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Thermal stability and structures of the gaseous GeB_2O_4 and $GeMo_2O_7$

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The stability of gaseous species GeB_2O_4 and $GeMo_2O_7$ was confirmed by Knudsen effusion mass spectrometry. The gas-phase reactions involving B_2O_3, Mo_2O_6, MoO_3, GeB_2O_4 and $GeMo_2O_7$ were studied. On the basis of equilibrium constants, the standard formation and atomization enthalpies of gaseous GeB_2O_4 (-1101 ± 18 kJ·mol^{-1} and 3600 ± 20 kJ·mol^{-1}) and $GeMo_2O_7$ (-1449 ± 41 kJ·mol^{-1} and 4810 ± 43 kJ·mol^{-1}) at 298 K were determined. To get structure parameters and vibrational frequencies of gaseous GeB_2O_4 and $GeMo_2O_7$ quantum chemical investigation of these molecules was undertaken. Formation enthalpies of gaseous $GeTaO_3$, $GeTiO_3$, $GeVO_3$ and $GePO_2$ were estimates.

1. Introduction

Gaseous oxyacid salts constitute a special class of gaseous inorganic compounds characterized by rather specific structure. Gaseous salt can be conceived as an interaction product of two oxides which differ in their acid-base properties. Interaction of oxides can take place both in condensed and gas phases.

To have a possibility to predict processes with participation of gaseous salts it is necessary to know their thermodynamic characteristics. At present the entropy values of gaseous compounds can be obtained with reasonable precision by quantum chemistry methods. Routine procedures exist as well for calculation of equilibrium geometric structures of gaseous salts. As for the standard formation enthalpies, quantum chemistry can certainly be used to calculate their values but for relatively large molecules involving transition metals the precision of such calculations is far from being satisfactory. Unfortunately, to set up an experiment to determine the required formation enthalpies is by no means easy if possible at all.

By now quite a bulk of experimental data concerning thermodynamic and structure characteristics of gaseous oxyacid salts is accumulated. High-temperature mass spectrometry method made a major contribution to this set of data. The combination of classic Knudsen effusion method with mass spectrometric analysis of the evaporation products has culminated in

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the discovery new types of molecules including ones unstable in the condensed phases which refuted completely the conception about high-temperature vapor as a medium low in molecular forms. By now quite many earlier unknown and complex molecules have been found and characterized and in a number of cases these molecules turned out to be the predominant vapor components.

Taking into account the importance of germanium compounds in different high-temperature technologies such as glass-work, in different solders and fluxes, etc, where germanium oxide goes to gas phase forming volatile compounds, it seems to be of considerable interest to study the question concerning the existence of volatile associates in high-temperature vapor.

In germanium-oxygen system the existence of two oxides, GeO and GeO_2, was established. The most stable form turned out to be germanium dioxide. On heating   germanium dioxide vaporizes with subsequent decomposition to gaseous GeO and O_2[1]. In vapor germanium dioxide was not detected.

Calculations of electronegativity values of oxides[2,3] show that germanium oxide GeO in reactions of gaseous salt formation can display amphoteric properties and may be both as anion- and cation-forming oxide. By now seven salts in which formation GeO plays a role of cation-forming oxide are known. They are $GePO_3$ [4] , $GeMoO_3$ [5], and $GeMoO_4$ [6], $GeWO_4$ and GeW_2O_7[7], $GeNbO_3$, and $GeTaO_3$ [5]. And only one gaseous salt in which formation GeO plays a role of anion-forming oxide are known. This salt is $BaGeO_2$ [8]. All of the aforementioned salts were obtained as a result of interaction of gaseous GeO with the corresponding gaseous oxides.

In paper[6] it was reported that in vapor over the mixture of oxides GeO_2 and MoO_3 taken in mole relation 1:1, besides GeO, Mo_2O_6, and Mo_3O_9 germanium molybdate $GeMoO_4$ was detected and its thermodynamic functions were determined. Values of partial pressures of vapor phase species were used to calculate the equilibrium constants of gas-phase reactions (1) and (2). In authors of paper[6] opinion the molecule $GeMo_2O_7$ was not detected because of low receptiveness of experimental equipment.

$$GeO + 1/2\ Mo_2O_6 = GeMoO_4 \tag{1}$$

$$GeO + 1/3\ Mo_3O_9 = GeMoO_4 \tag{2}$$

In paper[1] high-temperature mass spectrometry method was used to study thermodynamic properties of GeO_2-B_2O_3 system. Qualitative and quantitative vapor composition was determined and thermodynamic functions were evaluated at temperatures 1393 and 1483 K. In the vapor germanium borates were not found.

The major task of this work is to describe synthesis of gaseous germanium molybdate $GeMo_2O_7$ and germanium borate GeB_2O_4 and determination of their thermochemical properties.

2. Methods

2.1 Experimental

The Knudsen effusion technique combined with mass spectrometric analysis (standard model MS-1301 Construction Bureau, Academy of Science, St. Petersburg) of the vapor composition was employed. The samples were vaporized from molybdenum effusion cell, heated by electron impact. The temperature was measured by an optical pyrometer. Testing the instrument was conducted by measuring the vapor pressures of the gold metal.[9] The appearance energies (AE) of ions were measured by the vanishing current method with Au as a energy standard,[10] which was found to be accurate to within ±0.3 eV. The partial pressures of vapor components were determined by differential mass spectrometry using atomic cross sections taken from.[11]

2.2 Computational

Two different approaches to quantum chemical calculations of reaction enthalpies were employed. The first one is purely *ab initio* wave function based approach using explicitly correlated MP2-F12 method developed by Werner group[12-17]. All calculations were carried out with the MOLPRO suite of *ab initio* programs[18]. The second approach is density based and exploits DFT M06 method developed by Truhlar group[19]. All DFT calculations were performed with the GAUSSIAN'09 program set[20]. For boron, oxygen and germanium full-electron aug-cc-pvTZ basis set[21-22] was used. For molybdenum def2-TZVP basis set[23] with the corresponding effective core potential was chosen. Localization of energy stationary points and subsequent vibrational analysis were performed both in the frameworks of MP2 and DFT M06 methods. Molecular structures and normal vibrations were visualized with the aid of Chemcraft[24] and Avogadro[25] graphical programs. Natural Population Analysis[26] was employed to evaluate atomic charges and bond orders.

3. Results and discussion

The GeO^+, MoO_3^+, $Mo_2O_6^+$, $Mo_3O_9^+$, $GeMoO_4^+$ and $GeMo_2O_7^+$ ions were detected in the mass spectra over the mixture of GeO_2 and MoO_3 at the temperature range 1400 K to 1500 K. When we evaporated the mixture of GeO_2 and B_2O_3 from the molybdenum cell the GeO^+,

$B_2O_3^+$, $GeBO_2^+$ and $GeB_2O_4^+$ ions were found in the mass spectra. The relative intensities of these ions depended on the temperature and the evaporation time. To identify the origin of these ions in the mass spectra of the vapor over mixtures being evaporated, their appearance energies (AE) were measured. In temperature range of 1400 to 1500 K, the AEs of ions were as follows (± 0.3 eV): $GeO^+(10.2)$, $MoO_3^+(12.1)$, $Mo_2O_6^+(12.3)$, $Mo_3O_9^+(12.2)$, $GeMoO_4^+(11.0)$, $GeMo_2O_7^+(12.7)$, $B_2O_3^+(14.0)$, $GeBO_2^+(11.6)$ and $GeB_2O_4^+(11.2)$. The AEs for ions GeO^+, MoO_3^+, $Mo_2O_6^+$, $Mo_3O_9^+$ and $GeMoO_4^+$ coincide, within the experimental error, with the ionization energies of the respective molecules.[6, 10] The appearance energies of the $GeMo_2O_7^+$, $GeBO_2^+$ and $GeB_2O_4^+$ ions were determined for the first time. The values of AE ($GeMoO_7^+$) and ($GeB_2O_4^+$) were found to correlate with the AEs of parent ions $Ga_2Mo_2O_7^+$ $(11.8)^{[27]}$, $In_2MoO_4^+$ $(9.1)^{[28]}$, $GeW_2O_7^+$ $(12.5)^{[7]}$, $SnW_2O_7^+$ $(11.0)^{[29]}$, $PbMo_2O_7^+$ $(11.4)^{[30]}$, and $CaB_2O_4^+$ $(10.84)^{[31]}$ determined previously. The observed ion $GeBO_2^+$ is probably the fragment ion of GeB_2O_4 molecule. If the $GeBO_2^+$ ion was the parent ion of $GeBO_2$ molecule, their AE would be less than the corresponding value for ion $GeB_2O_4^+$ since with decrease of oxygen atom number in molecules of oxyacid salts the appearance energy of molecular ion is normally also decreases.[32]

Partial pressures of the vapor species were calculated by the ion current comparison method, eqn (3), using Au as external pressure standard.[9]

$$p_1 = \frac{p_2 \, I_1 \, T_1 \, \sigma_2 \, \gamma_2}{I_2 \, T_2 \, \sigma_1 \, \gamma_1} \tag{3}$$

In the equation above I_i is total ion current, T_i is temperature, σ_i is the ionization cross section, γ_i is the secondary electron multiplier gain factor, that is known to be proportional to the square root of the molecular mass of the corresponding molecule, p_i is partial pressure of the i species, while "1" and "2" indexes mean the sample and the standard correspondingly. Molecular cross sections were obtained by the additivity method, atomic cross sections being taken from Ref. 11. Cross section of $GeMo_2O_7$ and GeB_2O_4 molecules were multiplied by 0.7, according to suggestion of Guido $et\ al.$[33] for five and more atomic molecules. Cross section of Mo_2O_6 was calculated according to Meyer and Lynch rule[34] by eqn. 4.

$$\sigma_n/\sigma_1 = (1.5)^{n/2} \tag{4}$$

where σ_1 – cross section of the MoO_3 molecule.

Obtained values of partial pressures of vapor molecular forms enabled us to calculate the equilibrium constants of the gas phase reactions (5-7) using the eqn (8).

$$GeO + Mo_2O_6 = GeMo_2O_7 \tag{5}$$

$$GeO + 2\ MoO_3 = GeMo_2O_7 \tag{6}$$

$$GeO + B_2O_3 = GeB_2O_4 \tag{7}$$

$$\Delta_r H^0(0) = T[\Delta_r \Phi^0(T) - R \ln K_p(T)] \tag{8}$$

Here $\Delta_r H^0(0)$ and $\Delta_r \Phi^0(T)$ are changes in enthalpy and in reduced Gibbs potential of the reaction at temperatures 0 K and T, respectively, R is the gas constant, K_p is the reaction equilibrium constant. Thermodynamic functions of gaseous molybdenum, boron and germanium oxides were taken from the reference book,[35] and thermodynamic functions of $GeMo_2O_7$ and GeB_2O_4 were calculated by methods of statistical thermodynamics in "rigid rotor – harmonic oscillator" approximation. Partial pressures, equilibrium constants and reaction enthalpies obtained are listed in Table 1 and Table 2.

Table 1. The partial vapor pressures above GeO_2 - MoO_3 system and enthalpy values of reactions (5, 6)

T, K	p_i, atm				K_{eq} (non-dimensional)		$-\Delta_r H^0$ (0), kJ	
	GeO $\times 10^6$	MoO_3 $\times 10^7$	Mo_2O_6 $\times 10^6$	$GeMo_2O_7$ $\times 10^7$	(5)$\times 10^{-4}$	(6) $\times 10^{-11}$	(5)	(6)
1442	1.50	1.89	0.63	2.48	26.21	46.31	299.5	720.8
1447	1.50	1.60	0.69	2.34	22.60	60.90	298.7	726.5
1461	2.45	5.89	1.17	2.66	9.28	3.13	290.6	697.2
1478	2.71	9.39	1.18	4.48	14.04	1.87	298.9	698.6
1477	12.38	31.27	3.36	4.03	0.97	0.03.	265.9	648.6
1488	13.18	55.51	8.92	8.12	0.69	0.02.	263.6	646.9
1472	13.40	29.68	7.23	3.12	0.32	0.03	251.6	643.7
1449	12.14	17.53	11.58	7.91	0.56	0.21	254.6	659.3
1443	11.06	13.53	9.22	8.31	0.82	0.410	258.1	664.6
1434	10.65	18.80	4.30	5.22	1.14	0.14	260.6	647.7
1445	8.65	23.31	7.10	6.13	0.99	0.13	260.8	651.7
1442	8.29	18.90	10.37	5.68	6.61	0.19	255.4	655.0
1447	12.13	16.05	8.67	4.83	0.46	0.16	251.8	654.6
1435	11.34	28.94	6.88	6.53	0.84	0.07	257.0	639.8
1423	7.16	6.46	1.88	2.59	1.92	0.87	264.9	664.7
1425	2.96	9.48	1.88	1.73	3.11	0.65	270.9	662.2
1398	0.87	9.36	2.01	2.14	12.22	2.81	282.0	667.2
1398	0.77	4.68	0.67	0.52	10.13	3.08	279.7	668.3
1406	1.28	6.52	1.57	0.98	4.88	1.80	272.8	665.6
1407	1.25	6.88	1.63	0.65	3.19	1.10	268.0	660.3
1418	2.04	8.40	1.81	1.18	3.20	0.820	270.0	661.8
1413	1.80	6.55	1.81	1.38	4.24	1.79	272.4	668.7
1414	1.24	6.19	1.47	0.92	5.05	1.94	274.6	670.1
1414	1.35	5.46	1.36	1.05	5.72	2.61	276.1	673.6
1418	1.58	7.30	1.93	0.99	3.25	1.18	270.2	666.0
1424	1.59	8.07	2.39	1.26	3.32	1.22	271.5	669.1
1422	1.09	3.66	1.70	0.92	4.96	6.30	275.9	687.7
1425	1.30	6.24	1.08	0.99	7.05	1.96	280.6	675.2
1413	0.81	3.64	1.02	1.05	1.27	9.78	285.3	688.7
1420	0.65	4.75	1.02	0.79	11.94	5.39	285.9	684.9
1419	0.75	5.48	0.96	0.66	9.17	2.93	282.6	677.3
1419	0.71	1.46	0.74	0.46	8.76	30.42	282.0	704.9
1472	10.58	49.71	4.41	9.39	2.01	0.04	274.0	647.5
1486	11.03	52.58	5.16	10.34	1.82	0.03	275.2	652.6

1481	8.87	66.69	5.86	10.30	1.98	0.03	275.4	647.3
1483	9.94	62.01	6.22	10.31	1.67	0.03	273.6	648.5
1489	15.33	67.05	6.96	12.95	1.21	0.02	270.7	646.5
1495	14.68	48.09	5.20	6.93	0.91	0.02	268.1	650.0
1499	9.33	36.16	5.21	6.95	1.43	0.06	274.4	664.5
1486	10.68	31.55	3.38	3.88	1.07	0.04	268.7	653.5
1498	9.33	31.80	3.95	6.08	1.65	0.06	276.1	665.6
1499	8.62	24.59	2.51	1.82	0.84	0.03	267.8	658.4
Average values							273±12	667±20

Table 2. The partial vapor pressures above $GeO_2 - B_2O_3$ system and enthalpy values of reaction (7)

T, K	p, atm			K_{eq} (non-dimensional)	$-\Delta_r H^0(0)$ kJ/mol
	$GeO \times 10^4$	$B_2O_3 \times 10^5$	$GeB_2O_4 \times 10^7$		
1293	1.89	1.29	3.07	125.92	237.2
1351	32.32	7.13	24.25	10.52	219.6
1369	23.40	6.02	3.25	2.31	205.2
1357	15.46	6.36	4.11	4.18	210.1
1366	0.77	0.37	0.57	200.07	255.4
1283	0.72	0.13	0.68	726.50	254.3
1281	0.68	0.12	0.50	612.75	252.1
1287	0.73	0.19	0.58	418.17	249.1
1290	0.77	0.20	0.38	246.75	244.1
1386	2.00	0.34	0.13	19.12	232.5
1397	1.72	0.23	0.18	45.50	243.8
1461	2.11	0.34	0.19	26.48	247.9
1460	1.43	0.21	0.19	63.27	258.2
1460	1.30	0.23	0.10	33.44	250.1
1473	53.91	8.32	6.31	1.41	214.0
1473	49.10	8.32	6.02	1.47	214.6
1473	48.13	8.32	4.94	1.23	212.4
1472	49.06	8.07	5.75	1.45	214.3
1493	66.35	21.57	8.09	0.57	205.5
1494	75.18	14.89	10.52	0.94	211.9
1494	70.30	15.14	9.57	0.90	211.4
1495	70.35	14.90	10.86	1.04	213.3
1495	72.30	14.90	9.74	0.90	211.6
1495	69.37	14.90	1.03	0.10	212.8
1495	71.32	15.64	10.30	0.92	211.8
1494	68.35	14.89	8.35	0.82	210.2
1494	64.44	15.63	8.35	0.83	210.3
1494	62.49	15.63	8.35	0.85	210.7
1494	63.47	16.38	7.52	0.72	208.7
1425	3.61	1.67	1.29	21.40	239.6
1441	3.96	2.18	1.53	17.72	240.0
1445	2.23	2.30	1.54	30.03	246.9
1445	3.66	2.30	1.54	18.29	240.9

1464	4.51	3.44	2.11	13.60	240.4
1464	4.67	3.32	2.11	13.61	240.4
1465	4.68	3.56	2.20	13.20	240.2
1466	3.87	3.08	1.88	15.77	242.5
1466	3.71	3.20	1.65	13.90	241.0
1466	3.71	3.08	1.74	15.23	242.1
1495	4.44	5.64	2.34	9.34	240.6
1495	4.28	5.27	2.34	10.37	241.9
1494	4.27	5.39	2.34	10.17	241.5
1494	4.60	5.01	2.34	10.15	241.4
1494	4.44	5.14	2.34	10.25	241.6
1456	6.14	3.86	1.61	6.79	230.7
1457	7.53	3.67	1.75	6.33	230.0
1457	7.14	3.22	1.44	6.26	229.9
1468	6.64	3.43	1.62	7.11	233.1
1472	4.57	2.88	1.21	9.19	236.9
1472	3.89	2.88	1.18	10.53	238.5
1471	15.84	2.97	1.49	3.17	223.7
1471	3.45	2.88	0.31	3.12	223.6
1458	5.48	4.94	2.23	8.24	233.3
Average value					231±16

To get structure parameters and vibrational frequencies of gaseous GeO, B_2O_3, MoO_3, Mo_2O_6, GeB_2O_4, and $GeMo_2O_7$ quantum chemical investigation of these molecules was undertaken.

First full geometry optimization of the reacting species in their ground (singlet) states both on the MP2 and DFT M06 levels of theory was performed with subsequent vibrational analysis. In addition at the PES (potential energy surface) points corresponding to the MP2 equilibrium geometries explicitly correlated MP2-F12[12-17] method was used for more elaborate treatment of electronic correlation. The corresponding electronic and zero point energies are given in Table 3.

Table 3 Electronic and zero point vibrational energies calculated at the equilibrium geometries of the reacting species at the MP2 and DFT M06 levels of theory

Molecule	E_{MP2} (a.u.)	ZPE_{MP2} (a.u.)	$E_{MP2+f12}$ (a.u.)	E_{M06} (a.u.)	ZPE_{M06} (a.u.)
$GeO(C_{\infty v}, \Sigma^+)$	-2150.641537	0.002160	-2150.681578	-2152.219006	0.002303
$B_2O_3(C_{2v}, {}^1A_1)$	-275.116366	0.018569	-275.230839	-275.515892	0.019172
$MoO_3(C_{3v}, {}^1A_1)$	-293.257253	0.008153	-293.392987	-293.887477	0.008959
$Mo_2O_6(D_{2h}, {}^1A_g)$	-586.672861	0.018193	-586.950178	-587.951679	0.020710

Calculations of equilibrium geometries and electronic structure of diboron trioxide, molybdenum trioxide, and dimolibdenum hexaoxide in gas phase were already carried out at different levels of theory. For B_2O_3 molecule several local minima on its ground state PES were found[36,37] and V-shape geometric form of this molecule turned out to be the energetically favorable one and it was

confirmed by our calculations. Molybdenum oxides were also studied by different versions of DFT method.[38,39] For the germanium oxide in the selected basis aug-cc-pVTZ MP2 method slightly overestimates Ge-O bond length (1.664 Å against the experimental 1.625 Å[40]) and underestimates harmonic frequency (948 cm^{-1} against the experimental 985 cm^{-1} [40]). DFT M06 method gives the experimental value of Ge-O bond length but overestimates the vibrational frequency.

In order to be sure that for the correct description of reactions (5) - (7) it is unnecessary to take into account the excited states of the reacting species TDDFT method[41,42] was used to estimate the energy differences between their ground and the first excited states. In all cases the first excited states turned out to be the triplet ones separated from the ground states by the following energy gaps: 2.6 eV for MoO_3, 3.4 eV for Mo_2O_6, 4.0 eV for GeO, and 6.9 eV for B_2O_3.

On the ground singlet PES of GeB_2O_4 two minima were found. The corresponding optimal geometric structures are shown in Fig.1. In accordance to our calculations, structure I is energetically favorable. The corresponding electronic and zero point vibrational energies are listed in Table 4. Geometric parameters and harmonic frequencies of GeB_2O_4 (structure I) are given in Table S1.

Structure I   Structure II
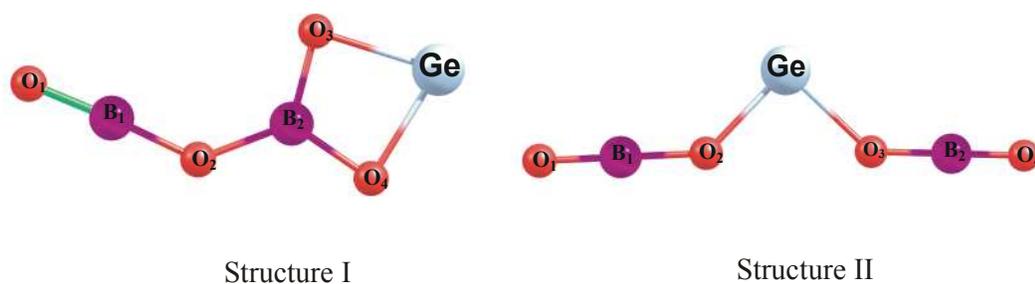
Fig. 1 The isomers of GeB_2O_4 found theoretically at the MP2 and DFT M06 levels of theory.

Table 4 Electronic and zero point vibrational energies calculated at two equilibrium geometries of GeB_2O_4 at the MP2 and DFT M06 levels of theory

	GeB_2O_4	
Energy (a.u.)	Structure I (C_S)	Structure II (C_S)
E_{MP2}	-2425.855418($^1A'$)	-2425.824407($^1A'$)
ZPE_{MP2}	0.024218	0.022290
$E_{MP2+fl2}$	-2426.010861($^1A'$)	-2425.980232($^1A'$)
E_{M06}	-2427.838686 ($^1A'$)	-2427.809021 ($^1A'$)
ZPE_{M06}	0.024769	0.023033

On the ground singlet PES of $GeMoO_4$ three equilibrium geometric structures were found. These structures are shown in Fig.2.

Structure I   Structure II   Structure III
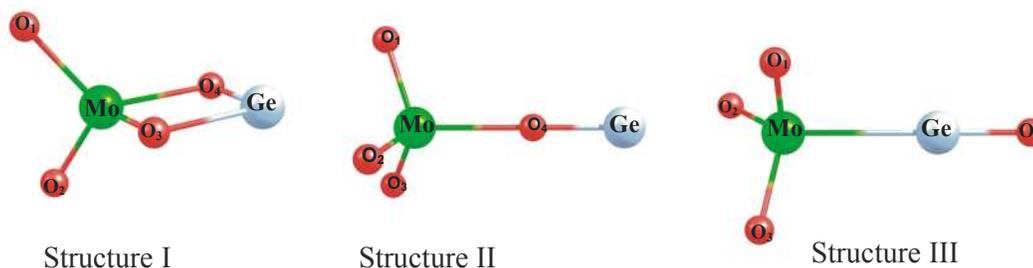
Fig. 2 The isomers of $GeMoO_4$ found theoretically at the MP2 and DFT M06 levels of theory.

Table 5 Electronic and zero point vibrational energies calculated at three equilibrium geometries of $GeMoO_4$ at the MP2 and DFT M06 levels of theory

	$GeMoO_4$		
Energy (a.u.)	Structure I (C_{2v})	Structure II (C_{3v})	Structure III (C_{3v})
E_{MP2}	-2444.021312 ($^1A_1$)	-2443.968093 ($^1A_1$)	-2443.927546 ($^1A_1$)
ZPE_{MP2}	0.012852	0.011597	0.011039

$E_{MP2+fl2}$	-2444.201826 ($^1A_1$)	-2444.145911 ($^1A_1$)	-2444.105426 ($^1A_1$)
E_{M06}	-2446.248807 ($^1A_1$)	-2446.192599 ($^1A_1$)	-2446.135060 ($^1A_1$)
ZPE_{M06}	0.013889	0.012825	0.012215

Geometric parameters and harmonic frequencies of energetically favorable structure I can be found in Table S2.

On the ground state of $GeMo_2O_7$ there exist at least two minimum points corresponding to equilibrium structures displayed in Fig. 3. In accordance to our calculations, structure I is energetically favorable. The corresponding electronic and zero point vibrational energies are listed in Table 6. Information about geometric structure and vibrational frequencies of $GeMo_2O_7$ ($^1A_1$) (structure I) can be found in Table S3.

Structure I   Structure II
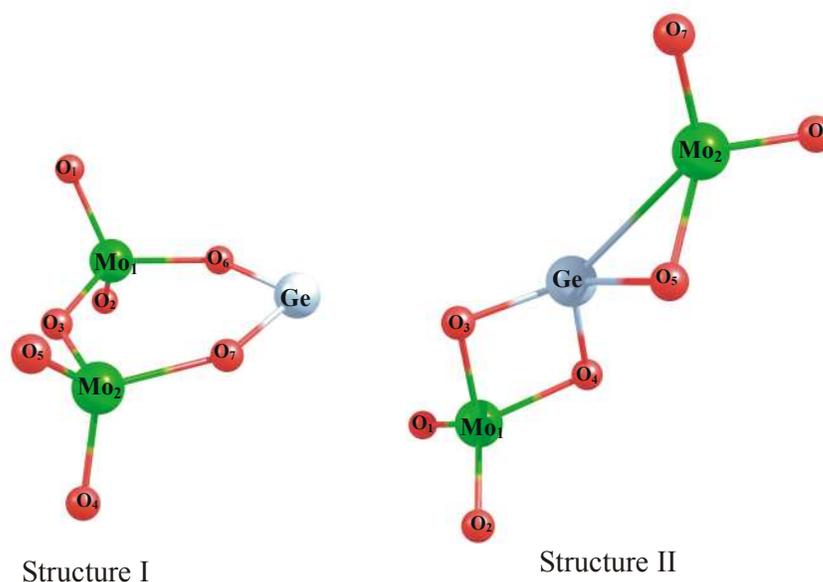
Fig. 3. The isomers of $GeMo_2O_7$ found theoretically at the MP2 and DFT M06 levels of theory.

Table 6. Electronic and zero point vibrational energies calculated at three equilibrium geometries of $GeMo_2O_7$ at the MP2 and DFT M06 levels of theory

	$GeMo_2O_7$	
Energy (a.u.)	Structure I (C_{2v})	Structure II (C_s)
E_{MP2}	-2737.411626 ($^1A_1$)	-2737.316839 ($^1A'$)
ZPE_{MP2}	0.022518	0.022137
$E_{MP2+fl2}$	-2737.729474 ($^1A_1$)	-2737.635697 ($^1A'$)
E_{M06}	-2740.280669 ($^1A_1$)	-2740.170335 ($^1A'$)

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ZPE_{M06}	0.024538	0.024371

In Table 7 natural atomic charges for the molecules under consideration are given.

Table 7 Natural atomic charges for energetically favorable isomers of GeB_2O_4, $GeMoO_4$, and $GeMO_2O_7$ calculated at the DFT M06 level of theory.

$GeB_2O_4(C_s)$		$GeMoO_4(C_{2v})$		$GeMO_2O_7(C_{2v})$	
Atom	Charge	Atom	Charge	Atom	Charge
O_1	-1.06	O_1, O_2	-0.49	O_1, O_2	-0.46
B_1	1.19	Mo	1.57	Mo_1, Mo_2	1.65
O_2	-0.87	O_3, O_4	-0.98	O_3	-0.78
B_2	1.24	Ge	1.38	O_4, O_5	-0.46
O_3	-0.83			O_6, O_7	-1.05
O_4	-1.04			Ge	1.43
Ge	1.37				

Using data from Tables 3-6 it is easy to estimate theoretical enthalpies of the aforementioned reaction and compare them with the experimental results. The corresponding enthalpy values (at 0 K) are presented in Table 8. It is seen that theoretical and experimental values are in a reasonable agreement.

Table 8 Calculated and experimental enthalpies of reactions (5)-(7) at 0 K.

Reaction	$-\Delta_r H^0(0)$, kJ mol^{-1}			
	MP2	MP2+f12	DFT M06	Expt
$GeO(^1\Sigma^+)+ B_2O_3(^1A_1)\rightarrow GeB_2O_4(^1A')$	247	249	264	231±16
$GeO(^1\Sigma^+)+MoO_3(^1A_1)\rightarrow GeMoO_4(^1A_1)$	315	327	367	
$GeMoO_4(^1A_1)+MoO_3(^1A_1)\rightarrow GeMo_2O_7(^1A_1)$	345	350	375	
$GeO(^1\Sigma^+)+2MoO_3(^1A_1)\rightarrow GeMo_2O_7(^1A_1)$	660	677	741	667±20
$MoO_3(^1A_1)+ MoO_3(^1A_1)\rightarrow Mo_2O_6(^1A_g)$	411	426	457	
$GeO(^1\Sigma^+)+ Mo_2O_6(^1A_g)\rightarrow GeMo_2O_7(^1A_1)$	250	251	285	273±12

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Combining the average values of the enthalpies of reactions (5-7), recalculated to the temperature 298 K, with the standard formation enthalpies (kJ/mol) of gaseous oxides Mo_2O_6 (-1140±40), MoO_3 (-364.4±15.0), B_2O_3 (-835.4±8.1), and GeO (-37.7±4.0), taken from the reference book,[35] allows us to calculate the standard formation and the standard atomization enthalpies of gaseous $GeMo_2O_7$ and GeB_2O_4 which are -1449±41 and -1101±18 $kJ·mol^{-1}$ respectively. Errors in values of calculated by us formation enthalpies is formed of errors of oxide formation enthalpies taken from the reference data and errors of reaction enthalpies involving errors of ionic current intensity measuring, pressure measuring by ionic current compare, and error in calculation of thermodynamic functions in the framework of "rigid rotator-harmonic oscillator" approximation.

In the isocation series of gaseous oxyacid salts the atomization enthalpy of gaseous salts has been shown[2] to be linearly dependent on the atomization enthalpy of gaseous anion-forming oxides, with the dependence being represented by the eq 9.

$$\Delta_{at}H^0(\text{salt, gas, 298}) = k \cdot \Delta_{at}H^0(\text{anion-forming oxide, gas, 298}) + b \qquad (9)$$

The data obtained in the present work allow us to plot such dependence (Fig. 4) for the isocation series of germanium salts. The coefficients k and b in eqn (9) are 0.941±0.017 and 1127±42, respectively. The high correlation coefficient (0.999) proves the adequacy of the results. Taking into account the high correlation coefficient we can expect our results to be reasonable.

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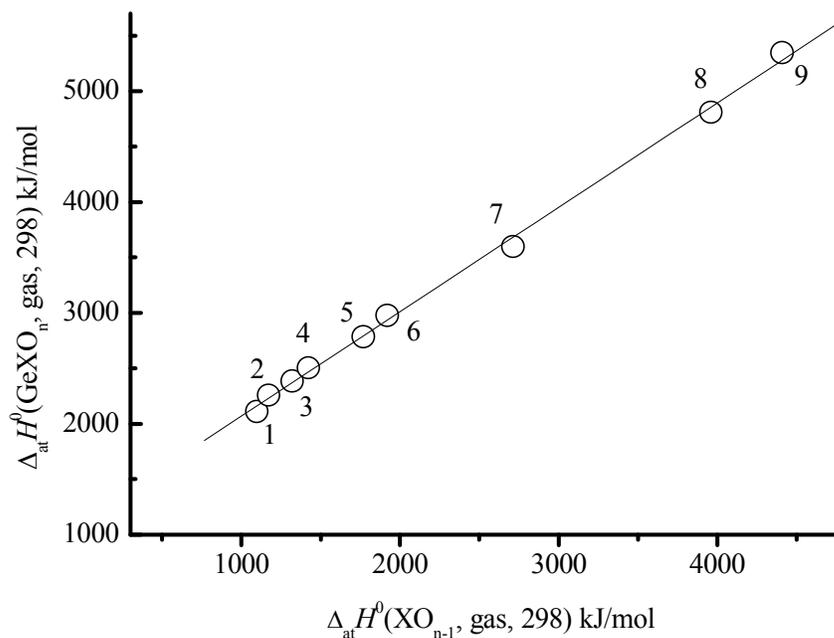
Fig. 4. Atomization enthalpies of gaseous germanium salts versus the atomization enthalpies of gaseous anion-forming oxides: (1) – $GePO_3$, (2) – $GeMoO_3$, (3) – $GeWO_3$, (4) – $GeNbO_3$, (5) – $GeMoO_4$, (6) – $GeWO_4$, (7) – GeB_2O_4, (8) – $GeMo_2O_7$, (9) – GeW_2O_7.

Consideration of the trends in atomization enthalpies in groups of salts forming isocationic series allows one to estimate atomization and formation enthalpies for yet unstudied compounds, including oxides, and also to correct experimental data falling out the linear dependence. Using eqn (9), we estimated the enthalpies of formation of gaseous germanium salts which have been detected in vapor but not characterized thermodynamically for some reasons, or are so far unknown. As new experimental data will be obtained, the coefficients k and b in eqn (9), as well as the enthalpies of formation of germanium gaseous salts may change. Enthalpies of formation of gaseous $GeTaO_3$, $GeTiO_3$, $GeVO_3$ and $GePO_2$ were estimated to be -592 ± 45, -751 ± 45, -664 ± 45 and -498 ± 45 kJ·mol^{-1}, respectively.

4. Conclusion

Gaseous germanium molybdates $GeMoO_4$, $GeMo_2O_7$ and borate GeB_2O_4 were detected in the vapor over the GeO_2-MoO_3 and GeO_2-B_2O_3 systems, respectively. $GeMo_2O_7$ and $In_2W_2O_7$ in the gas phase have been observed for the first time. The enthalpies of formation of these gaseous oxyacid salts were determined experimentally by Knudsen effusion mass spectrometry. The structures of gaseous $GeMoO_4$, $GeMo_2O_7$ and GeB_2O_4 were calculated by quantum chemistry methods. The structure of gaseous GeB_2O_4 is not the same as alkali earth metals borates.[31,43,44] The results obtained allowed to estimate the standard formation enthalpies of gaseous $GeTaO_3$, $GeTiO_3$, $GeVO_3$ and $GePO_2$.

Acknowledgments

References

1　　　M.M. Shultz, V.L. Stolyarova and G.A. Semenov, *Glass Phys. Chem*. 1978, **4**, 653.

2　　　S.I. Lopatin, *Rus. J. Gen. Chem.*, 2007, **77**, 1761.

3　　　S.I. Lopatin, A.I. Panin and S.M. Shugurov, *Dalton Trans.*, 2013, **42**, 8339.

4　　　S.I. Lopatin and G.A. Semenov, *Rus. J. Gen. Chem.*, 1995, **65**, 1060.

5　　　S.I. Lopatin, S.M. Shugurov and G.A. Semenov, *Vestnik SPbGU, Physic and Chemistry (Rus.)*, 2003, **2**, 50.

14

6   S.I. Lopatin, G.A. Semenov and T.S. Pilyugina, *Rus. J. Gen. Chem*., 2000, **70**, 529.

7   V. Plies, *Z. anorg. allg. Chem*., 1982, **484**, 165.

8   G.A. Semenov, *Rus. J. Phys. Chem.,* 1996, **70**, 997.

9   R.C. Paule and J. Mandel, *Pure Appl. Chem.*, 1972, **31**, 397.

10   *Energii razryva khimicheskikh svyazey: potentsialy ionizatsii i srodstvo k elektronu. Spravochnik. (Handbook on the Dissociation Energies of Chemical Bonds: Ionization Potentials and Electron Affinities)*, Nauka, Moscow, 1974.

11   *Recent Development in Mass Spectrometry,* Ogata K, Hayakawa T. (eds), Baltimore e.a., Univ. Park Press, 1970.

12   F.R. Manby, *J. Chem. Phys*., 2003, **119**, 4607.

13   A.J. May and F.R. Manby, *J. Chem. Phys*., 2004, **121**, 4479.

14   H.-J. Werner and F.R. Manby, *J. Chem. Phys*., 2006, **124**, 054114.

15   F.R. Manby, H.-J. Werner, T.B. Adler and A.J. May, *J. Chem .Phys*., 2006, **124**, 094103.

16   H.-J. Werner, *J. Chem. Phys*., 2008, **129**, 101103.

17   H.-J. Werner, T.B. Adler and F.R. Manby, *J. Chem. Phys*., 2007, **126**, 164102.

18   MOLPRO, version 2010.1, a package of ab initio programs.

19   Y. Zhao, D.G.Truhlar, *Theor. Chem. Account*, 2008, **120**, 215.

20   Gaussian 09, Revision D.01, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

21   R.A. Kendall, T.H. Dunning, Jr. and R.J. Harrison, *J. Chem. Phys*., 1992, **96**, 6796.

22   N.B. Balabanov and K.A. Peterson, *J. Chem. Phys.*, 2005, **123**, 064107.

23   F. Weigend and R. Ahlrichs, Phys. Chem. Chem. Phys., 2005,**7**, 3297.

15

24 http://www.chemcraftprog.com

25 M.D. Hanwell, D.E. Curtis, D.C. Lonie, T. Vandermeersch, E. Zurek and G.R. Hutchison, *J. Cheminform.*, 2012, **4**, 17.

26 A.E. Reed, L.A. Curtiss, F. Weinholt, *Chem. Rev.*, 1988, **88,** 899.

27 S.I. Lopatin, S.M. Shugurov and A.O. Gunina, *J. Phys. Chem. A*, 2009, **113**, 13469.

28 S.I. Lopatin, A.I. Panin and S.M.Shugurov, *Dalton Trans.*, 2013, **42**, 1210.

29 M.N. Bulova, A.S. Alikhanyan and A.M. Gas'kov, *Inorg. Materials.*, 2002, **38**, 688.

30 E.N. Nikolaev, K.V. Ovchinnikov and G.A. Semenov, *Rus. J. Gen. Ghem.*, 1984, **54**, 977.

31 V.I. Baranovskii, S.I. Lopatin and V.V. Sizov, *Rus. J. Gen. Chem.*, 2000, **70**, 1766.

32 S.I. Lopatin, *Rus. J. Gen. Ghem.*, 1999, **69**, 1417.

33 M. Guido and G. Gigli, *High Temp. Sci.,* 1975, **7**, 122.

34 R.T. Meyer and A.W. Lynch. *High Temp. Sci.*, 1973, **5**, 192.

35 *Termodinamicheskie Svoistva Individual'nykh Veschestv (Thermodynamic Properties of Individual Substances)*, V. P Glushko (ed), Nauka, Moscow, 1978−1982.

36 J.F. Chiang and D.R. Whitman, *Theor. Chin. Acta (Berl)*, 1970, **17**, 155.

37 L. Li and L. Cheng, *J. Chem. Phys.*, 2013, **138**, 094312.

38 F.-Q. Zhang, H.-S. Wu, Y.-Y. Xu, Y.-W. Li, and H. Jiao, *J. Mol. Model.*, 2006, **12**, 551.

39 Y.–P. Tong and Y.W. Lin, *J. Mol. Struct, (Theochem.)*, 2010, **952,** 61.

40 K.P. Huber and G. Herzberg "Constants of Diatomic Molecules" by (data prepared by J.W. Gallagher and R.D. Johnson, III) in NIST Chemistry WebBook, NIST Standard Reference Database Number 69**,** Eds. P.J. Linstrom and W.G. Mallard, National Institute of Standards and Technology, Gaithersburg MD, 20899, http://webbook.nist.gov, (retrieved April 14, 2014).

41 M.E. Casida, C. Jamorski, K.C. Casida, and D.R. Salahub, *J. Chem. Phys.*, 1998, **108**, 4439.

42 H. Eshuis, G.G. Balint-Kurti, and F.R. Manby, *J. Chem. Phys.*, 2008, **128**, 114113.

43 S.I. Lopatin, G.A. Semenov and S.M. Shugurov, *Rus. J. Gen. Chem.*, 2001, **71**, 68.

44 S.I. Lopatin, G.A. Semenov, V.I. Baranovskii, S.M. Shugurov and V.V. Sizov, *Rus. J. Gen. Chem.*, 2001, **71**, 1422.

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