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Thermochemical Study of Gaseous Salts of Oxygen-Containing Acids: XV.[1] Manganese Molybdates and Tungstates

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Abstract—The existence of gaseous manganese molybdates and tungstates $MnXO_4$ and $MnXO_3$ (X = Mo, W) was confirmed, and their standard enthalpies of formation and atomization were determined.

Gaseous salts of manganese(II) were unknown previously. It was found in [2] that the thermal stability of a gaseous salt depends on the difference in the acid–base properties between the oxides forming this salt, and it was suggested to use the ratio of the average orbital electronegativities of the cation- and anion-forming oxides as a quantitative stability criterion. Calculations of these values showed that gaseous salts formed by manganese(II) oxide and some typical anion-forming oxides should be thermally stable. Acid–base properties of manganese(II) oxides are similar to those of chromium(II) oxide, for which a number of gaseous salts are known [3]; therefore, the existence of similar salts should also be typical for MnO.

To study vaporization of low-volatile oxides at 1600–2700 K, effusion cells made of molybdenum and tungsten are used. Molybdenum and tungsten have weak reductive properties and at high temperatures react with oxide materials under study to give gaseous oxides XO, XO_2, XO_3 (here and hereinafter, X = Mo, W), and in some cases gaseous molybdates and tungstates [4–13]. Therefore, gaseous tungstates and molybdates form one of the most studied groups of gaseous salts. At present tungstates and molybdates of alkali and alkaline-earth metals, thallium, germanium, tin, chromium, lead, and europium, and also indium molybdate and boron tungstate, are known and their thermodynamic properties have been described. All these salts show high thermal stability and in some cases are major gas-phase components. Molybdenum and tungsten oxides XO_3 and XO_2, having acid properties, are typical anion-forming oxides and readily react with electropositive oxides to form salts. In this work, we provided conditions for coexistence of gaseous tungsten(IV, VI) and molybdenum(IV, VI) oxides with MnO, which allowed us to identify gaseous manganese(II) molybdates and tungstates and to determine their standard enthalpies of formation.

When $MnCO_3$ was evaporated from molybdenum and tungsten effusion cells at ~900 K, the mass spectrum of the vapor contained the only peak of CO_2^+ ions. At temperatures higher than 1800 K, the Mn^+, MnO^+, XO_3^+, XO_2^+, $MnXO_4^+$, and $MnXO_3^+$ ions were detected in the mass spectrum, with the relative intensities of their ion currents depending on the temperature and time of evaporation. As the temperature was increased with subsequent isothermal heating, the intensity of the MnO^+ current first decreased and then increased, whereas the intensities of the ion currents of XO_2^+, XO_3^+, $MnXO_4^+$, and $MnXO_3^+$ increased. Such a behavior may be due to gradual oxidation of the cell material and to successive formation of molybdenum or tungsten oxides in the condensed phase, and then of manganese molybdate or tungstate $MnXO_4$, which is the only stable compound in the $MnO–XO_3$ system [14].

To determine the nature of the ions of the mass spectrum, we have measured their appearance potentials by recording the curves of the ionization efficiency (eV, ±0.5): 7.3 (Mn^+), 7.8 (MnO^+), 11.5 (MoO_3^+), 10.7 (WO_3^+), 9.5 (MoO_2^+), 9.0 (WO_2^+), 8.9 ($MnWO_3^+$), 10.6 ($MnWO_4^+$), and 11.0 ± 1 ($MnMoO_4^+$). These ions are molecular, as their appearance potentials coincide with the ionization potentials of the corresponding molecules [15] within the limits of measurement errors. The appearance potential of the MnO^+ ion agrees well with the data from [16]. The

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

appearance potentials of the $MnWO_3^+$, $MnWO_4^+$, and $MnMoO_4^+$ ions were measured for the first time. The values obtained are comparable with the appearance potentials of tungstates of alkaline-earth metals [13], suggesting the molecular origin of these ions. We failed to measure the appearance potential of the $MnMoO_3^+$ ion owing to a low intensity of its ion current. Nevertheless, we found that this value is lower than the appearance potential of the $MnMoO_4^+$ ion, which confirms the molecular origin of the $MnMoO_3^+$ ion. As XO_2^+ ions can have a dual nature, to determine the contribution of the dissociative ionization of XO_3 to the total ion current of XO_2^+, we measured the intensity ratios XO_3^+/XO_2^+ at the ionizing electron energy of 25 eV, which exceeds the ionization threshold by 3 eV. The results of the measurements were taken into account when determining the partial pressures of XO_2^+ and XO_3^+. We did not introduce a correction for the fragmentation of Mn^+ (MnO), Mn^+ ($MnXO_3$), and Mn^+ ($MnXO_4$) as we failed to measure the intensities of ion currents of MnO^+, MnX_3^+, and MnX_4^+ at low ionizing voltages owing to their small values. However, it is known [16] that the ratio of intensities of fragmentation and molecular ions for oxides and salts of alkaline-earth metals, as a rule, does not exceed 1.0. The Mn–O bond is less ionic than the alkaline-earth metal–oxygen bond; therefore, the ratios of intensities Mn^+ (MnO)/MnO^+, Mn^+ (MnX_3^+)/MnX_3^+, and Mn^+ ($MnXO_4^+$)/$MnXO_4^+$ should be less than unity. As the partial pressures of manganese(II) oxide and molybdates (tungstates), which are proportional to the measured intensities of the corresponding ion currents, appear in the numerator and the denominator of the expression for the equilibrium constant $K_e(T)$, an additional error in determination of the enthalpies of reactions (1) and (2), connected with the neglect of the fragmentation of MnO, $MnXO_3$, and $MnXO_4$, is insignificant; according to our estimates, it does not exceed 1–1.5 kJ. The results of measuring the partial pressures of vapor components are given in Table 1.

Examination of the vapor mass spectra and appearance potentials of the ions shows that, when manganese(II) oxide is evaporated from a tungsten or molybdenum cell, the gas phase consists of MnO, XO_2, XO_3, $MnXO_3$, and $MnXO_4$ molecules and atomic manganese.

To determine the standard enthalpies of formation of manganese molybdates and tungstates, we measured the equilibrium constants of gas-phase reactions (1) and (2) and calculated their enthalpies.

$$MnXO_4 = MnO + XO_3, \quad (1)$$

$$MnXO_3 = MnO + XO_2. \quad (2)$$

The calculation was carried using Eq. (3). We studied the temperature dependence of the equilibrium constant for reaction (1) within a fairly wide temperature range and determined the enthalpies of the reactions also by Eq. (4).

$$\Delta_r H^0(0) = T[\Delta_r \Phi^0(T) - R\ln K_e(T)], \quad (3)$$

$$\Delta_r H^0(T) = -R\frac{\partial \ln K_e(T)}{\partial(1/T)}. \quad (4)$$

Here $\Delta_r H^0(0)$, $\Delta_r H^0(T)$, and $\Delta_r \Phi^0(T)$ are the enthalpy and reduced Gibbs potential of the reaction at 0 K and temperature T, respectively; R, gas constant; and K_e, equilibrium constant of the reaction. The thermodynamic functions of gaseous molybdenum(IV, VI), tungsten(IV, VI), and manganese(II) oxides necessary for the calculations were taken from [17, 18]. The thermodynamic functions of previously unknown gaseous manganese molybdates and tungstates were calculated by statistical thermodynamics methods in the approximation rigid rotator–harmonic oscillator. For the $MnXO_4$ molecules, we accepted a cyclic structure of the C_{2v} symmetry, with a distorted XO_4 tetrahedron and the manganese atom on the perpendicular to one of edges. This choice was based on the electron-diffraction study of the structure of $BaWO_4$ [19] and $BaMoO_4$ molecules [20], and also on the interpretation of the IR spectra of matrix-isolated $EuMoO_4$ and $EuWO_4$ molecules [10, 21]. Based on the above data, we chose the following values of structural parameters. For $MnMoO_4$: $r(Mo–O)_{cycl}$ 1.82, $r(Mo–O)_{term}$ 1.78 Å, $\angle OMoO_{cycl}$ 93°, and $\angle OMoO_{term}$ 100°; for $MnWO_4$: $r(W–O)_{cycl}$ 1.84, $r(W–O)_{term}$ 1.80 Å, $\angle OWO_{cycl}$ 90°, and $\angle OWO_{term}$ 100°. The normal mode frequencies for the groups MoO_3 and WO_4 are 920, 340, 310, 940, 790, 710, 500, 350, 320 and 920, 350, 320, 920, 790, 710, 490, 340, 310 cm^{-1}, respectively.

For $MnXO_3$ molecules, we accepted a cyclic structure of the C_{2v} symmetry similar to the structures of europium molybdate and tungstate [9, 10]. The OXO angle in the ring is 116°, and the interatomic distance r(X–O) is 1.85 Å in the ring and 1.75 Å for the terminal bonds. The normal mode frequencies of the XO_3 group of 800, 350, 960, 850, 300, 300 cm^{-1} were estimated from the frequencies of the XO_3^- ion using the ratio of frequencies in MNO_3 and NO_3^- [17] and taking into account splitting of E terms on passing from D_{3h} symmetry to C_{2v}.

As data on the interatomic distance and vibration frequencies of the Mn–O group are fully lacking, we have carried out quantum-chemical calculations of the geometric and electronic structure and vibration spectra of $MnXO_4$ molecules. The calculations were performed using the GAMESS program complex [22].

Table 1. Partial pressures of vapor components over the systems MnO–W and MnO–Mo and calculated enthalpies of reactions (1) and (2)

T, K	p, atm			$-\Delta H^0(0)$, kJ	T, K	p, atm			$-\Delta H^0(0)$, kJ
	MnO ($\times 10^7$)	WO_3 ($\times 10^6$)	$MnWO_4$ ($\times 10^7$)	Eq. (1)		MnO ($\times 10^7$)	WO_3 ($\times 10^6$)	$MnWO_4$ ($\times 10^7$)	Eq. (1)
1939	7.48	5.38	3.08	500.3	1886	3.65	3.53	1.28	483.1
1937	8.07	11.0	4.72	494.0	1943	8.19	8.35	2.72	482.5
1929	11.30	16.80	4.59	479.3	1944	8.19	8.67	2.63	481.5
1931	11.90	16.80	5.03	480.4	1945	8.20	8.36	2.44	481.2
1932	13.10	18.70	5.03	477.4	1950	7.71	8.38	2.45	483.4
1930	13.10	17.90	5.25	478.3	1946	7.69	8.68	2.45	481.8
1930	11.90	17.60	5.03	479.5	1884	3.02	3.95	1.02	480.4
1929	12.80	16.80	4.48	477.0	1883	3.09	4.21	0.94	477.5
1928	12.80	17.90	4.70	476.5			Average value		479.4 ± 7.4
1931	12.20	18.30	4.59	477.2	1939	10.59	11.73	3.66	476.6
1933	10.40	17.60	4.49	480.5	1945	13.13	14.51	4.13	473.1
1933	8.05	14.20	3.39	483.6	1955	14.14	14.98	4.38	474.7
1933	18.50	6.13	2.04	476.8	1971	13.94	17.09	4.42	476.7
1935	14.10	7.36	2.05	478.7	1985	14.67	18.01	5.15	480.8
1855	1.60	0.47	0.21	500.9			Average value		479.4 ± 7.4
1860	1.75	0.71	0.36	502.4		MnO ($\times 10^7$)	WO_2 ($\times 10^6$)	$MnWO_3$ ($\times 10^7$)	Eq. (2)
1858	2.01	1.70	0.46	490.3	1939	7.48	3.03	1.59	505.1
1852	2.80	2.10	0.57	483.6	1937	8.07	5.41	1.59	494.0
1862	2.91	2.28	0.61	485.3	1929	11.30	8.49	1.47	478.1
1860	2.91	2.52	0.61	483.2	1931	11.90	8.50	1.47	477.8
1861	3.20	2.19	0.54	482.2	1932	13.10	9.60	1.36	473.2
1853	2.32	2.14	0.57	486.4	1930	13.10	9.31	1.70	476.8
1869	1.95	1.18	0.29	491.8	1930	11.90	8.22	1.47	478.1
1869	1.95	1.18	0.29	491.8	1929	12.80	8.76	1.47	475.6
1975	14.50	11.68	3.76	480.6	1928	12.80	8.76	1.70	477.7
1964	13.01	10.44	3.36	479.7	1931	12.20	8.77	1.81	480.2
1948	9.77	8.02	2.43	479.6	1933	10.40	8.51	1.81	483.7
1918	7.56	6.46	2.02	477.1	1933	8.05	6.58	1.59	489.8
1883	5.06	4.09	1.36	476.0	1933	18.50	5.66	1.45	479.4
1892	5.42	4.82	1.62	477.2	1935	14.10	5.76	1.56	485.1
1914	6.85	5.88	1.89	478.1	1855	1.60	0.21	0.01	503.4
1931	7.26	7.81	2.28	479.8	1860	1.75	0.24	0.15	511.6
1942	5.01	1.05	1.02	507.9	1858	2.01	0.68	0.18	496.3
1964	10.20	5.59	2.58	489.6	1852	2.80	0.89	0.15	482.1
1948	6.63	7.15	1.92	484.0	1862	2.91	1.04	0.15	481.6
1880	2.45	2.28	1.18	493.5	1860	2.91	1.10	0.18	483.7
1881	2.75	2.69	1.09	488.1	1861	3.20	1.16	0.15	478.2
1881	3.49	3.32	1.27	483.6	1853	2.32	0.83	0.11	481.9
1882	3.57	3.32	1.27	483.5	1869	1.95	0.75	0.15	494.8
1879	3.49	3.62	1.36	482.8	1937	7.16	3.24	0.71	483.0

Table 1. (Contd.)

T, K	p, atm			$-\Delta H^0(0)$, kJ
	MnO ($\times 10^7$)	WO_3 ($\times 10^6$)	$MnWO_4$ ($\times 10^7$)	Eq. (1)
1955	14.14	6.36	1.55	478.1
1913	7.38	3.86	0.94	478.3
1895	5.48	2.89	0.58	475.7
1885	5.15	2.32	0.46	474.1
1903	6.42	3.28	0.81	478.5
1929	8.37	4.56	1.18	481.2
1939	10.59	5.73	1.42	479.2
1945	13.13	6.32	1.66	478.1
1955	14.14	6.93	1.79	479.0
1971	13.94	7.86	2.17	484.2
	Average value			477.5 ± 8.5
	MnO ($\times 10^7$)	MoO_3 ($\times 10^6$)	$MnMoO_4$ ($\times 10^7$)	Eq. (1)
1841	3.23	9.66	0.64	446.5
1826	3.44	11.36	0.90	444.9
1845	3.48	14.71	1.00	446.9
1848	3.91	12.57	1.28	451.9
1844	4.21	19.72	1.83	448.4
1849	2.14	28.16	1.74	453.7
1844	2.40	6.88	0.65	457.1
1837	2.39	8.90	0.92	457.0
1843	2.53	9.66	0.92	456.4
1847	3.40	23.59	2.13	451.9
1840	3.69	28.56	2.30	447.3
1844	3.51	29.71	2.49	449.6
1832	3.67	26.28	2.20	446.4
1842	3.08	26.42	2.03	449.8
1770	0.67	4.11	0.25	451.8
1784	0.91	4.44	0.40	456.7
1791	0.98	4.95	0.41	455.8
1787	1.01	4.94	0.45	456.0
1789	1.01	5.68	0.46	454.5
1787	1.05	6.04	0.51	454.1
1782	1.01	5.84	0.50	453.9
1784	1.01	6.39	0.55	454.5
1780	1.04	6.38	0.60	454.3
1799	1.16	6.45	0.56	456.2
1777	1.07	6.37	0.60	453.1
1786	1.18	6.58	0.56	452.2
1785	1.21	6.94	0.61	452.1
1810	2.36	24.09	1.59	444.0
1761	0.55	6.05	0.32	450.6

T, K	p, atm			$-\Delta H^0(0)$, kJ
	MnO ($\times 10^7$)	WO_3 ($\times 10^6$)	$MnWO_4$ ($\times 10^7$)	Eq. (1)
1774	0.54	6.82	0.38	454.6
1762	0.48	6.86	0.37	453.0
1762	0.48	5.42	0.27	451.9
1839	1.66	4.97	0.18	446.8
1833	2.27	6.55	0.53	453.1
1839	2.42	20.83	1.37	450.4
1833	5.29	10.91	1.96	452.4
1843	7.39	13.53	2.70	451.2
1876	14.58	29.03	5.39	447.3
1899	15.71	46.46	7.27	448.8
1870	9.14	38.33	5.79	450.0
1837	4.61	28.43	4.14	452.2
1803	4.52	9.30	1.02	440.1
1856	1.19	19.15	3.24	444.5
1846	2.08	6.04	0.59	460.6
1862	2.67	11.66	0.87	456.2
1871	3.73	22.04	1.41	450.8
1874	7.48	41.70	4.03	447.1
1853	5.03	44.18	3.45	445.1
1838	3.23	34.02	2.24	445.8
1813	1.82	24.92	1.43	446.5
1793	1.20	17.60	0.89	446.2
1763	0.55	10.38	0.38	445.5
1857	6.81	64.24	4.59	440.0
1833	4.09	54.84	2.36	434.5
1796	1.38	29.72	1.03	439.1
1777	0.81	21.93	0.70	441.2
1769	0.59	15.88	0.32	436.9
		Average value		449.8 ± 5.5
	MnO ($\times 10^7$)	WO_2 ($\times 10^6$)	$MnWO_3$ ($\times 10^7$)	Eq. (2)
1844	4.21	4.79	1.64	488.7
1849	2.14	8.17	2.59	499.1
1810	2.36	5.28	1.05	480.6
1816	2.20	5.19	0.79	479.2
1818	2.20	5.09	0.93	482.3
1812	1.03	4.23	0.39	482.2
1839	1.66	1.55	0.26	490.8
1833	2.27	1.85	0.53	492.6
1839	2.42	4.75	0.80	484.9
		Average value		486.7 ± 6.6

For the W, Mo, and Mn atoms, we used the Basch–Stevens–Krauss effective core potential [23–25], and for oxygen, the 6-31G* basis with polarizing functions [26]. The calculations were performed by the *ab initio* SCF method. It was found that the lowest state is sextet, with the spin density being concentrated on the Mn atom. The calculated data are given in Tables 2 and 3. Based on the calculation results, we accepted

Table 2. Geometric parameters of $MnXO_4$ molecules optimized by the SCF method

Parameter	$MnMoO_4$	$MnWO_4$
$r(X\text{–}O_{term})$, Å	1.680	1.699
$r(X\text{–}O_{cycl})$, Å	1.867	1.859
$r(Mn\text{–}O)$, Å	1.959	1.970
$\angle(O_{conc}XO_{term})$, deg	114	112
$\angle(O_{cycl}XO_{cycl})$, deg	89	89

Table 3. Vibrational frequencies of $MnXO_4$ molecules (cm^{-1}) calculated by the SCF method and their assignment

$MnMoO_4$	$MnWO_4$	Assignment
110	103	Torsion $Mn\text{–}O_{cycl}\text{–}X\text{–}O_{term}$
260	234	Torsion $O_{cycl}\text{–}X\text{–}O_{term}\text{–}O_{term}$
285	288	Bending $O_{cycl}\text{–}X\text{–}O_{cycl}$, asymm.
294	290	Bending $O_{term}\text{–}X\text{–}O_{cycl}$, symm.
359	354	Bending $O_{term}\text{–}X\text{–}O_{term}$
390	368	Bending $O_{term}\text{–}X\text{–}O_{term}$
470	461	Bending $O_{cycl}\text{–}Mn\text{–}O_{cycl}$
640	632	Bending $O_{cycl}\text{–}Mn\text{–}O_{cycl}$
706	701	Bending $O_{cycl}\text{–}Mn\text{–}O_{cycl}$
800	801	Bending $O_{cycl}\text{–}Mn\text{–}O_{cycl}$
1068	1496	Stretching $X\text{–}O_{term}$, asymm.
1102	1514	Stretching $X\text{–}O_{term}$, symm.

the interatomic Mn–O distance to be 1.97 Å, and the corresponding normal mode frequencies of the cation to be 456, 196, and 118 cm^{-1}. The interatomic distance r(Mn–O) of 1.96 Å was estimated as the sum of the ionic radius of Mn^{2+} [27] and the effective ionic radius of oxygen [28], which confirms our calculations.

The combination of the obtained enthalpies of reactions (1) and (2) with the enthalpies of formation of gaseous manganese(II), molybdenum(IV, VI), and tungsten(IV, VI) oxides allowed us to determine the standard enthalpies of formation of gaseous manganese molybdates and tungstates, which are presented in Table 4.

EXPERIMENTAL

This work was carried out by the method of high-temperature mass spectrometry on an MS-1301 mass spectrometer at the ionizing electron energy of 25 eV. Samples were evaporated from molybdenum and the tungsten effusion cells heated by electron impact. The temperature was measured with an EOP-66 optical pyrometer with an accuracy of ±5°C. The partial pressures of vapor components were determined by comparing the ion currents using gold as an internal reference of pressure [29]. The ionization cross sections were calculated by the additivity method using ionization cross sections of atoms [30]; the ionization cross sections of manganese tungstates were multiplied by 0.7 [31]. The device was preliminarily calibrated with CaF_2 vapor pressure [17].

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Table 4. Enthalpies of reactions (1) and (2) and standard enthalpies of formation of italicized gaseous manganese molybdates and tungstates as determined by Eqs. (3) and (4)

Reaction	T, K	$-\Delta_rH^0(T)$, kJ [(Eq. (4)]	$-\Delta_rH^0(298)$, kJ [(Eq. (4)]	$-\Delta_rH^0(298)$, kJ [(Eq. (3)]	$-\Delta_fH^0(298)$, kJ mol^{-1} [weighted average value; Eqs. (3), (4)]
$MnO + MoO_3 = \mathit{MnMoO}_4$	1761–1899	458 ± 38	448 ± 28	452.5 ± 5.5	654.5 ± 9.2
$MnO + MoO_2 = \mathit{MnMoO}_3$	–	–	–	488.7 ± 6.6	342.7 ± 8.2
$MnO + WO_3 = \mathit{MnWO}_4$	1852–1985	464 ± 43	446 ± 43	482.2 ± 7.4	634.9 ± 12.6
$MnO + WO_2 = \mathit{MnWO}_3$	–	–	–	479.8 ± 8.5	289.1 ± 9.8

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