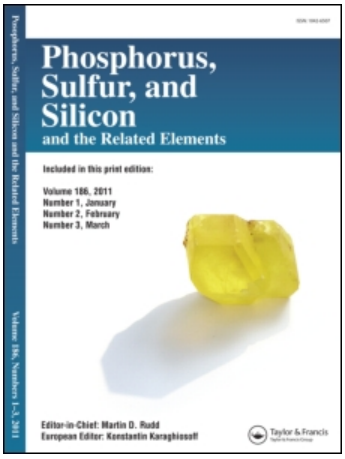

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THERMODYNAMIC STUDY OF GASEOUS MANGANESE PHOSPHATES $MnPO_3$ and $MnPO_2$

S. M. Shugurov[a]; A. Yu. Timoshkin[a]; S. I. Lopatin[a]
[a] Department of Chemistry, St. Petersburg State University, Staryi Peterhof, Russia

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S. M. Shugurov, A. Yu. Timoshkin, and S. I. Lopatin
Department of Chemistry, St. Petersburg State University, Staryi Peterhof, Russia

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In the present work, the stability of gaseous manganese-containing salts was proved by the high-temperature mass spectrometric method. New previously unreported species were found, $MnPO_3$ and $MnPO_2$. On the basis of equilibrium constants measured for gas-phase reactions the standard formation enthalpies for $MnPO_3$ and $MnPO_2$ were determined as -602.0 ± 10.0 kJ/mole and -299.0 ± 11.5 kJ/mole, respectively, and the standard atomization enthalpies as 1950 ± 14 kJ/mole and 1397 ± 14 kJ/mole, respectively.

Keywords: ab initio computations; double two-temperature cell; gaseous manganese phosphates; high-temperature mass spectrometry; $MnPO_{2(g)}$; $MnPO_{3(g)}$; thermodynamic functions

INTRODUCTION

The possibility of the existence of manganese-containing gaseous oxyacid salts as the one of the products in the steam environment of a severe reactor accident has been predicted previously.[1] This species may form in reactions between nuclear materials and various components of the cladding and structural materials. Stainless steel contains manganese, and manganese oxide (MnO) could be formed from this source in a steam environment at high temperatures and then react with any other oxides existing in the vapor phase. In order to predict the behavior of radiological hazardous fission products, knowledge of the

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Address correspondence to S. I. Lopatin, Department of Chemistry, St. Petersburg University, 198504 St. Petersburg, Staryi Peterhof, Universitetsky pr., 26, Russia. E-mail: transformer@lsi.ru

thermodynamic properties of the various components in the vapor is necessary. Before we started our investigation, the gaseous manganese-containing oxyacid salts were unknown. In the present work we obtained two new gaseous species, $MnPO_3$ and $MnPO_2$, and determined their thermodynamical characteristics.

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 vapor effusing from the cell was ionized with 25 eV electrons. In order to obtain a condition of coexistence of gaseous manganese and phosphorus oxides, the double two-temperature cell[2] was applied. This cell was made from molybdenum. It consists of two sections linked by a tube. The upper part was heated by electron impact and the lower part by heat transfer. The needed temperature gradient was obtained by changing the length of the link tube. MnO was placed in the upper part and $Mg_2P_2O_7$, which dissociates according to the equations[3]

$$3\ Mg_2P_2O_7 = 2\ Mg_3(PO_4)_2 + 2\ PO_2 + 0.5\ O_2 \quad (1)$$

and

$$Mg_3(PO_4)_2 = 3\ MgO + 2\ PO + 1.5\ O_2 \quad (2)$$

was placed in the lower part. The gaseous manganese and phosphorus oxides react with each other to form gaseous phosphates $MnPO_3$ and $MnPO_2$. In order to check that chemical equilibrium in the cell is attained, the equilibrium constants were measured with different ratios of the evaporated surface and effusion orifice area. The fact that equilibrium constants were the same at constant temperature proved that the chemical equilibrium is attained. The temperature was measured by an optical pyrometer EOP-66 with ± 5 K accuracy. The appearance energies (AE) of ions were measured by the vanishing current method with Au as an energy standard,[4] which was found to be accurate within ± 0.3 eV. The partial vapor pressures of the components were determined by differential mass spectrometry using atomic cross sections taken from Mann[5] with Au as internal standard[6] of pressure. The atomic cross section of $MnPO_3$ were multiplied by a factor 0.7, as recommended by Guido et al.[7] The experimental technique is described in detail elsewhere.[8]

RESULTS AND DISCUSSION

The Mn^+, MnO^+, PO^+, PO_2^+, $MnPO_3^+$, and $MnPO_2^+$ ions were detected in the mass spectrum at a temperature range of 1808–1881 K. The relative intensities of these ions depended on the temperature and evaporation time. The relative intensities of PO^+ and PO_2^+ ions were decreased, which corresponded to the transformation of magnesium diphosphate to monophosphate.[3] In addition, we detected MoO^+, MoO_2^+, MoO_3^+, and $MnMoO_4^+$ ions, which were formed as a result of interaction of the sample and the cell.

The appearance energies (AE, eV) of ions are as follows: Mn^+, 7.4 ± 0.3; MnO^+, 7.8 ± 0.3; PO_2^+, 11.3 ± 0.3; PO^+, 9.1 ± 0.3; $MnPO_3^+$, 10.5 ± 1; and $MnPO_2^+$, 8.1 ± 0.3. No breaks could be observed on the ionization efficiency curve of all ions. The values of the AE of Mn^+, PO^+, and PO_2^+ correspond to values of the ionization potential of the respective molecules.[4] The value of AE for MnO^+ is the same as that reported by Smoes and Drowart.[9] The AE of $MnPO_3^+$ and $MnPO_2^+$ ions are measured for the first time. However, these values are like to the corresponding values for AE of gallium and indium phosphates,[10,11] indicating that $MnPO_3^+$ and $MnPO_2^+$ are also parent ions.

The mass spectrum analysis and values of AE for ions indicate that the vapor over the studied system contains Mn, MnO, PO, PO_2, $MnPO_3$, and $MnPO_2$ molecules. The partial pressures of the vapor species were measured by the method of comparing ion currents. The enthalpy of formation of $MnPO_3$ and $MnPO_2$ were derived from a study of gas-phase reactions,

$$MnPO_3 = MnO + PO_2 \tag{3}$$

$$MnPO_2 = MnO + PO \tag{4}$$

The values of the enthalpies of the reactions in Equations (3) and (4) obtained from the third law of thermodynamics are listed in Table I. We failed to obtain the enthalpies from the second law because the temperature range of measurements was too narrow.

The thermodynamics functions for the species needed for the evaluation of reaction enthalpies were taken from literature data,[12,13] except for the case of $MnPO_3$ and $MnPO_2$. For these molecules thermodynamic functions (presented in Tables II and III) were calculated by the statistical thermodynamics method in a "rigid rotor–harmonic oscillator" approximation on the basis of the calculated molecular parameters (see section 4). The combination of enthalpies of reactions (3) and (4) with enthalpies of formation of gaseous oxides[12,13] allows us to obtain the standard enthalpies of formation and atomization

TABLE I Partial Pressures and Enthalpies of the Reactions in Equations (3) and (4) Over the $MnCO_3$—$MgHPO_4$ System

	p, atm					$-\Delta_rH^0$ (0 K), kJ	
T, K	MnO ($\cdot 10^7$)	PO ($\cdot 10^5$)	PO_2 ($\cdot 10^6$)	$MnPO_2$ ($\cdot 10^7$)	$MnPO_3$ ($\cdot 10^8$)	(3)	(4)
1808	0.99	2.19	1.73	0.18	2.52	488.2	418.5
1818	1.90	2.37	2.08	0.36	3.16	481.6	420.3
1819	1.45	2.37	2.03	0.34	3.17	486.3	423.7
1825	1.27	2.28	1.79	0.27	3.81	494.5	424.3
1825	4.48	—	2.16		6.74	481.2	—
1826	4.09	5.95	10.18	3.89	6.33	458.4	432.5
1826	2.04	5.55	9.65	2.26	5.43	467.4	435.8
1831	5.42	4.52	7.54	4.47	27.19	482.1	435.7
1836	0.26	—	2.25		0.25	476.5	—
1836	2.59	3.23	6.01	2.53	11.68	485.2	444.5
1837	3.88	4.7	7.94	4.48	19.48	482.8	441.6
1838	3.63	3.92	7.19	3.12	17.54	484	440.1
1840	5.19	5.14	8.33	5.27	23.42	481.2	439.0
1843	4.88	18.47	14.24	3.90	16.06	472.8	419.6
1846	4.89	13.70	10.70	3.22	11.49	472.8	421.8
1847	4.58	22.22	19.63	4.14	22.99	475.4	419.5
1847	4.28	19.13	17.84	3.68	16.09	472.4	421.0
1847	1.88	5.20	7.32	1.65	14.15	496.7	441.3
1849	2.82	6.77	9.62	2.83	25.96	496.1	439.8
1849	2.51	5.94	8.24	1.89	18.88	495.4	437.4
1850	3.37	12.30	12.06	1.84	9.21	474.3	421.5
1850	1.57	4.07	—	1.18	—	—	443.4
1851	4.90	20.21	18.33	3.69	18.43	473.0	419.0
1851	4.29	17.08	17.44	3.23	16.13	473.7	421.6
1852	4.09	—	6.64	—	6.84	472.5	—
1852	2.73	—	6.64	—	6.84	478.8	—
1852	3.37	12.62	14.31	2.07	9.22	472.1	423.4
1852	3.06	—	11.18	—	9.22	477.4	—
1852	3.77	8.37	10.55	4.02	28.37	492.4	438.2
1853	2.50	—	6.31	—	5.13	476.7	—
1855	5.69	—	4.98	—	10.28	478.9	—
1855	4.91	20.28	17.03	4.39	20.78	476.9	422.5
1856	4.33	4.75	7.31	4.28	8.57	474.6	443.6
1860	3.88	5.14	7.66	3.78	6.87	473.2	443.0
1866	0.26	2.03	1.94	0.02	0.38	492.9	416.9
1872	2.71	5.33	7.02	1.11	2.78	469.0	431.9
1873	1.97	4.53	5.04	0.74	1.86	473.1	433.3
1875	16.22	16.29	16.20	11.18	50.84	474.1	423.3
1880	18.97	14.10	11.54	13.25	50.98	478.3	426.8
1881	20.50	12.14	9.83	11.02	66.10	483.9	425.3
1881	13.56	14.50	14.96	7.14	30.60	471.7	422.2
Average value						479.2 ± 8.6	429.4 ± 9.0

TABLE II Thermodynamic Functions, Heat Capacity C_p°, Entropy S°, Free Energy Function Φ°, and Enthalpy Increment H(T)-H(0 K) of Gaseous $MnPO_3$ at Selected Temperatures in the Temperature Range 298.15–2500 K

T (K)	$\Phi_m^\circ(T)^a$ ($J \cdot K^{-1} \cdot mole^{-1}$)	$S_m^\circ(T)$ ($J \cdot K^{-1} \cdot mole^{-1}$)	H(T)-H(0 K) · ($J \cdot mole^{-1}$)	$C_{p,m}^\circ(T)$ ($J \cdot K^{-1} \cdot mole^{-1}$)
298.15	255.8	309.0	15851.6	53.2
1000	336.6	417.1	80495.2	80.5
1100	344.4	426.8	90686.8	82.4
1200	351.6	435.7	100972.0	84.1
1300	358.4	444.0	111331.0	85.6
1400	364.8	451.8	121750.0	87.0
1500	370.8	459.0	132218.0	88.2
1600	376.6	465.8	142726.0	89.2
1700	382.0	472.2	153267.0	90.2
1800	387.2	478.2	163837.0	91.0
1900	392.1	483.9	174431.0	91.8
2000	396.8	489.4	185046.0	92.5
2100	401.4	494.6	195679.0	93.2
2200	405.7	499.5	206327.0	93.8
2300	409.9	504.3	216988.0	94.3
2400	413.9	508.8	227662.0	94.9
2500	417.8	513.2	238346.0	95.3

[a] $\Phi_m^\circ(T) = \{G_m^\circ(T) - H_m^\circ(0\ K)\}/T$.

TABLE III Thermodynamic Functions, Heat Capacity C_p°, Entropy S°, Free Energy Function Φ°, and Enthalpy Increment H(T)-H(0 K)· of Gaseous $MnPO_2$ at Selected Temperatures in the Temperature Range 298.15–2500 K

T (K)	$\Phi_m^\circ(T)^a$ ($J \cdot K^{-1} \cdot mole^{-1}$)	$S_m^\circ(T)$ ($J \cdot K^{-1} \cdot mole^{-1}$)	H(T)-H(0 K) · ($J \cdot mole^{-1}$)	$C_{p,m}^\circ(T)$ ($J \cdot K^{-1} \cdot mole^{-1}$)
298.15	218.6	267.7	14651.2	49.1
1000	288.6	355.0	66428.3	66.4
1100	294.9	362.6	74391.1	67.6
1200	300.9	369.6	82407.8	68.7
1300	306.4	376.0	90467.1	69.6
1400	311.6	382.0	98560.7	70.4
1500	316.5	387.6	106682.0	71.1
1600	321.1	392.9	114826.0	71.8
1700	325.5	397.8	122990.0	72.4
1800	329.6	402.5	131170.0	72.9
1900	333.6	406.9	139363.0	73.4
2000	337.3	411.1	147568.0	73.8
2100	340.9	415.1	155783.0	74.2
2200	344.4	419.0	164007.0	74.6
2300	347.7	422.6	172238.0	74.9
2400	350.9	426.1	180476.0	75.2
2500	354.0	429.5	188720.0	75.5

[a] $\Phi_m^\circ(T) = \{G_m^\circ(T) - H_m^\circ(0\ K)\}/T$.

presented below:

$$\Delta_f H^\circ(298)MnPO_3 = -602.6 \pm 10.0 \quad \text{and}$$

$$\Delta_f H^\circ(298)MnPO_2 = -299.0 \pm 11.5 \text{ kJ/mole};$$

$$\Delta_{at} H^\circ(298)MnPO_3 = 1950 \pm 14 \quad \text{and}$$

$$\Delta_{at} H^\circ(298)MnPO_2 = 1397 \pm 14 \text{ kJ/mole}.$$

QUANTUM CHEMICAL COMPUTATIONS

Quantum chemical calculations have been carried out using the Gaussian 94 program package[14] at the Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia, USA. 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 B3LYP-functional[15,16] and second-order Møller-Plesset perturbation theory[17] have been used with adjunction of the full-electron basis sets of DZP and TZ2P quality.[18]

$MnPO_2$

For this molecule, two isomers are theoretically possible—structure with two bridging oxygen atoms $Mn(\mu\text{-}O)_2P$ and a chain structure O=Mn–P=O. Four-membered cycle $^5B_1$ $Mn(\mu\text{-}O)_2P$ (C_{2v} point group) is a global minimum at all levels of theory. It possesses the following structural parameters (B3LYP/TZ2P level of theory): r(Mn–O) = 0.1946 nm; r(P–O) = 0.1617 nm; r(Mn . . . P) = 0.2586 nm; ∠(OMnO) = 77.3°; ∠(OPO) = 97.52°; ∠(MnOP) = 92.56°. Relative energies of other considered species of $MnPO_2$ composition are given in Table IV.

TABLE IV Relative Energies of Several $MnPO_2$ Isomers, kJ mol^{-1}

Compound (point group)	Electronic state	UB3LYP		UMP2	
		pVDZ	TZ2P	pVDZ	TZ2P
$Mn(\mu\text{-}O)_2P$	$^1A_1$	327.7	290.8	595.7	540.6
(C_{2v})	$^3A_1$	157.1	137.1	371.2	360.0
	$^5B_1$	0.0	0.0	0.0	0.0
OMnPO (C_s)	$^5A''$	221.3	206.3	[a]	[a]

[a]Geometry optimization of this compound not converged.

$MnPO_3$

For this molecule, three structural isomers have been considered: Mn(μ-O)$_2$P=O with two bridging oxygen atoms, O=Mn–PO$_2$ with direct Mn–P bond, and Mn(μ-O)$_3$P with three bridging oxygen atoms. Among all considered species, the most stable is C_s symmetric Mn(μ-O)$_2$P=O, in which P=O bond lies out of the Mn(μ-O)$_2$P plane. It possess the following major structural parameters (B3LYP/TZ2P level of theory): r(Mn–O) = 0.1813 nm; r(P–O) = 0.1640 nm; r(P=O) 0.1477 nm; r(Mn. . .P) = 0.2499 nm; ∠(OMnO) = 81.9°; ∠(OPO) = 92.9°; ∠(MnOP) = 92.5°; ∠(MnPO) = 134.0°.

We also calculated atomization enthalpies of the most stable isomers of $MnPO_2$ and $MnPO_3$ and model molecules O_2, PO, and PO_2. Standard atomization enthalpies and entropies predicted at B3LYP and MP2 levels of theory are summarized in Table V. Note that increasing the size of the basis set (from pVDZ to TZ2P) improves agreement between theoretical and experimental values. Our best B3LYP/TZ2P values for atomization enthalpies of PO and PO_2 are underestimated by 13 and 70 kJ mol^{-1} compared to experimental data. For $MnPO_2$ and $MnPO_3$, theoretical values are overestimated by 25 kJ mol^{-1} and underestimated by 155 kJ mol^{-1}, respectively. MP2 level of theory performs similar to B3LYP for O_2 and PO_2 molecules but significantly underestimates atomization enthalpy of $MnPO_2$ even with TZ2P basis set. Due to limited computer resources, we were not able to use MP2 level of theory for $MnPO_3$. Data in Table V indicate first that the size of the basis set is

TABLE V Calculated Standard Atomization Enthalpies $\Delta_{at}H^{\circ}_{(298)}$, kJ mol^{-1} and Entropies $\Delta_{at}S^{\circ}_{(298)}$, J mol^{-1} K^{-1} for the Investigated Species

	UB3LYP/pVDZ (UMP2/pVDZ)		UB3LYP/TZ2P (UMP2/TZ2P)		Exp.	
Compound	$\Delta_{at}H^{\circ}_{(298)}$	$\Delta_{at}S^{\circ}_{(298)}$	$\Delta_{at}H^{\circ}_{(298)}$	$\Delta_{at}S^{\circ}_{(298)}$	$\Delta_{at}H^{\circ}_{(298)}$	$\Delta_{at}S^{\circ}_{(298)}$
O_2	527.3 (497.8)	100.1 (99.8)	502.3 (495.2)	99.9 (99.5)	498.4[a]	117.0[a]
PO	559.5 (490.6)	97.4 (97.8)	580.4 (554.1)	97.5 (97.4)	593.5[a]	101.6[a]
PO_2	1021.4 (968.5)	212.7 (213.7)	1059.2 (1054.3)	213.1 (213.7)	1129.4[a]	231.8[a]
$MnPO_2$	1446.2 (1222.1)	337.8 (333.6)	1421.3 (1327.8[c])	334.3	1397 ± 14[b]	
$MnPO_3$	1663.2	456.3	1796.4	463.6	1950 ± 14[b]	

[a]Calculated using data in Data bank IVTANTHERMO.[13]
[b]Experimental data obtained in the present work.
[c]Values for $\Delta_{at}E^{\circ}_{(0)}$ (vibrational analysis has not been completed).

extremely important, and second that B3LYP level of theory significantly underestimates atomization energy of $MnPO_3$. Probably the use of more sophisticated levels of theory (such as MP4, CCSD(T)) is necessary to satisfactorily describe the thermodynamic properties of $MnPO_2$ and $MnPO_3$, but these advanced calculations lie outside the scope of this article and should be the subject of a special investigation.

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