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Thermochemical Study of Gaseous Salts of Oxygen-Containing Acids: XX.[1] Germanium Salts

S. I. Lopatin, S. M. Shugurov, A. I. Panin, and K. A. Emel'yanova

St. Petersburg State University, Universitetskii pr. 26, St. Petersburg, 198504 Russia
e-mail: sergeylopatin2009@yandex.ru

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Abstract—Reactions of the gas-phase synthesis of germanium vanadate, borate, and molybdate have been studied. Standard enthalpies of formation and atomization of gaseous salts GeV_2O_6, GeB_2O_4, and $SnMo_2O_7$ have been determined.

Keywords: high-temperature mass-spectrometry, gaseous germanium salts, gas-phase reactions

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The presence of two oxides GeO and GeO_2 in the germanium-oxygen system [2] was determined. Gas phase above GeO, GeO_2, and GeO_2–Ge mixtures was repeatedly studied [3–6]. Germanium dioxide passes in vapor in the temperature range 1300–1500 K according to Eq. (1).

$$GeO_2(cr) = GeO(gas) + 0.5\ O_2(gas). \quad (1)$$

Evaporation of the GeO_2–Ge mixture proceeds at lower temperatures (870–960 K), and in addition to GeO the molecules Ge_2O_2 and Ge_3O_3 were detected in vapor, their partial pressures bringing essential contribution to the total vapor pressure above the mixture [7]. IR spectra of the molecules isolated in inert matrices upon evaporation of GeO, GeO_2, and the GeO_2–Ge mixture were studied and structures of gaseous molecules $(GeO)_n$ (n = 1–4) were determined [8].

Gaseous germanium oxide GeO is amphoteric, as it can fulfill the roles of both anion- and cation-forming oxides in reactions of gas-phase synthesis of gaseous oxyacid salts. The existence of a gaseous salt, in which germanium functions as an anion-forming component, was detected experimentally: the molecule $BaGeO_2$ was found in vapor above the BaO–GeO_2 system [9]. Gaseous germanium salts were found in studies of vaporization products in the systems GeO_2–P_2O_5 [10], GeO_2–WO_3 [11], GeO_2–MoO_3 [12], and GeO_2–Nb_2O_5 [13]. At present it is known that the gaseous salts $GePO_3$, $GeWO_3$, $GeWO_4$, GeW_2O_7, $GeMoO_3$, $GeMoO_4$, and $GeNbO_3$ exist, as well as tin and lead gaseous borates and vanadates, which were thermodynamically characterized [1, 14].

As germanium is the tin and lead analog, the probability of germanium borate and vanadate existence in vapor is rather high. The synthesis of these gaseous salts would require conditions to be created for coexistence of GeO with B_2O_3 and V_4O_{10} in vapor, respectively [15].

Germanium vanadate. Vaporization of the GeO_2 mixture with V_2O_5 was carried out from an effusion cell made of zirconium dioxide. Necessity of using a cell made of this very material is described in detail in [1]. Peaks of the ions Ge^+, GeO^+, $V_4O_{10}^+$, and $GeV_2O_6^+$ were detected in the vapor mass spectrum in the temperature range 1550–1700 K. The intensity of the peak of $V_4O_{10}^+$ ions permanently decreased during vaporization, which is caused by V_2O_5 partial thermal dissociation. After decrease in the intensity of ionic currents to a noise level the temperature was lifted up to 2000 K and peaks of the ions VO_2^+ and $V_2O_4^+$ were detected, which confirms the results of [16].

To determine molecular precursors of the ions observed in the mass spectrum, we have measured their appearance energies, eV: 16.0±0.5 (Ge^+), 10.2±0.3 (GeO^+), 10.5±0.3 ($V_4O_{10}^+$), and 11.5±0.5 (GeV_2O_6). The value of gold ionization energy (9.2 eV)

[1] For communication XIX, see [1].

was used as the reference [17]. The comparison of appearance energies of ions in the mass spectrum of vapor above the mixture of GeO_2 and V_2O_5 with ionization energies of the corresponding molecules [17] has shown that the ions GeO^+, $V_4O_{10}^+$, and $GeV_2O_6^+$ are products of direct ionization of these molecules.

The appearance energy of GeO^+ coincides with the reference value of the GeO ionization energy [17]. The appearance energy of $V_4O_{10}^+$ (11.8 eV) was determined experimentally [18, 19]. According to our quantum-chemical calculations, ionization energies of V_4O_{10} and GeV_2O_6 are equal to 11.9 and 11.5 eV, respectively. In our experimental conditions the appearance energy of Ge^+ is much higher than the ionization energy of monatomic germanium, which allows us to state that this ion is a product of the dissociative GeO ionization.

The enthalpy of the reaction involving gaseous germanium vanadate was determined by Eq. (2).

$$\Delta_r H^0(0) = T\Delta_r \Phi^0(T) - RT\ln K_p(T). \quad (2)$$

Here $\Delta_r H^0(0)$, $\Delta_r H^0(T)$, and $\Delta_r \Phi^0(T)$ are changes in the enthalpy and reduced Gibbs energy of the reaction at 0 and T, K, respectively; R is the gas constant; K_p is reaction equilibrium constant.

To find standard formation enthalpies of gaseous germanium vanadate, we have determined equilibrium constants of reaction (3).

$$GeO(gas) + 0.5\ V_4O_{10}(gas) = GeV_2O_6(gas). \quad (3)$$

Thermodynamic functions of GeO and V_4O_{10} necessary for the calculation of the reaction (3) enthalpy were taken from the handbook [20], and those for GeV_2O_6 were calculated by the statistical thermodynamics method in the approximation rigid rotator–harmonic oscillator. Necessary molecular parameters and germanium vanadate structure were determined by quantum-chemical calculations. The results are presented in Table 1.

Germanium borate. A mixture of GeO_2 and B_2O_3 was evaporated from a molybdenum effusion cell. In the temperature range of 1300-1500 K peaks of Ge^+, GeO^+, $B_2O_3^+$, $GeBO_2^+$, and $GeB_2O_4^+$ ions were detected in the vapor mass spectra. Values of the appearance energy of the ions are, eV: 16.0±0.5 (Ge^+), 10.2±0.3 (GeO^+), 14.0±0.3 ($B_2O_3^+$), 11.6±0.5 ($GeBO_2^+$) and 11.2±0.5 ($GeB_2O_4^+$). The appearance energies of GeO^+ and $B_2O_3^+$ ions coincided within the limits of experimental error with the values of ionization energies of the GeO and B_2O_3 molecules [17]. The appearance energies of the ions $GeBO_2^+$ and $GeB_2O_4^+$ were measured for the first time. The ion $GeB_2O_4^+$ is a product of the direct ionization of the corresponding molecule, as the value of its appearance energy correlates with the value of the CaB_2O_4 ionization energy found by quantum-chemical calculations [21]. The ion $GeBO_2^+$ is a product of dissociative ionization of the GeB_2O_4 molecule [Eq. (4)]. If the ion $GeBO_2^+$ were a product of the molecule $GeBO_2$ direct ionization, its appearance energy would be considerably lower than that of GeB_2O_4 [22]. For example, ionization energies of the CaB_2O_4 and $CaBO_2$ molecules are equal to 10.84 and 6.53 eV, respectively [21].

$$GeB_2O_4 + e^- = GeBO_2^+ + BO_2 + 2e^-. \quad (4)$$

To determine the standard formation enthalpy of gaseous germanium borate, we have measured equilibrium constants of reaction (5) and have calculated enthalpy of this reaction by Eq. (2).

$$GeO(gas) + B_2O_3(gas) = GeB_2O_4(gas). \quad (5)$$

Thermodynamic functions of gaseous GeO and B_2O_3 necessary for the calculation of the reaction (5) enthalpy were taken from the handbook [20], and those for GeB_2O_4 were calculated by the statistical thermodynamics method in the approximation rigid rotator–harmonic oscillator. Necessary molecular parameters and structure of germanium borate were found by quantum-chemical calculations. The results are presented in Table 2.

Germanium molybdate $GeMo_2O_7$. In vapor above a mechanical mixture of GeO_2 and WO_2 in the temperatures range of 1258–1383 K molecules $GeWO_4$ and GeW_2O_7 were detected [11], and in vapor above a mixture of GeO_2 and MoO_3 taken in a molar ratio 1 : 1 only germanium molybdate $GeMoO_4$ was found in addition to GeO, Mo_2O_6, and Mo_3O_9 [12]. It is not excluded that the molecule $GeMo_2O_7$ has not been detected because of low instrument sensitivity, which has not allowed us to detect $GeMo_2O_7^+$ ions.

In the mass spectra of vapor above a GeO and MoO_3 mixture in the temperature range of 1380–1500 K peaks of the ions Ge^+, GeO^+, MoO_3^+, $Mo_2O_6^+$, $Mo_3O_9^+$, $GeMoO_4^+$, and $GeMo_2O_7^+$ were detected. Measured appearance energies of the ions, eV: 16.0±0.5 (Ge^+), 10.2±0.3 (GeO^+), 12.1±0.3 (MoO_3^+), 12.3±0.3 ($Mo_2O_6^+$), 12.2±0.3 ($Mo_3O_9^+$), 11.0±0.3 ($GeMoO_4^+$), and 12.7±0.5 ($GeMo_2O_7^+$).

Table 1. Partial pressures (p_i, atm) of vapor molecular species above the system GeO_2–V_2O_5 and enthalpies of reaction (3) at 0 K

T, K	$p(GeO) \times 10^{-4}$	$p(V_4O_{10}) \times 10^{-7}$	$p(GeV_2O_6) \times 10^{-7}$	$-\Delta_r H^0(0)$, kJ
1571	4.42	25.10	1.30	94.3
1574	4.92	17.84	4.21	78.2
1572	4.91	16.20	4.21	77.5
1573	4.72	11.35	3.91	75.7
1573	4.13	10.54	3.61	74.5
1577	3.75	12.19	3.02	76.7
1580	2.37	9.77	2.11	74.0
1579	2.37	14.65	1.81	78.7
1580	0.74	4.34	1.61	57.1
1611	10.90	68.23	11.04	86.7
1614	10.46	73.62	12.36	85.3
1626	11.46	68.87	11.79	87.3
1631	9.66	21.26	11.17	78.0
1635	4.61	1.95	7.25	57.8
1634	4.01	10.12	5.93	69.7
1582	4.86	67.01	9.56	76.4
1647	2.73	5.25	6.50	59.2
1661	1.93	3.44	5.90	53.3
1660	1.10	3.71	5.89	46.0
1702	1.48	1.63	3.69	64.8
1614	1.16	0.47	0.29	72.2
1613	1.36	0.99	0.43	74.0
1610	0.71	0.47	0.29	65.4
1677	1.15	0.30	0.52	63.4
1684	1.05	0.20	0.60	57.6
Average value				71.9±11.8

Analysis of the vapor mass spectra and of the appearance energies of ions has allowed us to conclude that all above-listed ions, except for Ge^+, are products of ionization of corresponding molecules. Appearance energies of the ions GeO^+, MoO_3^+, $Mo_2O_6^+$, and $Mo_3O_9^+$ coincide with ionization energies of the corresponding molecules within the limits of experimental errors [17]. The origin of the $GeMoO_4^+$ ion is described in detail in [12]. The $GeMo_2O_7^+$ ion is also molecular, as its appearance energy agrees well with ionization energies of the molecules $GeW_2O_7^+$ (12.5 eV) [11], $SnW_2O_7^+$ (11.0 eV) [23], and $PbMo_2O_7^+$ (11.4 eV) [24]. Thus, it has been found that in vapor above GeO and MoO_3 oxides the molecule $GeMo_2O_7$ exists in addition to the molecules GeO, MoO_3, Mo_2O_6, and $GeMoO_4$. Enthalpies of reactions (6), (7) involving $GeMo_2O_7$ were determined by Eq. (2).

$$GeO + Mo_2O_6 = GeMo_2O_7, \quad (6)$$

$$GeO + 2MoO_3 = GeMo_2O_7. \quad (7)$$

Thermodynamic functions of the gaseous molecules GeO, MoO_3, and Mo_2O_6 necessary for the calculation of enthalpies of reactions (6), (7) were taken from the handbook [20], and those for $GeMo_2O_7$ were calculated by the statistical thermodynamics method in the approximation rigid rotator–harmonic oscillator. Necessary molecular parameters and germanium borate structure were determined by quantum-chemical calculations. The values of partial pressures of vapor components and enthalpies of reactions are presented in Table 3.

Quantum-chemical calculations of structures and molecular parameters of gaseous germanium salts. Calculations of equilibrium geometries and frequencies of normal modes and also estimation of reactions enthalpies were carried out using two various approaches. The first approach described in [25–30] is

Table 2. Partial pressures (p_i, atm) of vapor molecular species above the system GeO_2–B_2O_5 and enthalpies of reaction (5) at 0 K

T, K	$p(GeO) \times 10^4$	$p(B_2O_3) \times 10^5$	$p(GeB_2O_4) \times 10^7$	$-\Delta_r H^0(0)$, kJ
1293	1.89	1.29	3.07	237.2
1351	32.32	7.13	24.25	219.6
1369	23.40	6.02	3.25	205.2
1357	15.46	6.36	4.11	210.1
1366	0.77	0.37	0.57	255.4
1283	0.72	0.13	0.68	254.3
1281	0.68	0.12	0.50	252.1
1287	0.73	0.19	0.58	249.1
1290	0.77	0.20	0.38	244.1
1386	2.00	0.34	0.13	232.5
1397	1.72	0.23	0.18	243.8
1461	2.11	0.34	0.19	247.9
1460	1.43	0.21	0.19	258.2
1460	1.30	0.23	0.10	250.1
1473	53.91	8.32	6.31	214.0
1473	49.10	8.32	6.02	214.6
1473	48.13	8.32	4.94	212.4
1472	49.06	8.07	5.75	214.3
1493	66.35	21.57	8.09	205.5
1494	75.18	14.89	10.52	211.9
1494	70.30	15.14	9.57	211.4
1495	70.35	14.90	10.86	213.3
1495	72.30	14.90	9.74	211.6
1495	69.37	14.90	1.03	212.8
1495	71.32	15.64	10.30	211.8
1494	68.35	14.89	8.35	210.2
1494	64.44	15.63	8.35	210.3
1494	62.49	15.63	8.35	210.7
1494	63.47	16.38	7.52	208.7
1425	3.61	1.67	1.29	239.6
1441	3.96	2.18	1.53	240.0
1445	2.23	2.30	1.54	246.9
1445	3.66	2.30	1.54	240.9
1464	4.51	3.44	2.11	240.4
1464	4.67	3.32	2.11	240.4
1465	4.68	3.56	2.20	240.2
1466	3.87	3.08	1.88	242.5
1466	3.71	3.20	1.65	241.0
1466	3.71	3.08	1.74	242.1
1495	4.44	5.64	2.34	240.6
1495	4.28	5.27	2.34	241.9
1494	4.27	5.39	2.34	241.5
1494	4.60	5.01	2.34	241.4
1494	4.44	5.14	2.34	241.6
1456	6.14	3.86	1.61	230.7
1457	7.53	3.67	1.75	230.0

Table 2. (Contd.)

T, K	$p(GeO) \times 10^4$	$p(B_2O_3) \times 10^5$	$p(GeB_2O_4) \times 10^7$	$-\Delta_r H^0(0)$, kJ
1457	7.14	3.22	1.44	229.9
1468	6.64	3.43	1.62	233.1
1472	4.57	2.88	1.21	236.9
1472	3.89	2.88	1.18	238.5
1471	15.84	2.97	1.49	223.7
1471	3.45	2.88	0.31	223.6
1458	5.48	4.94	2.23	233.3
Average value				231±16

based on the use of the wave functions of many-electron systems and is a modification of either variation perturbation theory or of coupled-cluster method. To take into account electronic correlation effects, this approach uses wave functions explicitly depending on interelectron distances. These methods were named explicitly correlated or F12-methods by their authors. In particular, the methods MP2-F12 [30] and CCSD (*T*)-F12 [31] were developed. In this work we used the MP2-F12 version in the form recommended in [32]. All calculations were carried out using the MOLPRO *ab initio* program set [33].

The second mode of calculation is based on the density functional method and uses the hybrid functional M06 developed for the calculation of atomization enthalpies and enthalpies of reactions of molecules containing transition elements [34.] The M06 calculations were fulfilled by the GAUSSIAN'09 program set [35]. For boron, oxygen, germanium, and vanadium full-electron the aug-cc-pvTZ Gaussian basis set [36, 37] were used. For molybdenum we took the def2-TZVP basis [38] with a corresponding effective core potential. Localization of points of the total energy minimum (equilibrium geometries) followed by calculation of frequencies of normal modes was carried out by the MP2 and DFT M06 methods. Visualization of geometries and normal modes was realized by means of graphical programs Chemcraft [39] and Avogadro [40].

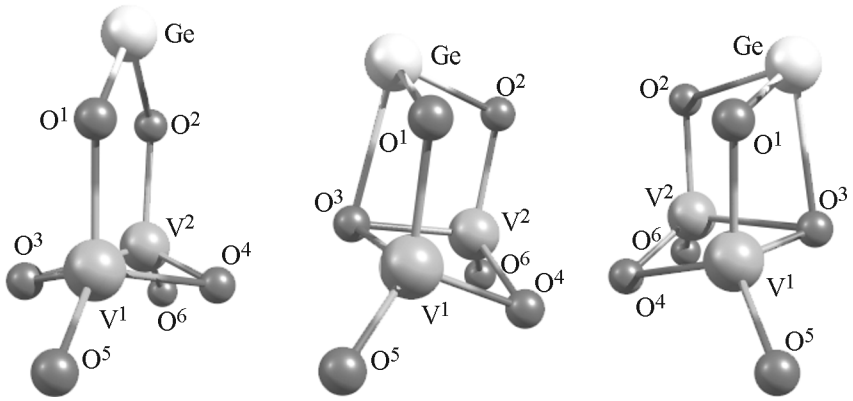
At the first step we fulfilled a complete optimization of structures of the reacting molecules GeO, B_2O_3, MoO_3, and Mo_2O_6 in their ground (singlet) states by the MP2 and DFT M06 methods with the subsequent calculation of normal mode frequencies. The corrections to total energies were calculated by the MP2-F12 method in points of potential energy surfaces (PES) corresponding to equilibrium geometries found by the MP2 method. The molecule V_4O_{10} is the exception, geometry of which was optimized in the chosen basis only by the DFT M06 method because of limited accessible computer resources.

The MP2 method slightly overestimates the Ge–O bond length of 1.664 Å (experimental value is 1.625 Å [41]) and underestimates the normal mode frequency of 948 cm^{-1} (experimental value is 985 cm^{-1}). The DFT M06 method gives the bond length value practically coincident with the experimental value, but overestimates the normal mode frequency (1011 cm^{-1}). Several minima on the ground state PES of the B_2O_3 molecule were found. The V-shaped geometry of the C_{2v} symmetry corresponds to the lowest energy, which agrees with available published data [42, 43]. Much less information is known about the properties of the gaseous V_4O_{10} molecule. It is reasonable to suggest that the geometric structure of this molecule is similar to that of the P_4O_{10} molecule, i.e. it belongs to the T_d symmetry group. Quantum-chemical calculations confirm this assumption. Vertical ionization energy (E_I) and electron affinity (E_A) of V_4O_{10} molecules calculated by the DFT M06 method as differences of total energies of a neutral molecule, a cation, and an anion at a fixed equilibrium geometry of a neutral particle [E_I(M06) 11.8 and E_A(M06) 3.97 eV] agree well with the experimental data [18, 19].

Gaseous molybdenum trioxide was studied experimentally and theoretically several times [44–47]. The geometry of its ground state has the C_{3v} symmetry with the bond length r(Mo–O) of 1.73 Å and the OMoO angle of 99º. The optimization by the DFT M06 method results in r(Mo–O) of 1.70 Å and OMoO angle of 110º, and by the MP2 method, r(Mo–O) of 1.75 Å and OMoO angle of 106º. It is necessary to note that the experimental values of the bond length and the angle were more likely estimated by analogy to oxides

Table 3. Partial pressures (p_i, atm) of vapor molecular species above the system GeO_2–MoO_3 and enthalpies of reactions (6) and (7) at 0 K

T, K	$p(GeO) \times 10^6$	$p(MoO_3) \times 10^7$	$p(Mo_2O_6) \times 10^6$	$p(GeMo_2O_7) \times 10^7$	$-\Delta_r H^0(0)$, kJ	
					reaction (6)	reaction (7)
1442	1.50	1.89	0.63	2.48	299.5	720.8
1447	1.50	1.60	0.69	2.34	298.7	726.5
1461	2.45	5.89	1.17	2.66	290.6	697.2
1478	2.71	9.39	1.18	4.48	298.9	698.6
1477	12.38	31.27	3.36	4.03	265.9	648.6
1488	13.18	55.51	8.92	8.12	263.6	646.9
1472	13.40	29.68	7.23	3.12	251.6	643.7
1449	12.14	17.53	11.58	7.91	254.6	659.3
1443	11.06	13.53	9.22	8.31	258.1	664.6
1434	10.65	18.80	4.30	5.22	260.6	647.7
1445	8.65	23.31	7.10	6.13	260.8	651.7
1442	8.29	18.90	10.37	5.68	255.4	655.0
1447	12.13	16.05	8.67	4.83	251.8	654.6
1435	11.34	28.94	6.88	6.53	257.0	639.8
1423	7.16	6.46	1.88	2.59	264.9	664.7
1425	2.96	9.48	1.88	1.73	270.9	662.2
1398	0.87	9.36	2.01	2.14	282.0	667.2
1398	0.77	4.68	0.67	0.52	279.7	668.3
1406	1.28	6.52	1.57	0.98	272.8	665.6
1407	1.25	6.88	1.63	0.65	268.0	660.3
1418	2.04	8.40	1.81	1.18	270.0	661.8
1413	1.80	6.55	1.81	1.38	272.4	668.7
1414	1.24	6.19	1.47	0.92	274.6	670.1
1414	1.35	5.46	1.36	1.05	276.1	673.6
1418	1.58	7.30	1.93	0.99	270.2	666.0
1424	1.59	8.07	2.39	1.26	271.5	669.1
1422	1.09	3.66	1.70	0.92	275.9	687.7
1425	1.30	6.24	1.08	0.99	280.6	675.2
1413	0.81	3.64	1.02	1.05	285.3	688.7
1420	0.65	4.75	1.02	0.79	285.9	684.9
1419	0.75	5.48	0.96	0.66	282.6	677.3
1419	0.71	1.46	0.74	0.46	282.0	704.9
1472	10.58	49.71	4.41	9.39	274.0	647.5
1486	11.03	52.58	5.16	10.34	275.2	652.6
1481	8.87	66.69	5.86	10.30	275.4	647.3
1483	9.94	62.01	6.22	10.31	273.6	648.5
1489	15.33	67.05	6.96	12.95	270.7	646.5
1495	14.68	48.09	5.20	6.93	268.1	650.0
1499	9.33	36.16	5.21	6.95	274.4	664.5
1486	10.68	31.55	3.38	3.88	268.7	653.5
1498	9.33	31.80	3.95	6.08	276.1	665.6
1499	8.62	24.59	2.51	1.82	267.8	658.4
Average value					273±12	667±20



I (C_{2v}) **II** (C_s) **III** (C_s)

Fig. 1. Possible structures of gaseous germanium vanadate.

of other metals than were directly determined [47]. The same is applicable to the frequencies of normal modes.

Much less is known about properties of the gaseous oxide Mo_2O_6. We can only say with confidence that Mo_2O_6 has the equilibrium geometry of the ground state corresponding to the D_{2h} symmetry point group.

To find out how much the effective core potential and the corresponding basis used for molybdenum are suitable for the description of thermodynamic values, we have calculated the atomization enthalpy of the MoO_3 molecule: $MoO_3(^1A_1) \rightarrow Mo(^7S) + 3O(^3P)$. The resulting value 1740.7 kJ/mol (at 0 K) agrees perfectly with the experimental value of 1740.1±21.3 kJ/mol [46].

To be sure that the correct description of the reactions under study does not require the consideration of excited states of reacting particles, we have estimated the energies of transition from ground states to lowest excited states using the TDDFT method [48, 49]. For all molecules under consideration the first excited states appeared to be triplet offset by 4.0 (GeO), 6.9 (B_2O_3), 3.25 (V_4O_{10}), 2.6 (MoO_3), and 3.4 eV (Mo_2O_6) from ground states.

Three minima on the ground state PES were found for the GeV_2O_6 molecule. Structures **I–III** corresponding to these minima are depicted in Fig. 1. Structures **II** and **III** have equal energies and are enantiomers. Very shallow potential wells correspond to them, and the lowest energy (when the DFT M06 method is used) has structure **I**. It can be assumed that the germanium atom can move rather freely in the O_3–Ge–O_4 plane.

On the PES of the ground singlet state of the GeB_2O_4 molecule two energy minima were detected. Geometries corresponding to them are depicted in Fig. 2. The energy difference between these isomers is ~80 kJ.

Unlike tin vanadate [1], gaseous germanium vanadate $Ge_2B_2O_5$ was not detected in vapor above a mixture of GeO_2 and B_2O_3. Isomers of this compound were calculated by a quantum-chemical method. On the ground state PES of $Ge_2B_2O_5$ three minima were found. Structures corresponding to them are presented in Fig. 3. Energies of structures **I, II** are very close to each other (ΔE ~12 kJ), structure **III** is offset by ~138 kJ from the first structure.

On the ground state PES of the $GeMoO_4$ molecule three minima were found. Geometries corresponded to them are presented in Fig. 4. Structure **I** is most favorable in energy and lays on the energy scale lower than structure **II** by ~148 kJ and lower than structure **III** by ~299 kJ. Calculation of $GeMoO_4$ thermodynamic functions in [12] was based on structure **I**.

On the ground state PES of the $GeMo_2O_7$ molecule two structures corresponding to energy minima were found. These structures are presented in Fig. 5. The second structure lays higher in energy by ~249 kJ than the first (ground) structure.

Calculated theoretically and found experimentally enthalpies of reactions (2), and (5)–(7) at 0 K are presented in Table 4. The combination of these enthalpies reduced to 298 K with the formation enthalpies of gaseous oxides of germanium GeO, vanadium V_4O_{10}, boron B_2O_3, and molybdenum MoO_3 and Mo_2O_6 has allowed us to determine standard formation enthalpies of gaseous germanium vanadate, borate, and molybdates, which are shown in Table 5.

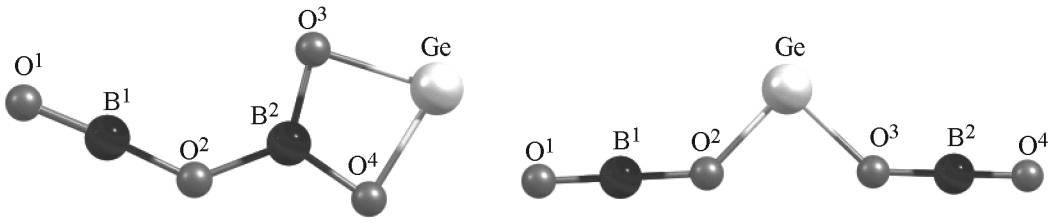


Fig. 2. Isomers of GeB_2O_4 derived theoretically by MP2 and DFT M06 methods.

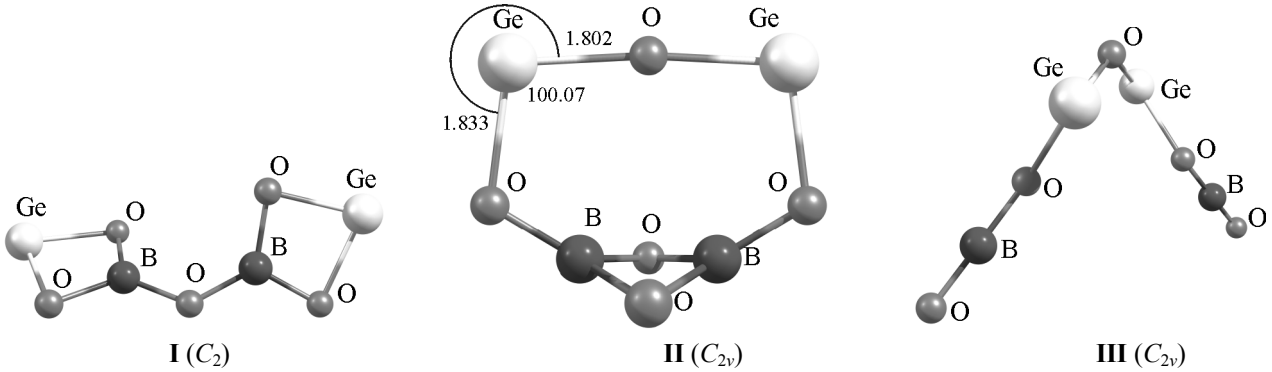


Fig. 3. Isomers of $Ge_2B_2O_5$ derived theoretically by MP2 and DFT M06 methods.

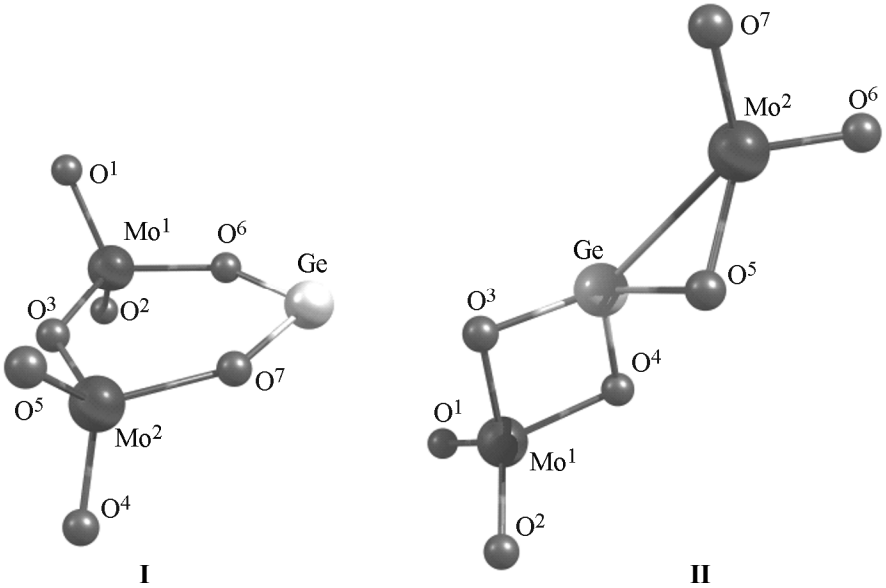


Fig. 4. Isomers of $GeMoO_4$ derived theoretically by MP2 and DFT M06 methods.

The values of formation and atomization enthalpies of gaseous $GeMo_2O_7$ found in the present work in combination with known atomization enthalpies of gaseous $GePO_3$ [10], $GeMoO_3$, $GeWO_3$, $GeNbO_3$ [13], $GeWO_4$, and GeW_2O_7 [11], and also of $GeMoO_4$ [12] have allowed us to derive a dependence of atomization enthalpies of gaseous germanium salts on the atomization enthalpies of gaseous anion-forming oxides. The dependence presented in Fig. 6 is described by Eq. (8).

$$\Delta_{at}H^0(\text{salt, gas, 298}) = k\Delta_{at}H^0(\text{anion-forming oxide, gas, 298}) + b. \quad (8)$$

For isocation germanium series coefficients k and b are equal to 0.9522±0.014 and 1112.7±35.0,

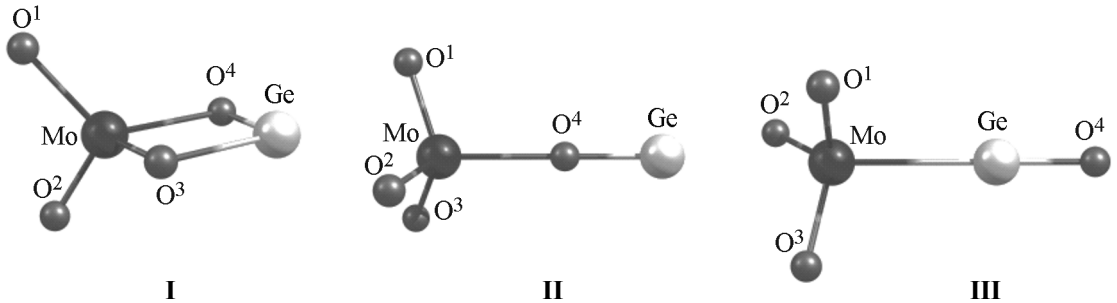


Fig. 5. Isomers of $GeMo_2O_7$ derived theoretically by MP2 and DFT M06 methods.

respectively, the correlation coefficient is –0.9992. The value of atomization enthalpy of gaseous germanium vanadate is absent from Fig. 6 because of the absence of the published value of the formation enthalpy of the anion-forming oxide V_2O_5(gas). Equation (8) derived for isocation series of tin and lead salts [1] makes it possible to estimate this value at –1160 kJ/mol. Results of the present work allow us to refine the value of the formation enthalpy of V_2O_5(gas): it is equal to –1168 kJ/mol.

EXPERIMENTAL

Mass spectra were recorded on an MS-1301 mass spectrometer at the energy of ionizing electrons of 30 eV. Mixtures of the oxides GeO_2–MoO_3 and GeO_2–B_2O_3 were evaporated from a molybdenum cell heated by a resistance furnace. Temperature was measured by a platinum–platinum–rhodium thermocouple. A mixture of GeO_2–V_2O_5 was evaporated from an effusion cell made of zirconium dioxide. The cell was heated by

Table 4. Theoretical and experimental values of enthalpies of reactions (3) and (5)–(7) at 0 K

Gas-phase reaction[a]	$-\Delta_rH^0(0)$, kJ			
	quantum-chemical calculations, method			experimental data
	DFT M06	MP2	MP2+f12	
$GeO(^1Y^+) + 0.5V_4O_{10}(^1A_1) = GeV_2O_6(^1A_1)$	66			72
$GeO(^1Y^+) + B_2O_3(^1A_1) = GeB_2O_4(^1A_1)$	264	247	249	231
$GeO(^1Y^+) + MoO_3(^1A_1) = GeMoO_4(^1A_1)$	367	315	327	363 [12]
$GeMoO_4(^1A_1) + MoO_3(^1A_1) = GeMo_2O_7(^1A_1)$	375	345	350	317 [12, our data]
$GeO(^1Y^+) + 2MoO_3(^1A_1) = GeMo_2O_7(^1A_1)$	741	660	677	667
$GeO(^1Y^+) + Mo_2O_6(^1A_g) = GeMo_2O_7(^1A_1)$	285	250	251	273

[a] Symbols in parentheses denote terms of ground states of molecules.

Table 5. Enthalpies of reactions (3), (5)–(7) (kJ) and standard enthalpies of formation (kJ/mol) of gaseous germanium salts

Gas-phase reaction	$-\Delta_rH^0(298)$	$-\Delta_fH^0$ (salt, 298, gas)	Recommended value of $-\Delta_fH^0$(salt, 298, gas)
$GeO + 1/2V_4O_{10} = GeV_2O_6$	71±12	1522±16	1522±16
$GeO + B_2O_3 = GeB_2O_4$	228±16	1101±18	1101±18
$GeO + 2MoO_3 = GeMo_2O_7$	667±20	1459±42	
$GeO + Mo_2O_6 = GeMo_2O_7$	272±12	1433±26	1449±41

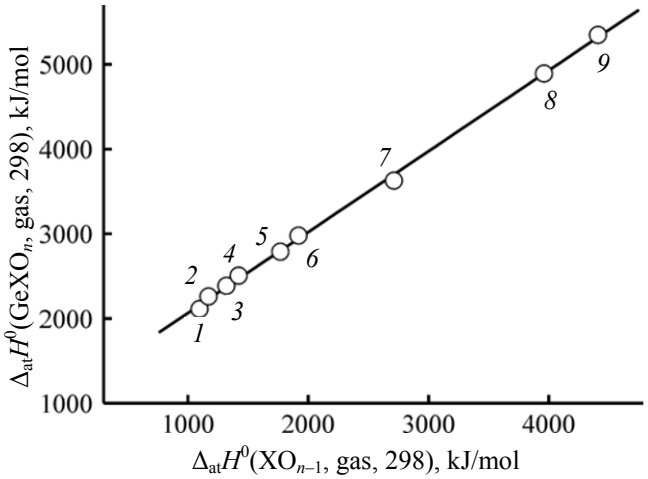


Fig. 6. Dependence of atomization enthalpies of gaseous germanium salts on the atomization enthalpies of gaseous anion-forming oxides. (*1*) $GePO_3$, (*2*) $GeNbO_3$, (*3*) $GeMoO_3$, (*4*) $GeWO_3$, (*5*) $GeMoO_4$, (*6*) $GeWO_4$, (*7*) GeB_2O_4, (*8*) $GeMo_2O_7$, (*9*) GeW_2O_7.

electron bombardment, temperature was measured by an EOP-66 optical pyrometer. Partial pressures of vapor components were measured by the method of comparing ionic currents using silver [50] or gold [51] as pressure standards. Partial pressures of molecular vapor species were determined by the method of comparing ionic currents, ionization cross-sections of molecules were calculated by the additivity method using the values of atomic ionization cross-sections from [52]. A correcting coefficient 0.7 was applied in the calculation of ionization cross-sections of gaseous germanium salts with V_4O_{10} [53].

To determine vapor molecular composition, we measured appearance energies of ions in mass spectra by the method of disappearing ionic current, using values of gold and silver ionization energies as standards [17]. The instrumentation was preliminarily calibrated against vapor pressure of CaF_2 [20].

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