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Thermodynamic Properties of the Gaseous Gallium Molybdates and Tungstates

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A number of gaseous oxyacid salts have been identified by Knudsen effusion mass spectrometry by vaporizing Ga_2O_3 from molybdenum and tungsten cells. The stability of gaseous molecules Ga_2MoO_4, Ga_2WO_4, $Ga_2Mo_2O_7$, and $Ga_2W_2O_7$ was deduced from the measurements. The structures and molecular parameters of all salts investigated were obtained using quantum chemical calculations. On the basis of equilibrium constants measured for gas-phase reactions, the standard formation enthalpies were determined to be -827 ± 26, -843 ± 26, -1578 ± 32, and -1525 ± 34 kJ·mol^{-1} for Ga_2MoO_4, Ga_2WO_4, $Ga_2Mo_2O_7$, and $Ga_2W_2O_7$, respectively.

Introduction

Gaseous oxyacid salts of type M_mXO_n are of interest for understanding of the chemical bonding in a large number of high-temperature vapors. Only gaseous gallium phosphates $GaPO_2$ and $GaPO_3$ had been known[1] before our investigations. Four new gaseous species, Ga_2MoO_4, Ga_2WO_4, $Ga_2Mo_2O_7$, and $Ga_2W_2O_7$, have been identified in the present work, and their thermochemical characteristics have been determined.

Gallium according to its position in the periodic table can form two oxides Ga_2O_3 and Ga_2O. The most stable compound in the condensed phase is Ga_2O_3, whereas Ga_2O oxide can be formed as a result of condensation of the mixture of gaseous Ga_2O_3 and metallic gallium.[2] The most stable component in the gas phase is Ga_2O, which is formed as a result of high-temperature oxidation−reduction of Ga_2O_3.[3] It was indicated[4,5] that Ga_2O can be produced by heating Ga_2O_3 to 1500−1600 K. At this temperature, gallium(III) oxide is decomposed to gallium(I) oxide and oxygen. The GaO molecule, of which the dissociation energy is 240 kJ·mol^{-1},[6] was observed by spectroscopic methods. A relatively more recent handbook[7] gives a much larger value of dissociation energy (~377 kJ·mol^{-1}).

Indium molybdate was obtained in vapor[8] by heating In_2O_3 with metallic molybdenum. Using the results of this study, IR absorption spectra of the vapor over the mixture of gallium, indium, and thallium oxides with molybdenum were analyzed.[9] The obtained absorption bands were attributed to gallium, indium, and thallium molybdates, respectively. It was noticed that in the IR spectra of the vapor over the thallium oxide−molybdenum mixture, the Tl_2O bands were missing, but in the IR spectra of the vapor over similar mixtures with gallium and indium oxides, the bands corresponding to antysymmetric vibrational frequencies ν_3 of Ga_2O and In_2O molecules were present. This observation testifies that gallium, indium, and thallium oxides when heated evaporate as M_2O and also that the vapor over Ga_2O_3−Mo and In_2O_3−Mo contains products of gallium and indium molybdates dissociation. The lowering of vibration frequencies of M−O and MoO_4 groups in molybdates in comparison with the corresponding ones in M_2O and Mo_3O_9 molecules were explained by the bicyclical structure of gaseous molybdates. The electron diffraction investigation[10] of the vapor over indium molybdates was also confirmed by the bicyclical structure with two cycles of In−O−O−Mo lying in perpendicular planes of In_2MoO_4 molecule. The structure of gaseous gallium, indium, and thallium molybdates and tungstates is the same as that of alkali metals molybdates and tungstates.[11]

The evaporation of Ga_2O_3 from molybdenum or tungsten cells leads to the formation of gaseous gallium molybdates or tungstates, respectively. These salts may also be obtained by the evaporation of mixtures of Ga_2O_3 and molybdenum or tungsten oxides, but this method is more technically laborious, particularly because of the fact that the double two-temperature cell[12] must be used because of the great difference in volatility between gallium and molybdenum and tungsten oxides.

Experimental Section

The Knudsen effusion technique with mass spectrometric analysis (standard model MS-1301 Construction Bureau, Academy of Science, St. Petersburg) of the vapor composition was employed. The molybdenum and tungsten twin effusion cells heated by electron bombardment were used. The temperature was measured with an accuracy of ±5 K using an optical pyrometer EOP-66 of high precision. The ratio of the vaporization area to the effusion hole area was ~200. Molecules effusing from the Knudsen cell were ionized by electron impact. The energy of electrons was 25 eV. To prove the composition of an ion, isotopic abundances were measured and compared with the theoretical abundances for possible ions of a particular mass. The appearance energies (AEs) of ions were obtained by the vanishing current method with Au as an energy standard,[13] which was found to be accurate within 0.3 eV. The partial vapor pressures of the gaseous species were determined by the method of ion currents comparison

$$p_i = p_{Au}\frac{I_i T_i \sigma_{Au}\gamma_{Au}}{I_{Au} T \sigma_i \gamma_i} \tag{1}$$

where I_i is the total ion current of the i-species; σ_i is the i-molecule ionization cross-section; and γ_i is the secondary electron multiplier gain factor that is inversely proportional to the square root of the molecular mass of the i-molecule. The use of eq 1 excludes the sensitivity constant because it presents in numerator and in denominator.

Atomic cross sections used were taken from Mann[14] and were equal to 1.27, 5.94, 6.91, and 9.24 × 10^{-24} cm^2 for oxygen, gallium, molybdenum, and tungsten, respectively. The cross

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TABLE 1: Equilibrium Data for the Gas-Phase Reactions 3 and 4 for the Ga_2O−Mo System

	p_i (atm)				$-\Delta_r H^0(0)$ (kJ)	
T (K)	$Ga_2O \times 10^{-6}$	$MoO_3 \times 10^{-7}$	$Ga_2MoO_4 \times 10^{-7}$	$Ga_2Mo_2O_7 \times 10^{-8}$	eq 3	eq 4
1612	5.2	2.0	4.6		380.4	
1601	3.6	1.3	2.8		382.5	
1607	4.0	1.8	3.9		382.7	
1610	5.5	3.1	6.9		378.9	
1631	7.5	2.8	5.2		376.9	
1623	6.3	2.2	4.3		378.4	
1615	5.4	1.8	3.3	4.8	377.5	786.9
1621	5.6	1.9	3.5	7.1	378.7	792.9
1608	4.0	1.5	2.7	6.1	380.3	795.7
1616	4.2	1.4	2.5	5.8	381.0	800.0
1617	3.6	1.2	2.9	5.2	386.7	805.2
1643	8.6	3.1	6.0	14.2	378.1	793.3
1640	9.0	2.6	4.5	8.2	375.5	788.6
1637	7.7	2.4	2.7	7.5	371.8	790.4
1643	8.1	2.5	3.9	9.2	376.3	794.1
1645	3.9	1.3	1.8	4.3	385.5	812.5
1625	5.4	2.4	2.6	3.7	373.0	780.2
1604	4.9	1.3	1.7	4.8	371.9	791.8
1634	5.6	2.1	2.7	8.6	376.8	798.8
1628	5.0	2.0	2.7	7.8	390.3	797.6
1614	4.6	1.8	2.7	6.6	375.8	792.8
1628	5.4	2.0	3.6	10.0	380.2	799.9
1618	4.6	1.7	2.9	8.9	379.4	800.2
1631	5.6	2.1	3.2	9.7	378.5	799.1
1636	5.4	2.5	3.6	11.2	379.2	799.1
1653	6.8	5.1	4.4	14.0	372.7	787.2
1649	5.7	2.0	1.8	3.8	374.4	795.6
1585	6.7	2.0	3.6	8.2	367.9	774.5
1580	4.0	1.6	3.6	8.2	377.0	784.9
1623	7.9	4.5	11.1	32.4	378.4	786.4
1622	9.6	4.5	10.1	28.3	374.3	781.5
1618	9.1	4.3	9.4	26.2	373.9	780.6
		average value			378 ±5	796 ± 9

sections of Mo_3O_9, Ga_2MoO_4, Ga_2WO_4, $Ga_2Mo_2O_7$, and $Ga_2W_2O_7$ were obtained by the additivity method and multiplied by a factor 0.7, as recommended by Guido et al.[15] The experimental technique is described in detail elsewhere.[16,17]

Results and Discussion

The mixture of Ga_2O and MoO_3 was evaporated to obtain gaseous molybdates. The Ga^+, Ga_2^+, Ga_2O^+, $Mo_3O_9^+$, $Ga_2MoO_3^+$, and $Ga_2MoO_4^+$ ions were detected in the mass spectra of the vapor over the mixture of Ga_2O_3 and MoO_3 at the temperature range from 1516 to 1592 K. The relative intensities of these ions depended on the temperature and the evaporation time. However, the composition of the condensed phase rapidly changed, and equilibrium was not achieved. This fact did not allow us to obtain reliable results. But thermodynamic data from this system were also taken into account during the determination of formation enthalpy of Ga_2MoO_4.

When we evaporated Ga_2O_3 from the molybdenum or tungsten cells, the sample reacted with the material of the cell and the Ga^+, Ga_2^+, Ga_2O^+, XO_2^+, XO_3^+, $Ga_2XO_3^+$, $Ga_2XO_4^+$, and $Ga_2X_2O_7^+$ ions were detected in the mass spectra in the temperature range of 1558−1711 K.

The appearance energies of ions are Ga^+ (6.0), Ga_2^+ (12.8), Ga_2O^+ (7.6), MoO_2^+ (9.5), MoO_3^+ (12.1), WO_2^+ (10.0), WO_3^+ (11.6), $Ga_2MoO_3^+$ (13.8), $Ga_2WO_3^+$ (13.6), $Ga_2MoO_4^+$ (11.8), $Ga_2WO_4^+$ (11.5), and $Ga_2Mo_2O_7^+$ (11.8). The AEs for ions Ga^+, Ga_2O^+, MoO_2^+, MoO_3^+, WO_2^+, and WO_3^+ coincide within the experimental error, with the ionization energies of the respective molecules.[13] The AEs of $Ga_2XO_4^+$ were determined for the first time. The values found correlate with the AEs of molecular ions determined previously in the vapor over the alkali metal molybdates and tungstates.[18] The AE was not measured for $Ga_2W_2O_7^+$ ion because of the low ion current intensity. The observed ions of Ga_2^+, $Ga_2MoO_3^+$, and $Ga_2WO_3^+$ are the fragment ions of Ga_2O and Ga_2XO_4 molecules, respectively.[5]

To determine the standard enthalpies of formation for gallium molybdates and tungstates, we derived the equilibrium constants K_p and enthalpies for gaseous reactions 2−4 using eq 5.

$$Ga_2O + 1/3\ Mo_3O_9 = Ga_2MoO_4 \tag{2}$$

$$Ga_2O + XO_3 = Ga_2XO_4 \tag{3}$$

$$Ga_2O + 2\ XO_3 = Ga_2X_2O_7 \tag{4}$$

$$\Delta_r H^0(0\ K) = T[\Delta_r \Phi^0(T) - R \ln K_p(T)] \tag{5}$$

Here $\Delta_r H^0(0)$ and $\Delta_r \Phi^0(T)$ are the changes of the enthalpy and free-energy function of the reaction at temperature 0 and T, respectively; R is the gas constant; and K_p is the equilibrium constant of the reaction. The partial pressures and standard enthalpies of reactions 2−4 are presented in Tables 1−4. The free-energy function and heat capacity of gaseous oxides necessary for the calculation of the enthalpies of reactions and evaluation to standard temperature 298 K were taken from ref 19. The free-energy function and heat capacity of gaseous gallium salts (presented in Tables 5−8) were calculated by the

TABLE 2: Equilibrium Data for the Gas-Phase Reaction 3 for the Ga_2O-W System

	p_i (atm)			$-\Delta_rH^0(0)$ (kJ)
T (K)	$Ga_2O \times 10^{-6}$	$WO_3 \times 10^{-8}$	$Ga_2WO_4 \times 10^{-7}$	3
1570	2.8	0.4	2.7	430.6
1573	3.0	0.8	2.7	422.0
1572	3.0	0.8	2.8	422.8
1568	2.9	1.0	2.7	418.5
1567	2.5	0.7	2.2	422.4
1626	7.7	2.3	4.8	416.0
1625	5.6	1.9	3.1	416.7
1626	5.8	1.7	3.1	418.0
1625	5.3	1.4	3.0	421.1
1625	4.7	1.3	2.6	422.1
1663	8.4	2.6	3.5	417.8
1558	1.2	0.3	1.0	430.7
1632	8.9	1.4	1.8	409.6
1620	5.3	1.1	1.5	413.5
1635	2.6	1.1	1.0	421.0
1625	6.0	2.4	33.0	445.2
1633	4.3	2.2	23.4	448.8
1651	4.6	2.4	25.0	452.2
1646	3.5	2.1	19.3	452.7
1644	3.3	1.9	18.0	453.4
1645	3.3	1.7	18.0	455.0
1647	3.5	2.1	19.3	452.9
1658	1.2	3.1	6.5	450.6
1565	2.6	0.8	1.6	414.2
1566	1.5	0.8	1.9	425.2
1581	1.5	0.3	1.6	438.1
1603	4.8	1.3	2.6	417.3
1613	4.1	1.3	2.0	418.3
1613	3.3	1.1	2.0	422.9
1616	3.3	1.2	2.0	422.9
1619	3.2	1.0	1.7	424.6
1624	2.7	0.8	1.4	427.6
1614	1.9	0.9	1.0	424.6
		average value		429 ± 14

TABLE 3: Equilibrium Data for the Gas-Phase Reaction 4 for the Ga_2O-W System

	p_i (atm)			$-\Delta_rH^0(0)$ (kJ)
T (K)	$Ga_2O \times 10^{-5}$	$WO_3 \times 10^{-7}$	$Ga_2W_2O_7 \times 10^{-6}$	*4*
1677	5.1	6.9	2.1	799.1
1677	3.8	8.6	2.1	797.0
1673	4.1	6.9	1.9	798.9
1674	1.9	5.2	1.7	816.4
1711	2.5	8.8	1.7	815.6
1668	5.0	10.5	1.8	781.5
1670	4.7	8.4	2.8	795.6
1673	5.4	8.4	2.3	792.3
1673	4.1	10.5	2.8	792.6
1676	3.6	10.6	2.3	792.8
1675	2.9	8.4	1.8	798.4
1673	2.1	6.3	1.4	806.5
1629	7.2	6.7	2.1	773.7
1611	4.2	4.0	2.6	789.5
1641	7.2	6.8	2.7	782.1
1640	7.0	6.8	2.5	780.9
1653	8.8	8.2	3.3	782.3
1648	7.5	8.2	3.1	781.4
1646	7.2	8.2	2.7	779.2
1647	6.8	6.8	2.7	785.5
1648	6.3	6.8	2.2	784.2
1685	9.2	11.1	3.8	789.4
1677	7.6	9.7	3.5	791.1
1676	7.9	9.7	3.5	790.1
1684	6.1	8.4	3.0	779.2
1686	3.6	5.6	2.7	817.3
		average value		793 ± 12

TABLE 4: Equilibrium Data for the Gas-Phase Reaction 2 for the Ga_2O-MoO_3 System

	p_i (atm)			$-\Delta_rH^0(0)$ (kJ)
T (K)	$Ga_2O \times 10^{-5}$	$Mo_3O_9 \times 10^{-6}$	$Ga_2Mo_2O_7 \times 10^{-6}$	
1564	1.82	1.23	2.82	81.3
1581	2.66	1.86	3.46	78.0
1573	2.34	1.65	2.54	75.8
1633	7.57	2.78	5.12	69.4
1635	6.17	1.28	3.42	70.2
1679	7.24	1.54	3.67	69.6
1675	4.69	0.44	1.27	73.3
1549	2.32	2.37	2.65	73.9
1560	1.97	2.17	2.67	76.9
1562	1.60	1.30	1.60	75.3
1562	1.72	1.08	1.92	77.5
1573	2.48	1.20	1.88	72.5
1617	9.56	2.69	6.36	68.8
1545	0.41	0.46	2.07	99.8
1543	2.46	0.36	0.33	54.0
1513	0.97	0.16	0.58	75.6
1511	0.95	0.10	0.44	74.1
1536	1.84	0.30	1.08	73.6
1530	2.34	0.34	1.47	73.7
1540	0.67	0.28	1.38	90.2
1542	1.64	0.22	1.18	77.8
1543	2.26	0.34	1.38	73.9
1552	2.47	0.34	1.84	76.7
1548	2.57	0.60	2.03	74.9
1536	2.40	0.50	1.47	72.0
1548	1.05	0.60	1.83	85.2
1554	0.99	0.55	1.73	85.9
1565	1.63	0.97	2.98	84.5
1566	1.32	1.02	3.19	88.1
1563	0.96	0.65	3.28	94.4
1571	0.89	0.65	1.75	87.6
1561	0.71	0.51	1.64	90.2
1609	3.60	2.86	6.34	81.3
1594	3.32	1.04	3.14	77.0
1592	3.31	1.04	3.13	76.9
1592	3.23	0.66	2.40	75.7
		average value		78 ± 8

TABLE 5: Thermodynamic Functions: Heat Capacity, $C_p{}^0$, Entropy, S^0, Free-Energy Function, Φ^0, and Enthalpy Increment, $H(T) - H(0\ K)$, of Gaseous Ga_2MoO_4 at Selected Temperatures in the Temperature Range 298.15−1900 K

T	$\Phi^0{}_m(T)$	$S^0{}_m(T)$	$H(T) - H(0\ K)$	$C_{p,m}{}^0(T)$
K	$J \cdot K^{-1} \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$
298.15	330.3	418.9	26.4	88.7
1000	462.8	590.8	128.1	128.1
1100	475.1	605.5	143.4	130.4
1200	486.5	618.9	158.8	132.4
1300	497.2	631.3	174.3	134.1
1400	507.2	642.8	189.8	135.6
1500	516.6	653.5	205.4	136.9
1600	525.5	663.6	221.0	138.1
1700	533.9	673.1	236.6	139.2
1800	541.9	682.0	252.2	140.1
1900	549.5	690.5	267.9	141.0

statistical thermodynamic method in the rigid rotor−harmonic oscillator approximation on base of molecular parameters and vibrational frequencies obtained by quantum chemistry computation. The calculations were performed using the PC GAMESS version[20] of the GAMESS(US) QC package.[21] The quantum-chemical calculations of the geometries, electronic structures, and vibrational spectra of the gaseous salts formed by Ga(I) oxide that were identified in this work are performed for the first time. These data hadn't been found in the literature. Structures of all molecules have been fully optimized with subsequent vibrational analysis and correspond to minima on the potential energy surface (PES). Density functional theory in form of the B3LYP functional[22,23] have been used with adjunction of the following basis sets: (1) full electron basis set 6-31G(3df)[24,25] for oxygen, (2) ECP basis sets aug-cc-pVQZ-PP[26] (Ga_2MoO_4 molecule), SBKJC[27] (Ga_2WO_4 molecule), and SDB-aug-cc-pVTZ[28] ($Ga_2X_2O_7$ molecules) for gallium, (3) ECP

TABLE 6: Thermodynamic Functions: Heat Capacity, C_p^0, Entropy, S^0, Free-Energy Function, Φ^0, and Enthalpy Increment $H(T) - H(0\ \mathrm{K})$ of Gaseous Ga_2WO_4 at Selected Temperatures in the Temperature Range 298.15−2100 K

T	$\Phi^0_{\mathrm{m}}(T)$	$S^0_{\mathrm{m}}(\mathrm{T})$	$H(T) - H(0\ \mathrm{K})$	$C_{p,\mathrm{m}}^0(T)$
K	$J\cdot K^{-1}\cdot mol^{-1}$v	$J\cdot K^{-1}\cdot mol^{-1}$	$kJ\cdot mol^{-1}$	$J\cdot K^{-1}\cdot mol^{-1}$
298.15	331.8	420.0	26.3	88.2
1000	463.9	591.6	127.8	127.8
1100	476.1	606.3	143.1	130.1
1200	487.6	619.7	158.6	132.1
1300	498.2	632.1	174.0	133.9
1400	508.2	643.6	189.6	135.4
1500	517.6	654.3	205.1	136.7
1600	526.4	664.4	220.7	137.9
1700	534.8	673.8	236.3	139.0
1800	542.8	682.8	251.9	140.0
1900	550.4	691.2	267.6	140.8
2000	557.6	699.3	283.2	141.6
2100	564.6	706.9	298.9	142.3

TABLE 7: Thermodynamic Functions: Heat Capacity, C_p^0, Entropy, S^0, Free-Energy Function, Φ^0, and Enthalpy Increment, $H(T) - H(0\ \mathrm{K})$ of Gaseous $Ga_2Mo_2O_7$ at Selected Temperatures in the Temperature Range 298.15−2000 K

T	$\Phi^0_{\mathrm{m}}(T)$	$S^0_{\mathrm{m}}(T)$	$H(T) - H(0\ \mathrm{K})$	$C_{p,\mathrm{m}}^0(T)$
K	$J\cdot K^{-1}\cdot mol^{-1}$	$J\cdot K^{-1}\cdot mol^{-1}$	$kJ\cdot mol^{-1}$	$J\cdot K^{-1}\cdot mol^{-1}$
298.15	404.5	541.8	41.0	137.4
1000	614.3	819.8	205.5	205.5
1100	634.1	843.6	230.4	209.5
1200	652.5	865.4	255.5	213.0
1300	669.6	885.6	280.8	216.0
1400	685.7	904.3	306.0	218.6
1500	700.9	921.8	331.4	221.0
1600	715.2	938.2	356.8	223.0
1700	728.8	953.6	382.2	224.8
1800	741.7	968.2	407.7	226.5
1900	754.0	982.0	433.2	228.0
2000	765.7	995.1	458.7	229.4

TABLE 8: Thermodynamic Functions: Heat Capacity, C_p^0, Entropy, S^0, Free-Energy Function, Φ^0, and Enthalpy Increment $H(T) - H(0\ \mathrm{K})$ of Gaseous $Ga_2W_2O_7$ at Selected Temperatures in the Temperature Range 298.15−2100 K

T	$\Phi^0_{\mathrm{m}}(\mathrm{T})$	$S^0_{\mathrm{m}}(T)$	$H(T) - H(0\ \mathrm{K})$	$C_{p,\mathrm{m}}^0(T)$
K	$J\cdot K^{-1}\cdot mol^{-1}$	$J\cdot K^{-1}\cdot mol^{-1}$	$kJ\cdot mol^{-1}$	$J\cdot K^{-1}\cdot mol^{-1}$
298.15	417.2	554.9	41.06	137.7
1000	626.9	832.0	205.2	205.2
1100	646.6	855.8	230.1	209.2
1200	665.0	877.6	255.2	212.7
1300	682.1	897.8	280.4	215.7
1400	698.2	916.5	305.7	218.3
1500	713.3	934.0	331.0	220.7
1600	727.7	950.4	356.4	222.7
1700	741.2	965.8	381.8	224.6
1800	754.1	980.4	407.3	226.3
1900	766.4	994.1	432.8	227.8
2000	778.1	1007.0	458.3	229.1
2100	789.3	1020.0	483.8	230.4

basis sets LANL2DZ[29] ($Ga_2Mo_2O_7$ molecule) and Stuttgart RSC 1997[30] (Ga_2MoO_4 molecule) for molybdenum, and (4) ECP basis set LANL2DZ[29] for tungsten for all investigated molecules.

The structure optimizations for all molecules were performed without symmetry restriction (C_1 symmetry). The ground state of molecules has singlet multiplicity.

For Ga_2XO_4 molecules, two four-membered cycles Ga-(μ-O)$_2$X lying in orthogonal planes (D_{2h} point group, Figure 1a) are the global minima of theory. They possess the following structural parameters: r(Ga−O) = 0.2157 nm, r(Mo−O) = 0.1795 nm, and $\angle(O_{cycl}MoO_{cycl})$ = 116.1° for Ga_2MoO_4 and r(Ga−O) = 0.2174 nm, r(W−O) = 0.1799 nm, and $\angle(O_{cycl}\text{-}WO_{cycl})$ = 116.1° for Ga_2WO_4 molecules. As discovered experimentally, gaseous alkali metals[11] and indium[10] molybdates and tungstates have the same structures. Frequencies calculated are 54, 54, 120, 123, 181, 244, 275, 303, 304, 392, 412, 821, 823, 864, and 869 cm^{-1} for Ga_2MoO_4 and 55, 55, 138, 140, 188, 232, 278, 296, 296, 402, 404, 825, 827, 856, and 908 cm^{-1} for Ga_2WO_4. In ref 9, absorption bands 760 and 930 cm^{-1} were interpreted as vibration frequencies of the MoO_4 group of Ga_2MoO_4. There are no equal or at least close frequencies among the calculated ones. However, if we compare frequencies obtained in ref 9 for In_2MoO_4 (760 and 930 cm^{-1}) with frequencies obtained in later works[30,31] (839 and 829.5 cm^{-1}), then we shall see that they are not similar at all. Therefore, the comparison of our results of calculation and the corresponding experimental data is hardly possible.

Four structural isomers have been considered for $Ga_2X_2O_7$ molecules. Their structures are presented in Figure 1b−e. Among all considered species, the most stable one is (μ−O) (O = XGa(μ-O)$_2$)$_2$ (C_{2v} point group, Figure 1b). The energy of isomers was compared using the B3LYP functional and following basis sets: ECP basis set SBK for gallium, molybdenum, and tungsten and full electron basis set 6-31G for oxygen. For $Ga_2Mo_2O_7$, the energy of structure c (Figure 1) is higher than energy of structure b by 61 kJ, the energy of structure d is higher by 21 kJ, and the energy of structure e is higher by 25 kJ. For $Ga_2W_2O_7$, the energy of structure c (Figure 1) is higher than the energy of structure b by 60 kJ, the energy of structure d is higher by 18 kJ, and the energy of structure e is higher by 19 kJ.

The $Ga_2Mo_2O_7$ molecule possesses the following major structural parameters: r(Ga−O) = 0.2149 nm, r(Mo−O′) = 0.1927 nm, r(Mo−O″) = 0.1707 nm; r(Mo−O) = 0.1789 nm, and $\angle$(MoO′Mo) = 113.9°. The $Ga_2W_2O_7$ molecule possesses the following major structural parameters: r(Ga−O) = 0.2054 nm, r(W−O′) = 0.1923 nm, r(W−O″) = 0.1723 nm, r(W−O) = 0.1795 nm, and $\angle$(WO′W) = 108.6°. The Ga−O distances are similar in all molecules, which is connected to the ion-pair conception of gaseous salts structure. It is typical that the Mo−O distances are similar to analogous W−O distances. Frequencies calculated are 24, 34, 57, 100, 111, 133, 139, 172, 182, 190, 193, 197, 285, 286, 286, 293, 300, 340, 344, 596, 646, 774, 853, 859, 878, 990, and 997 cm^{-1} for $Ga_2Mo_2O_7$ and 20, 22, 62, 95, 99, 117, 138, 170, 178, 181, 193, 193, 287, 295, 295, 302, 306, 343, 344, 593, 685, 784, 856, 889, 900, 1003, and 1009 cm^{-1} for $Ga_2W_2O_7$.

Using the enthalpies of reactions 2−4 together with the formation enthalpies of gaseous gallium, molybdenum, and tungsten oxides,[19] we determined the standard formation and atomization enthalpies of gaseous Ga_2MoO_4, Ga_2WO_4, $Ga_2Mo_2O_7$, and $Ga_2W_2O_7$ molecules. The resulting values are listed in the Table 9.

Also, the reaction enthalpies of eqs 3 and 4 were calculated from the results of quantum chemical calculations. The values obtained are: −359 and −439 kJ in reaction 3 for molybdate and tungstate, respectively, and −685 and −825 kJ in reaction 4 for molybdate and tungstate, respectively. These values are not in a good agreement with the values obtained experimentally, especially for gallium molybdates, but for tungstates, they coincide with calculating error.

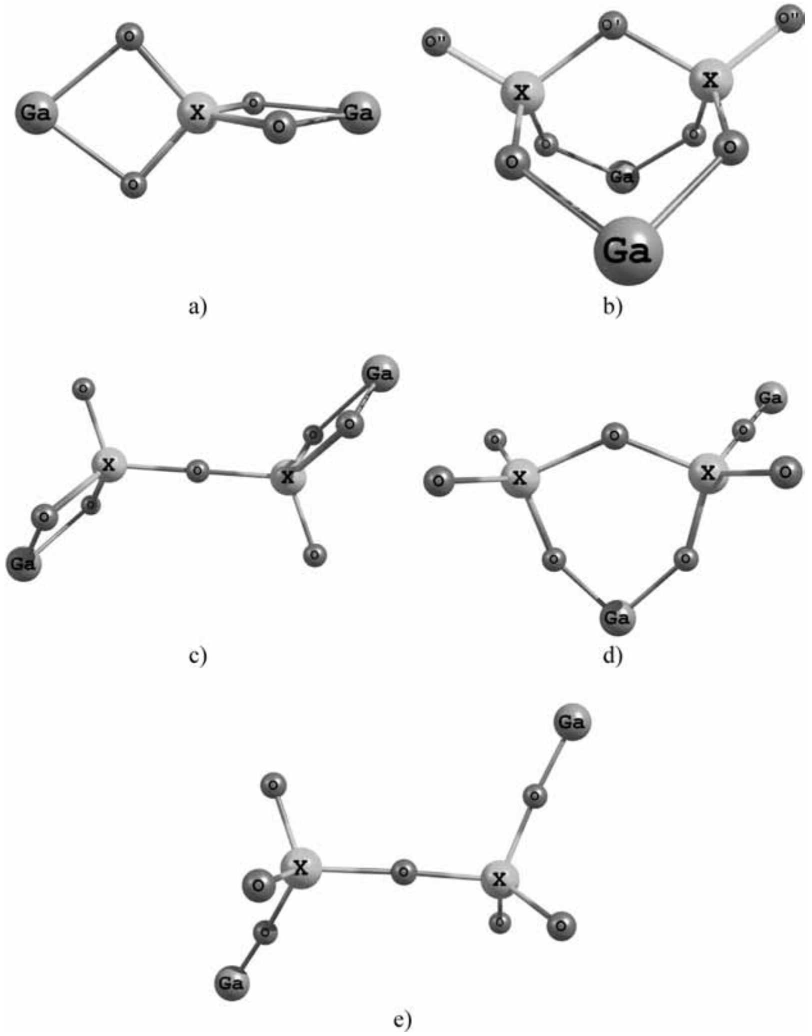

Figure 1. Structures of gaseous gallium molybdates and tungstates ((a) Ga_2XO_4, (b−e) $Ga_2X_2O_7$).

TABLE 9: Reaction Enthalpies Studied, Standard Formation, and Atomization Enthalpies of Gaseous Gallium(I) Underlined Salts

reaction	$-\Delta_r H^0(298)$ kJ	$-\Delta_f H^0(298)$ kJ·mol^{-1}	$-\Delta_f H^0(298)$ kJ·mol^{-1} (recommended value)	$\Delta_{at} H^0(298)$ kJ·mol^{-1}
$Ga_2O + 1/3Mo_3O_9 = \underline{Ga_2MoO_4}$	78 ± 12	817 ± 29	827 ± 26	3021 ± 28
$Ga_2O + MoO_3 = \underline{Ga_2MoO_4}$	379 ± 11	839 ± 22		
$Ga_2O + 2MoO_3 = \underline{Ga_2Mo_2O_7}$	790 ± 22	1578 ± 32	1578 ± 32	5181 ± 34
$Ga_2O + WO_3 = \underline{Ga_2WO_4}$	428 ± 17	843 ± 26	843 ± 26	3235 ± 28
$Ga_2O + 2\ WO_3 = \underline{Ga_2W_2O_7}$	791 ± 34	1525 ± 34	1525 ± 34	5515 ± 36

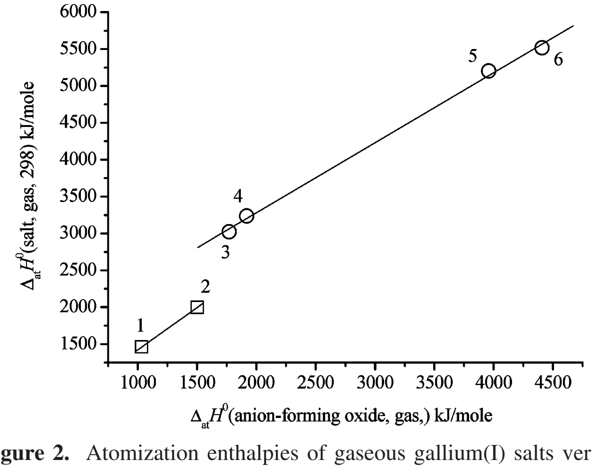

Figure 2. Atomization enthalpies of gaseous gallium(I) salts versus the atomization enthalpies of gaseous anion-forming oxides: (1) $GaPO_2$, (2) $GaPO_3$, (3) Ga_2MoO_4, (4) Ga_2WO_4, (5) $Ga_2Mo_2O_7$, and (6) $Ga_2W_2O_7$.

In the isocationic series of gaseous oxyacid salts, the atomization enthalpies of salts are linear functions of the atomization enthalpies of the gaseous anion-forming oxides.[32] These functions can be represented by eq 6

$$\Delta_{at}H^0(\text{salt, gas, 298}) = k\Delta_{at}H^0(\text{anion-forming oxide, gas, 298}) + b \quad (6)$$

The atomization enthalpies of gaseous gallium salts determined in this work were used to plot the function for the isocationic series of gaseous gallium(I) salts (Figure 2). If the molecule of a gaseous salt includes two atoms of gallium, then the coefficients k and b in eq 5 are 0.946 ± 0.025 and 1387 ± 80, respectively. The high correlation coefficient (0.999) proves the adequacy of the results.

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