × 10 ⁻⁷
Sb ₄ O ₆	Sb ₄ O ₆ ⁺ , Sb ₃ O ₄ ⁺ , SbO ⁺ , Sb ⁺	2.8 × 10 ⁻⁶
PbSb ₂ O ₄	Sb ₂ PbO ₄ ⁺ , SbPbO ₂ ⁺	3.6 × 10 ⁻⁷

where p_i = the partial pressure of component i , c = the proportionality factor, $\sum I_i$ = the intensity of all of the ions formed by the ionisation and fragmentation of a gaseous molecule of i , T = the temperature, σ_i = the ionisation cross section and S_i = the electron multiplier efficiency. The approximated eqn (6) can be used in most cases (the procedure of simplification is described elsewhere¹⁷):

$$p_i = c \sum I_i T \quad (6)$$

The proportionality factors c_1 and c_2 were determined by a calibration experiment for both systems and were found to be $c_1 = 3.6 \times 10^{-10}$ and $c_2 = 3.4 \times 10^{-11}$ bar K⁻¹.

The mass spectrometric measurements of pure oxides As₂O₃ and Sb₂O₃ were used for the calibration. The proportional factors c_1 and c_2 were determined within the error of a factor of 8 and 7 respectively.

Using the c_1 and c_2 values, the relative intensities $\sum I_i$, and applying eqn (6), the partial pressures of the gaseous molecules in the two equilibrium gaseous mixtures PbO–As₂O₃ and PbO–Sb₂O₃ can be calculated (Table 2). It was taken into account that arsenic and antimony oxides were constantly evaporating at lower temperatures (423 K and 673 K, respectively) and when they passed by lead oxide at higher temperatures (900 K and 1110 K, respectively). Tables 2 and 3 present the parent ions, their fragments, which contributed to the gaseous molecules, and the partial pressures of these molecules. We assumed equilibrium inside the Knudsen cell in the systems under consideration. The equilibrium in the Knudsen cell was confirmed by vaporisation of As₂O₃ oxide.¹⁴ The equilibrium in the gas phase was investigated in the Knudsen cell over Sb₂O₃ and PbO oxides too.^{3–5,8,9,15}

Using the partial pressures, we determined the equilibrium constants of the formation of the arsenic–lead and antimony–lead ternary oxides, which will be given later in this paper.

2.2. Density functional theory computations

The def2-TZVP/RI-BP86 method allows a good correlation between the calculated values and the experimental data for many oxides to be obtained. We successfully used the method employed previously for studying oxide systems containing molybdenum, tungsten, tellurium and antimony oxides.^{1,2} We also used the def2-TZVP/RI-BP86 method in the current study and showed the correlation between the experimental and calculated data for arsenic, antimony and lead oxides.

First, the oxides PbO, Pb₂O₂, Pb₃O₃, Pb₄O₄, and X₄O₆ (where X = As or Sb) were quantum chemically investigated. Total energies, thermal energies, point groups of the molecules and geometrical structures of pure lead, arsenic and antimony oxides are given in Table 4.

Monomers and oligomers of lead oxide, arsenic oxide and antimony oxide have also been theoretically studied elsewhere.^{18–20} The calculated geometrical structures with their point groups, bond lengths and angles in that study agree well with our calculations. Table 5 presents a comparison of the experimental structural data from the literature and our calculated structural data for lead, arsenic and antimony oxides. The geometric parameters for gaseous As₄O₆ and Sb₄O₆ obtained by electron diffraction agree well with the calculated values. The experimental data are also in good agreement.

The experimental and calculated vibration spectra of gaseous As₄O₆, Sb₄O₆, Pb₂O₂ and Pb₄O₄ are presented in Table 6. The experimental frequencies and our calculated frequencies for As₄O₆, Sb₄O₆, Pb₄O₄, Pb₂O₂ and PbO are in

Table 4 Symmetries, total energies and thermal energies of the molecules (def2-TZVP/RI-BP86, scaling factor = 1.053)



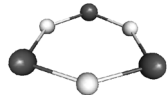

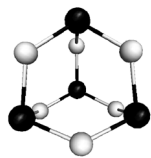

Molecule	Point group	Structure	E_{tot} (a.u.)	E_{298}^{therm} (kJ mol ⁻¹)
PbO	$C_{\infty v}$		-267.940878	10.99
Pb ₂ O ₂	D_{2h}		-536.690429	26.83
Pb ₃ O ₃	D_{3h}		-805.068223	44.09
Pb ₄ O ₄	T_d		-1073.497158	60.50
As ₄ O ₆	T_d		-9396.461653	89.58
Sb ₄ O ₆	T_d		-1413.450842	85.86
AsO	$C_{\infty v}$		-2311.386123	12.42

Table 5 Experimental and calculated geometric parameters of gaseous molecules

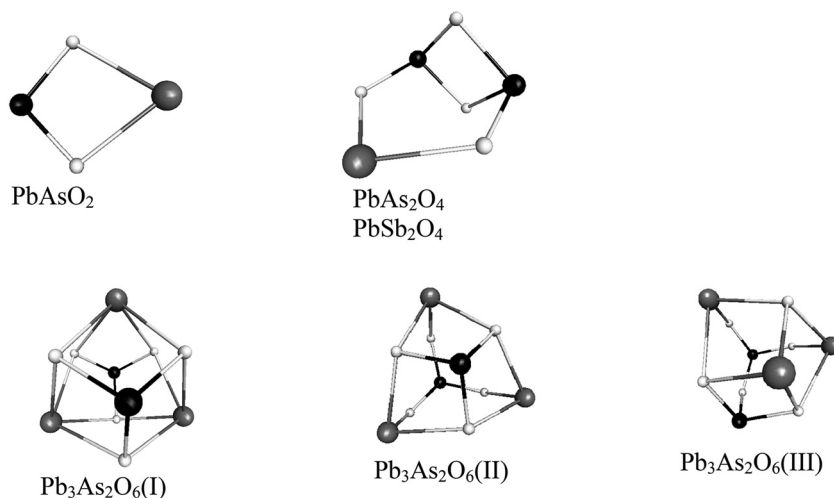
		$r(\text{M-O})$ Å	$\angle(\text{O-M-O})$	$\angle(\text{M-O-M})$
Pb ₄ O ₄	Exp. ²¹	—	86°	94°
	Calc.	2.265	81.7°	97.8°
Pb ₂ O ₂	Exp. ²¹	—	80°	—
	Calc.	2.138	83.3°	—
As ₄ O ₆	Exp. ²²	1.80 ± 0.02	100 ± 1.5°	126 ± 3°
	Calc.	1.817	100.2°	125.8°
Sb ₄ O ₆	Exp. ²³	2.00 ± 0.02	98°	129.0 ± 2.5
	Calc.	1.986	98.6°	128.3°

Table 6 Observed and calculated vibrational frequencies for gaseous As₄O₆, Sb₄O₆, Pb₄O₄, Pb₂O₂ and PbO (scaling factor = 1)

		Vibrational frequencies (cm ⁻¹)			
As ₄ O ₆	Exp. ²⁴	255.0	372.9	495.6	833.2
	Calc.	239.3	350.3	470.0	779.1
Sb ₄ O ₆	Exp. ²⁵	172.2	292.4	415.6	785.0
	Calc.	165.2	270.7	401.5	741.4
Pb ₄ O ₄	Exp. ²¹	—	372	464	—
	Calc.	113.3	353.3	451.8	—
Pb ₂ O ₂	Exp. ²¹	—	463	558	—
	Calc.	86.6	455.2	542.7	—
PbO	Exp. ²¹	714	—	—	—
	Calc.	724.0	—	—	—

Table 7 Symmetries, total energies and thermal energies of the molecules (def2-TZVP/RI-BP86, scaling factor = 1.053)

Molecule		E_{tot} (a.u.)	E_{298}^{therm} (kJ mol ⁻¹)
PbAs ₂ O ₄	C_s	-4966.580578	58.57
PbAsO ₂	C_1	-2579.790596	28.36
Pb ₃ As ₂ O ₆ (I)	D_{3h}	-5503.395177	92.3
Pb ₃ As ₂ O ₆ (II)	C_{3v}	-5503.369471	90.72
Pb ₃ As ₂ O ₆ (III)	C_s	-5503.364595	91.88
PbSb ₂ O ₄	C_s	-975.065646	56.49

**Fig. 1** Structures of the ternary oxides PbAs₂O₄, PbAsO₂, Pb₃As₂O₆, PbSb₂O₄ and Pb₃AsO₄.

good agreement but almost all of the experimental frequencies (except PbO) insignificantly (5–6%) exceed the calculated values. Therefore vibrational wave numbers were calibrated using scaling factor = 1.053.

Total energies, thermal energies and point groups for the ternary oxides PbAs₂O₄, Pb₃As₂O₆, PbSb₂O₄ and the hypothetical molecule PbAsO₂ are presented in Table 7, and the structures are shown in Fig. 1. For Pb₃As₂O₆, several structural isomers were found, and the optimised geometries and total energies of the isomers were also calculated and are presented in Table 7 ($E_{\text{tot(I)}} < E_{\text{tot(II)}} < E_{\text{tot(III)}}$) and in Fig. 1.

Transitions between the isomers of Pb₃As₂O₆ at the experimental temperature of 900 K can be characterised by Gibbs free energy: $\Delta_i G_{900(\text{II} \rightarrow \text{I})} = -51.9$ kJ mol⁻¹ and $\Delta_i G_{900(\text{III} \rightarrow \text{I})} = -66.1$ kJ mol⁻¹. According to the values of $\Delta_i G_{900}$, the ratio of the partial pressures of the isomers can be calculated at a temperature of 900 K: $p(\text{Pb}_3\text{As}_2\text{O}_6(\text{I})) : p(\text{Pb}_3\text{As}_2\text{O}_6(\text{II})) : p(\text{Pb}_3\text{As}_2\text{O}_6(\text{III})) = 6843 : 7 : 1$. Because the partial pressures of Pb₃As₂O₆(II) and Pb₃As₂O₆(III) are insignificant in the gas phase, we will not consider them further.

The total energies of the cations X₄O₆⁺, PbO⁺, PbX₂O₄⁺, PbAsO₂⁺ and Pb₃As₂O₆⁺ (X = As or Sb) were computed in a doublet spin state in the geometry of a neutral molecule to determine the vertical ionisation energies (IE) of the corresponding molecules (Table 15 ES1†). The first IE was determined as the difference between the total energy of the cation in a doublet state and the energy of the neutral molecule. Known experimental IE and AE values for the lead, arsenic and antimony oxides and AE values for PbAs₂O₄⁺ and PbAsO₂⁺ from the present study were compared with computed theoretical IE values (Table 8). The experimental AE values are in good agreement with theoretical IE values for all molecules except PbAsO₂. This agreement confirms that the PbAs₂O₄⁺ ion was formed by ionisation of ternary oxides rather than by fragmentation processes. If PbAs₂O₄⁺ is a fragment of Pb₃As₂O₆⁺, the AE(PbAs₂O₄⁺) is expected to be much higher. Our measured AE values for PbAsO₂⁺ and AsO⁺ greatly exceeded the

Table 8 The calculated vertical first ionisation energies (IE) (def2-TZVP/RI-BP86) and experimental appearance energies (AE)

Molecule	IE (eV) QC	AE, IE (eV) Exp.
PbO	9.65	9.4 ± 0.3 (EI, AE) ²⁶ 9.0 ± 0.5 (EI, AE) ⁵
Pb ₂ O ₂	8.41	8.8 ± 0.5 (EI, AE) ⁵
As ₄ O ₆	9.60	10.05 ± 0.05 (PE, IE) ²⁷
Sb ₄ O ₆	8.92	9.31 ± 0.05 (PE, IE) ²⁷
AsO	8.48	9.0 ± 0.3 (EI, AE) ⁶
PbAs ₂ O ₄	9.07	9.7 ± 0.5 (EI) ^a
PbAsO ₂	6.74	10.0 ± 0.5 (EI) ^a
Pb ₃ As ₂ O ₆ (l)	8.47	—
PbSb ₂ O ₄	8.49	—

^aThis work; EI – electron ionisation, PE – photoelectron ionisation.

calculated values, which means that these ions were formed by fragmentation.

Thermodynamic values for all of the compounds were obtained using the FREEH module and a scaling factor of 1.053 with a temperature range from the standard temperature to the temperature of the mass spectrometric experiments of 298–1000 K. The entropy, S_T^0 , can be approximated as a function of temperature:

$$S_T^0 = S_{298}^0 + \int_{298}^T c_{p,T}^0 \frac{dT}{T} \quad (7)$$

where $c_{p,T}^0 = a + b \times 10^{-3} \times T + c \times 10^6 \times T^{-2}$

The a , b and c coefficients of the heat capacity function $c_{p,T}^0$ were calculated mathematically by fitting ten values of S_T^0 in the temperature range of 298–1100 K. Calculated entropies for gaseous PbO, As₄O₆, and Sb₄O₆ were compared with the experimental literature values to demonstrate the adequacy of the calculation method chosen (Table 9) for the study of thermodynamics. The calculated and experimental values of S_{298}^0 and S_{1000}^0 are in good agreement. The experimental and calculated values of coefficient b of the $c_{p,T}^0$ function differ from each other but yield correct entropy values. Therefore, the calculated coefficients a , b and c for the ternary oxides are acceptable and can be used in the calculations. The calculated entropy values and the values of coefficients a , b and c for the ternary oxides are presented in Table 10.

The thermodynamics of gaseous monomer and oligomer molecules of lead oxides have been studied elsewhere.^{3–5} The enthalpies of oligomerisation for the lead oxides from the literature and our calculated values are compared in Table 11.

Table 9 Experimental²⁸ and calculated thermodynamic characteristics of lead, arsenic and antimony oxides (def2-TZVP/RI-BP86, scaling factor = 1.053)

Molecule	S_{298}^0 (J mol ⁻¹ K ⁻¹) (exp./QC)	S_{1000}^0 (J mol ⁻¹ K ⁻¹) (exp./QC)	$c_{p,T}^0 = a + b \times 10^{-3} \times T + c \times 10^6 \times T^{-2}$ (exp./QC)		
			a	b	c
PbO(g)	240.0//240.1	282.7//282.2	36.18//35.14	1.05//2.00	-0.36// -0.34
As ₄ O ₆ (g)	409.3//409.0	659.6//659.0	212.81//218.22	18.57//12.86	-3.98// -4.52
Sb ₄ O ₆ (g)	444.2//454.0	699.8//709.1	217.64//220.99	14.11//10.39	-3.47// -3.83

The calculated standard enthalpies of dimerisation and tetramerisation are in very good agreement with the literature values. The literature values of the enthalpy of the trimerisation process differ from each other and had an error of ±25 kJ mol⁻¹; our standard enthalpy value falls between the experimentally obtained ones. Thus, our method gives satisfactory results for the calculations of the enthalpies of reactions and can be used to investigate the thermodynamic characteristics of the ternary oxides.

Table 12 presents the reactions for the formation of the ternary lead–arsenic and lead–antimony oxides as well as the calculated enthalpies, entropies and equilibrium constants at standard and experimental temperatures for these reactions.

The calculated standard enthalpies of formation $\Delta_f H_{298}^0$ of the ternary oxides have been obtained with the help of the reaction enthalpies $\Delta_r H_{298}^0$ of the processes from Table 12 and the experimental values of $\Delta_f H_{298}^0(\text{PbO}) = 70.3 \text{ kJ mol}^{-1}$,²⁸ $\Delta_f H_{298}^0(\text{As}_4\text{O}_6) = -1196.1 \text{ kJ mol}^{-1}$,²⁸ and $\Delta_f H_{298}^0(\text{Sb}_4\text{O}_6) = -1215.5 \text{ kJ mol}^{-1}$ ²⁸ and are as follows:

$$\Delta_f H_{298}^0(\text{PbAs}_2\text{O}_4, \text{QC}) = -668.5 \text{ kJ mol}^{-1},$$

$$\Delta_f H_{298}^0(\text{PbSb}_2\text{O}_4, \text{QC}) = -653.4 \text{ kJ mol}^{-1}, \text{ and}$$

$$\Delta_f H_{298}^0(\text{Pb}_3\text{As}_2\text{O}_6, \text{QC}) = -1107.8 \text{ kJ mol}^{-1}.$$

2.3. Experimental determination of the standard enthalpies of formation of $\Delta_f H_{298}^0$

The equilibrium constant $K_{p,T}$ is related to the reaction enthalpy, reaction entropy and temperature by the van't Hoff equation. The experimental reaction enthalpies $\Delta_r H_T^0$ for processes 1', 2' and 3 are calculated with eqn (8) and presented in Table 13. The values of the reaction entropies $\Delta_r S_T^0$ are calculated using quantum chemical values of entropy for ternary oxides and the experimental entropies S_T^0 of PbO(s), PbO(g), As₄O₆(g), and Sb₄O₆(g) obtained from eqn (7) and the $c_{p,T}^0$ function.²⁸

$$\Delta_r H_T^0(\text{exp.}) = -RT \ln K_{p,T} + T \Delta_r S_T^0 \quad (8)$$

$$\Delta_f H_T^0 = \Delta_f H_T^0 + \int_T^{T'} c_{p,T}^0 dT \quad (9)$$

The enthalpies of formation ($\Delta_f H_T^0$) of the ternary oxides (Table 14) were obtained using the determined enthalpies of reactions $\Delta_r H_T^0$ (Table 13) and enthalpies of formation $\Delta_f H_T^0$ of PbO(g), PbO(s), As₄O₆(g) and Sb₄O₆(g) oxides at experimental

Table 10 Calculated thermodynamic characteristics of lead–arsenic and lead–antimony oxides (def2-TZVP/RI-BP86, scaling factor = 1.053)

Molecule	S_{298}^0/S_T^0 (J mol ⁻¹ K ⁻¹)	$c_{p,T}^0 = a + b \times 10^{-3} \times T + c \times 10^6 \times T^{-2}$		
		<i>a</i>	<i>b</i>	<i>c</i>
PbAs ₂ O ₄	407.9//563.4 ^a	148.99	7.92	-2.79
PbSb ₂ O ₄	424.2//614.7 ^b	151.03	6.12	-2.48
Pb ₃ As ₂ O ₆ (l)	514.0//773.9 ^a	218.22	12.86	-4.52

^a *T* = 900 K. ^b *T* = 1110 K.**Table 11** Comparison of the calculated and experimental values for the standard enthalpies of the equilibrium reactions of the lead oxides (def2-TZVP/RI-BP86, scaling factor = 1.053)

Reaction	$\Delta_r H_{298}^0$ (kJ mol ⁻¹) QC	$\Delta_r H_{298}^0$ (kJ mol ⁻¹) Exp. ^a
2PbO(g) ⇌ Pb ₂ O ₂ (g)	-258.3	-250.6 ± 6 ³ -265.4 ± 17 ⁵
3PbO(g) ⇌ Pb ₃ O ₃ (g)	-470.4	-419.5 ± 25 ³ -529.2 ± 25 ⁵
4PbO(g) ⇌ Pb ₄ O ₄ (g)	-816.7	-835.0 ± 15 ³ -845.7 ± 42 ⁵

^a Mass spectrometric experiment.

temperatures, which were obtained from eqn (9) and the experimental $c_{p,T}^0$ function²⁸ ($\Delta_f H_{900}^0(\text{PbO(s)}) = -187.2$ kJ mol⁻¹, $\Delta_f H_{900}^0(\text{As}_4\text{O}_6(\text{g})) = -1070.3$ kJ mol⁻¹, $\Delta_f H_{900}^0(\text{AsO}(\text{g})) = 75.6$ kJ mol⁻¹, $\Delta_f H_{1110}^0(\text{PbO}(\text{g})) = 99.4$ and $\Delta_f H_{1110}^0(\text{Sb}_4\text{O}_6(\text{g})) = -1039.2$ kJ mol⁻¹). Then, the calculated enthalpies of formation $\Delta_f H_T^0$ of the ternary oxides were converted into the standard enthalpies of formation $\Delta_f H_{298}^0$ using eqn (9) and the calculated *a*, *b* and *c* coefficients of the $c_{p,T}^0$ function (Table 10). The deviations of the experimental values are discussed in the next section. The experimental enthalpies $\Delta_f H_T^0$ and $\Delta_f H_{298}^0$ and the quantum chemical values of $\Delta_f H_{298}^0$ of the ternary oxides are presented in Table 14 for comparison.

2.4. Error estimation by the determination of the experimental standard enthalpies of formation

In the present section we estimate errors in the determination of the standard enthalpy of formation. The proportional factors *c*₁ and *c*₂ were determined within the errors of a factor of 8 and 7 respectively. The errors of proportional factors lead to the errors of equilibrium constant $K_{p,T}$ and give the

Table 12 Calculated standard enthalpies, entropies of reaction and equilibrium constants for the equilibrium processes in which the lead–arsenic and lead–antimony oxides participate (def2-TZVP/RI-BP86, scaling factor = 1.053)

Reaction	$\Delta_r H_T^0$ (kJ mol ⁻¹) 298// <i>T</i>	ΔS_T^0 (J mol ⁻¹ K ⁻¹) 298// <i>T</i>	ln $K_{p,T}$ 298// <i>T</i>
1 PbO(g) + 1/2 As ₄ O ₆ (g) ⇌ PbAs ₂ O ₄ (g)	-140.7//−138.4 ^a	-36.7//−32.7 ^a	52.4//14.6 ^a
2 3 PbO(g) + 1/2 As ₄ O ₆ (g) ⇌ Pb ₃ As ₂ O ₆ (g)	-720.6//−703.1 ^a	-410.7//−378.9 ^a	241.5//48.4 ^a
3 PbO(g) + 1/2 Sb ₄ O ₆ (g) ⇌ PbSb ₂ O ₄ (g)	-115.9//−112.7 ^b	-42.9//−37.8 ^b	41.6//7.7 ^b

^a *T* = 900 K. ^b *T* = 1110 K.**Table 13** Experimental equilibrium constant and enthalpies of reaction

Reaction	ln $K_{p,T}$	$\Delta_r H_T^0$ (kJ mol ⁻¹)
1' PbO(s) + 1/2 As ₄ O ₆ (g) ⇌ PbAs ₂ O ₄ (g)	-5.4 ± 1.4 ^a	149.1 ± 19.5 ^a
2' 3 PbO(s) + 1/2 As ₄ O ₆ (g) ⇌ Pb ₃ As ₂ O ₆ (g)	-7.9 ± 1.2 ^a	132.3 ± 18.0 ^a
3 PbO(g) + 1/2 Sb ₄ O ₆ (g) ⇌ PbSb ₂ O ₄ (g)	7.7 ± 1.4 ^b	-112.8 ± 18.5 ^b

^a *T* = 900 K. ^b *T* = 1110 K.

deviation of ln $K_{p,T} \pm 1.1$ for reactions 1', 2' and ± 1.0 for reaction 3. The error of the sum of ions $\sum I_i$ (eqn (6)) could reach 20%. That contributes to the errors of ln $K_{p,T}$ the values ± 0.3 , ± 0.1 and ± 0.4 for reactions 1', 2' and 3 respectively.

The error in determination of enthalpy of reaction $\Delta_r H_T^0$ includes both the error of equilibrium constant and the error of entropy of reaction according to eqn (8). The error of entropy of reaction 3 is lower than errors of entropy of reactions 1' and 2', because the entropies of reactions $\Delta_r S_T^0(1')$ and $\Delta_r S_T^0(2')$ include both experimental and quantum chemical calculated entropies and $\Delta_r S_T^0(3)$ is a quantum chemical value. We estimate the errors of $\Delta_r S_T^0(1')$ and $\Delta_r S_T^0(2')$ to be ± 10 J mol⁻¹ K⁻¹ and the error of $\Delta_r S_T^0(3)$ to be ± 5 J mol⁻¹ K⁻¹.

Then the total errors of enthalpy of reactions 1', 2' and 3 are equal to ± 19.5 , ± 18.0 and ± 18.5 kJ mol⁻¹ respectively. The errors of standard enthalpy of formation $\Delta_f H_{298}^0$ have corresponding deviations and are given in Table 14. The differences between the calculated and experimental enthalpies of formation are not very large. The biggest difference of $\Delta_f H_{298}^0(\text{exp}) - \Delta_f H_{298}^0(\text{QC})$ is for the Pb₃As₂O₆ molecule and is equal to 17.5 kJ mol⁻¹.

3. Experimental

3.1. Samples

Yellow lead monoxide (grade puriss. p.a), arsenic trioxide (grade puriss. p.a) and antimony trioxide (grade puriss. p.a) were used in the present study.

3.2. Mass spectrometry

Mass spectrometric measurements were carried out using a modified Finnigan type mass spectrometer. The vapours effusing from the Knudsen cell were ionised with 70 eV

Table 14 Experimental enthalpies of formation for lead–arsenic and lead–antimony oxides

Compound	$\Delta_f H_f^0$ (kJ mol ⁻¹) Exp.	$\Delta_f H_{298}^0$ (kJ mol ⁻¹) Exp.	$\Delta_f H_{298}^0$ (QC) kJ mol ⁻¹	$\Delta_f H_{298}^0$ (exp.) – $\Delta_f H_{298}^0$ (QC) kJ mol ⁻¹
PbAs ₂ O ₄	–573.2 ± 19.5	–659.5 ± 19.5	–668.5	9.0
Pb ₃ As ₂ O ₆	–964.4 ± 18.0	–1090.3 ± 18.0	–1107.8	17.5
PbSb ₂ O ₄	–549.9 ± 18.5	–669.9 ± 18.5	–653.4	–16.5

Q5 ^a $T = 900$ K. ^b $T = 1110$ K.

electrons and accelerated to 3000 V. Ion currents were detected by an electron multiplier at 1.6–2.0 kV. Two systems were experimentally investigated in the gas phase: X₂O₃–PbO, where X = As or Sb. A quartz double Knudsen cell (described elsewhere²⁹) with an effusion orifice 1 mm in diameter was employed in the investigation of these systems. Temperature was measured with a Pt–Pt/Rh thermocouple. X₂O₃ oxides were continuously evaporated (As₂O₃ at 423 K and Sb₂O₃ at 673 K) and flowed through solid lead oxide, which was heated to 900 K and 1110 K, respectively. The reaction products leaving the Knudsen cell were analysed by mass spectrometry. The same method with a double Knudsen cell was previously applied in the study of the Sb₂O₃–WO₃ system.¹ Appearance energies (AEs) of the ions of the ternary oxides were obtained by varying the electron energy to determine the onset of the ions.

3.3. Quantum chemical calculations

Quantum chemical calculations were performed using the TURBOMOLE program package.³⁰ All of the structures of the molecules were fully optimised using density functional theory (DFT) with the BP86 functional and the def2-TZVP triple split valence basis set with a polarisation function and small core ECP functions. RI-treatment was also applied. All computational details have been described in our previous studies.^{1,2}

4. Conclusions

The existence of three novel ternary lead–arsenic and lead–antimony oxides (PbAs₂O₄, Pb₃As₂O₆ and PbSb₂O₄) in the gas phase was proven by means of mass spectrometry. The gas phase of both systems primarily contained X₄O₆ and PbX₂O₄ oxides (X = As or Sb). The PbAs₂O₄ and PbSb₂O₄ oxides are isostructural, have two-coordinate atoms of Pb and three-coordinated atoms of X. Similar structures have been observed for the Sb₂MoO₆ and Sb₂WO₆ oxides.^{1,2} The Pb₃As₂O₆ oxide has a cage-like structure with high symmetry D_{3h} and contains four-coordinate atoms of Pb (Fig. 1). The Pb₂X₂O₅ oxides were not detected. The oxidation state of Pb is 2+ and that of X is 3+ as in PbO and X₄O₆ oxides. The maximum number of metallic atoms found in these gaseous ternary compounds was five, similar to the results of our previous studies on antimony–molybdenum and antimony–tungsten ternary oxides.¹

It is known that SnPO₂, which is isoelectronic with PbAsO₂, is a stable species.¹¹ AsO⁶ also existed in the gas phase. The PbAsO₂⁺ and AsO⁺ ions have large intensities in our mass spectrum, which allowed us to suspect the presence of PbAsO₂ in the gas phase. However, the determination of the appearance energy of PbAsO₂⁺ did not confirm our assumptions.

The PbO–As₂O₃ system has different compounds in the solid state and the gas phase. As was mentioned above, two solid compounds PbAs₂O₄ and Pb₂As₂O₅ were reported.¹³ Our study did not confirm the presence of Pb₂As₂O₅ in the gas phase, but Pb₃As₂O₆ which is not known in the solid state was detected in the gas phase.

The enthalpies of formation of the ternary oxides in the gas phase were determined using mass spectrometry and were compared with quantum chemical calculations. The experimental and calculated standard enthalpies of formation are in very good agreement.

The partial pressures of the ternary lead–arsenic species are about 3 to 4 order of magnitude higher than the partial pressures of pure lead monoxide at the same temperature. The fraction of lead-containing species is enhanced in the presence of As₄O₆ by a factor of 5000.

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