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Thermochemical Study of Gaseous Salts of Oxygen-Containing Acids: XVI.[1] Iron(II) Salts

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Abstract — Existence of gaseous salts formed by iron oxide FeO was established, and their standard enthalpies of formation and atomization were determined.

At present, only two iron-containing gaseous salts are known. When studying flames containing oxygen, hydrogen, potassium, and iron, Farber *et al*. [2] detected $KHFeO_2$ and K_2FeO_2 molecules and estimated the standard enthalpy of formation of K_2FeO_2. A study of the vaporization of $Fe(PO_3)_3$, $Fe_2P_2O_7$, $FePO_4$, and $Fe_3(PO_4)_2$ [3] from a one-temperature cell showed that they dissociate thermally, and phosphorus oxides pass into the vapor. Gaseous iron phosphates were not detected in this case.

According to the criterion of the reactivity of gaseous oxides suggested in [4], FeO should have amphoteric properties and react with both anion- and cation-forming oxides to form gaseous salts. For this reaction to occur, it is necessary to create conditions for the coexistence of FeO in vapor with anion- and cation-forming oxides stable at high temperatures. First of all, these are oxides of molybdenum MoO_2 and MoO_3, of tungsten WO_2 and WO_3, of phosphorus PO and PO_2, and of alkaline-earth metals.

To obtain gaseous iron molybdates and tungstates, we used the analogy with molybdates and tungstates of chromium [5], manganese [6], and alkaline-earth metals [7] and studied Fe_3O_4 vaporization from molybdenum and tungsten effusion cells. Iron oxides Fe_2O_3 and Fe_3O_4 dissociate on heating to evolve oxygen and to form FeO [8], which, in turn, passes into vapor mainly as atomic iron and oxygen [9–14]. The relative content of FeO in the vapor is low and does not exceed 1–3%.

In the mass spectra of the vapor in the temperature range 1870–2075 K, we recorded the peaks of Fe^+, FeO^+, XO_2^+, XO_3^+, and $FeXO_4^+$ ions (hereinafter, X = Mo, W) with the relative intensities dependent on the temperature and vaporization time. To create conditions for coexistence of phosphorus and iron oxides in the vapor, we applied the two-temperature cell technique [15]. The peaks of Fe^+, FeO^+, PO^+, PO_2^+, $FePO_3^+$, and $FePO_2^+$ ions were recorded in the mass spectrum of vapor over the system Fe_3O_4 (high-temperature compartment)–$MgHPO_4$ (low-temperature compartment) at 1720–1850 K. To obtain gaseous strontium and barium ferrates, we carried out the vaporization of Fe_3O_4 mixtures with SrO and BaO. In this case, peaks of Fe^+, FeO^+, Sr^+, SrO^+, Ba^+, BaO^+, $SrFeO_2^+$, and $BaFeO_2^+$ ions were detected in the vapor mass spectra at 1880–2058 K.

To determine the origin of ions in the mass spectra, we measured their appearance potentials (eV, ±0.3): 7.8 (Fe^+), 9.1 (FeO^+), 11.5 (MoO_3^+), 10.7 (WO_3^+), 9.5 (MoO_2^+), 9.0 (WO_2^+), 11.4 (PO_2^+), 9.7 (PO^+), 12.5±1 ($FeMoO_4^+$), 11.5±1 ($FePO_3^+$), 9.0±1 ($FePO_2^+$), 5.7 (Sr^+), 6.0 (SrO^+), 5.4 (Ba^+), 6.5 (BaO^+), 10.5±1 ($SrFeO_2$), and 10.7 ($BaFeO_2^+$). The appearance potentials of XO_3^+, XO_2^+, FeO^+, SrO^+, BaO^+, Sr^+, Ba^+, and Fe^+ ions coincide with the ionization potentials of the corresponding molecules within the limit of experimental errors [9, 10, 16]. The appearance potentials of the $FeXO_4^+$, $FePO_3^+$, $FePO_2^+$, $SrFeO_2^+$, and $BaFeO_2^+$ ions, which were measured for the first time, agree well with those for molybdates, tungstates, and phosphates of alkaline-earth metals [7], chromium [5], and manganese [6], which suggests molecular origin of the above ions. The appearance potentials of the $SrFeO_2^+$ and $BaFeO_2^+$ ions exceed the corresponding value for barium chromate $BaCrO_2$ by 2.0 eV [17, 18], but the absence of $MFeO_3^+$ ions from the mass spectrum and the fact that the ionization potential of iron is higher than that of chromium also suggest the molecular origin of the $SrFeO_2^+$ and $BaFeO_2^+$ ions.

An examination of the vapor mass spectra and

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

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appearance potentials of ions shows that the vapor phase over the systems under study contains atomic iron, strontium, and barium, the oxides FeO, MoO_2, MoO_3, WO_2, WO_3, PO, PO_2, SrO, and BaO, and also the salts $FeMoO_4$, $FeWO_4$, $FePO_2$, $FePO_3$, $SrFeO_2$, and $BaFeO_2$ formed by iron oxide.

To find the standard enthalpies of formation of iron molybdate, tungstate, and phosphates and of strontium and barium ferrates, we determined the equilibrium constants (K_e) and enthalpies [$\Delta_r H^0(0)$] of gas-phase reactions (1)–(4) by Eq. (5).

$$FeO + XO_3 = FeXO_4, \quad (1)$$

$$FeO + PO_2 = FePO_3, \quad (2)$$

$$FeO + PO = FePO2, \quad (3)$$

$$MO + FeO = MFeO_2, \quad (4)$$

$$\Delta_r H0(0) = T[\Delta_r \Phi^0(T) - R\ln K_e(T)], \quad (5)$$

$$\Delta_r H^0(T) = -R\frac{\partial \ln K_e(T)}{\partial(1/T)}. \quad (6)$$

Here M = Sr, Ba; $\Delta_r H^0(0)$, $\Delta_r H^0(T)$, and $\Delta_r \Phi^0(T)$ are the enthalpies (at 0 K and temperature T, respectively) and reduced Gibbs potential (at temperature T) of a reaction; R is the gas constant; and K_e is the equilibrium constant of a reaction.

We studied the temperature dependence of the equilibrium constant of reaction (4) with M = Ba in a sufficiently wide temperature range and calculated the enthalpy of the reaction by Eq. (6). We measured the partial pressures of the vapor components by comparing the ion currents using gold as an internal reference of pressure [19]. To determine the contribution of dissociative ionization to the integral intensities of ion currents of XO_2^+ and PO^+, we measured the intensity ratios XO_3^+/XO_2^+ and PO_2^+/PO^+ at the ionizing voltage of 25 V and at a voltage exceeding the ionization threshold by 3 V. The results of the measurements were taken into account when determining the partial pressures of PO, PO_2, XO_2, and XO_3. We did not introduce a correction for the fragmentation of Fe^+ (FeO) and of the salts under study, as the ion currents of FeO^+, $FePO_3^+$, and $FeXO_4^+$ at low ionizing voltage were too small to be measured. However, it is known [20] that the contribution of dissociative ionization for oxides and salts of alkaline-earth metals does not exceed 50% of the total ion current. The iron–oxygen bond is less ionic than that in compounds of alkaline-earth metals; therefore, the intensity ratios $Fe^+(FeO)/FeO^+$, $Fe^+(FeXO_4)/FeXO_4^+$, $Fe^+(FePO_3)/FePO_3^+$, and $Fe^+(FePO_2)/FePO_2^+$ should be less than unity. The partial pressures of FeO and iron salts, which are proportional to the measured intensities of the corresponding ion currents, appear in the numerator and denominator of the expression for the equilibrium constants $K_e(T)$ of gas-phase reactions (1)–(4); therefore, the error in the determination of the enthalpies for these reactions, associated with the neglect of the fragmentation of FeO and gaseous salts, decreases and, according to our estimates, does not exceed 1–1.5 kJ. The partial pressures of vapor components and enthalpies of reactions (1)–(4) are given in Tables 1–3. The thermodynamic functions of gaseous oxides, required for the calculation, were taken from the handbooks [21, 22]. The related values for the gaseous salts were calculated by statistical thermodynamics methods in the rigid rotator–harmonic oscillator approximation.

As published data on the structure and molecular parameters of gaseous salts formed by iron oxide FeO are fully lacking, we performed quantum-chemical calculations of the geometric and electronic structure and vibrational spectra of $FeXO_4$, $FePO_3$, and $FePO_2$ molecules. The calculations were carried out by *ab initio* SCF method using the GAMESS program complex [23]. For the W, Mo, and Fe atoms, we used the Basch–Stevens–Krauss effective core potential [24–26]. For oxygen and phosphorus, we took the 6-31G* basis set with polarizing functions [27]. The molecular geometry was optimized without imposing restrictions on the symmetry and also within the framework of the C_{2v} symmetry. The C_{2v} structure, which represents a distorted XO_4 tetrahedron with an iron atom bound to two oxygen atoms in the bidentate mode, is minimal in energy for $FeXO_4$ molecules. For the $FePO_3$ and $FePO_2$ molecules, the planar C_{2v} structure with an iron atom bound to two oxygen atoms in the bidentate mode is minimal in energy. The lowest-energy state for $FeXO_4$ molecules is quintet, and for the $FePO_3$ and $FePO_2$ molecules, quartet, with the spin density concentrated on the Fe atom.

To obtain a set of molecular parameters of FeO_2 anionic group, we performed quantum-chemical calculations for the $CaFeO_2$ molecule, which is a structural analog of strontium and barium ferrates. For calcium ferrate, when the 6-31G** basis with the polarizing functions [27] was used, the planar C_{2v} structure with iron and calcium atoms bound to oxygen atoms in the bidentate mode appeared to be minimal in energy. The lowest-energy state is singlet. The effective charge of iron in the $CaFeO_2$ molecule is higher than in the molecules of iron phosphates, molybdate, and tungstate. The results of the quantum-chemical calculations are presented in Tables 4–6.

Published data on the structures of XO_4, PO_3, and PO_2 molecules obtained by gas-phase electron diffrac-

tion and by IR spectroscopy of matrix-isolated molecules [6, 28] allowed us to choose for these anionic groups a set of molecular parameters which we used in the calculation of thermodynamic functions of gaseous molybdates, tungstates, and phosphates of alkaline-earth metals, chromium, and manganese [5–7]. The parameters chosen agree well with the results of quantum-chemical calculations. We estimated the iron–oxygen interatomic distance in gaseous salts at 1.93 Å as a sum of Fe^{2+} ionic radius [29] and effective ionic radius of oxygen [30]; it agrees well with the calculated values for iron molybdate and tungstate. The normal mode frequencies for the iron–oxygen bonds of 456, 196, and 118 cm^{-1} are taken the same as for iron molybdate in which the iron–oxygen distance is the closest to the calculated value. The interatomic distances and normal mode frequencies for the Sr–O and Ba–O bonds were taken the same as in the molecules of molybdates and tungstates of alkaline-earth metals [7].

Using Eq. (6), we found that the enthalpy of reaction (4) involving barium oxide and ferrate is -375 ± 36 kJ mol^{-1} for the middle of the range of measurements (1946 K). The recalculation of this value to the standard temperature of 298 K gives -368 ± 36 kJ mol^{-1}. The weighted mean enthalpy of this reaction determined by Eqs. (5) and (6) is -386.7 ± 4.0 kJ mol^{-1}.

A combination of the obtained enthalpies of reactions (1)–(4), recalculated to 298 K, with the enthalpies of formation of gaseous oxides of iron(II), molybdenum(IV, VI), tungsten (IV, VI), phosphorus(II, IV), strontium, and barium allowed us to obtain the standard enthalpies of formation of gaseous iron molybdate and tungstate, iron phosphates, and strontium and barium ferrates (Table 7).

The enthalpies of atomization of gaseous $FePO_2$, $FePO_3$, $FeMoO_4$, and $FeWO_4$, which we have determined, allowed us to construct a correlation between the enthalpies of atomization of gaseous iron salts and gaseous anion-forming oxides (see figure). A high correlation coefficient of the linear relationship [Eq. (7); r 0.99991, k 1.053 ± 0.010, b 785.7 ± 14.5], confirms the reliability of our results and allows estimation of the enthalpies of atomization for gaseous iron salts that were not studied experimentally.

$$\Delta_f H^0(FeXO_n,\ \text{gas},\ 298\ \text{K}) = k\Delta_f H^0(XO_{n-1},\ \text{gas},\ 298\ \text{K}) + b. \qquad (7)$$

The enthalpies of atomization of gaseous $SrFeO_2$ and $BaFeO_2$ also fit linear relationships (7) con-

Table 1. Partial pressures of vapor components over the systems Fe_3O_4–W and Fe_3O_4–Mo and enthalpies of reaction (1)

T, K	p, atm			$-\Delta_r H^0(0)$, kJ
	FeO, $\times 10^7$	WO_3, $\times 10^6$	$FeWO_4$, $\times 10^8$	
2002	3.82	4.47	2.19	486.2
2002	3.91	5.17	2.92	488.1
1999	2.95	5.16	2.19	487.3
2067	6.90	10.19	5.28	492.3
2067	6.24	10.92	6.04	495.2
2067	4.60	10.56	4.53	496.1
2069	3.95	10.20	4.53	499.8
2071	2.96	9.12	3.78	504.0
2074	3.16	9.13	3.79	503.6
2013	5.81	4.60	1.76	477.5
2006	4.80	5.01	2.33	482.4
2014	4.49	5.34	2.34	484.4
2014	3.82	5.34	1.76	482.3
2015	3.33	5.04	1.93	487.5
2015	2.83	5.16	1.66	487.2
2014	2.83	4.60	1.66	488.8
	FeO, $\times 10^7$	MoO_3, $\times 10^5$	$FeMoO_4$, $\times 10^8$	
			Average	490.2 ± 7.7
1874	4.11	0.73	3.55	453.1
1878	3.91	0.67	3.56	456.1
1905	5.01	0.86	4.51	462.5
1882	4.47	1.87	5.49	445.6
1894	3.83	1.74	6.90	455.6
1911	5.06	1.59	8.41	459.8
1901	5.16	1.38	6.69	455.8
1897	4.51	1.38	9.66	462.8
1913	4.54	1.63	8.35	461.4
1920	5.34	1.80	9.58	461.1
1904	4.91	1.42	9.50	462.3
1937	6.54	1.82	7.38	457.6
1932	6.81	1.88	7.36	455.2
1935	7.38	1.96	8.60	456.4
1918	6.19	2.08	9.74	456.3
1932	6.52	1.88	7.36	455.9
1938	6.12	1.89	7.99	459.6
1929	6.23	1.81	7.34	456.5
1935	5.68	1.82	6.75	458.0
1932	5.10	1.05	4.90	462.7
1930	3.34	1.34	6.41	469.4
1935	3.90	1.51	8.84	471.3
1936	4.09	1.78	11.25	472.0
1936	4.09	1.92	12.06	471.9
1940	4.28	1.93	12.89	473.2
1940	3.91	2.02	11.28	471.7
1939	3.72	1.81	9.66	471.5
1940	2.24	1.65	5.64	472.8
			Average	461.7 ± 7.3

Table 2. Partial pressures of vapor components over the system Fe_3O_4–$Mg_2P_2O_7$ and enthalpies of reactions (2) and (3)

T, K	*p*, atm					$-\Delta_r H^0(0)$, kJ	
	FeO, $\times 10^7$	PO, $\times 10^5$	PO_2, $\times 10^6$	$FePO_2$, $\times 10^8$	$FePO_3$, $\times 10^8$	Eq. (2)	Eq. (3)
1768	7.33	3.73	–	8.38	–	419.0	401.0
1771	7.81	2.04	–	4.58	–	452.0	400.8
1770	6.40	2.14	2.17	4.96	2.24	452.0	403.9
1759	5.12	1.43	1.85	2.65	1.73	451.1	401.4
1764	2.02	1.54	1.73	1.52	1.24	462.0	406.9
1724	2.14	1.15	1.36	2.24	0.42	438.6	406.6
1733	2.21	0.64	0.88	1.5	0.29	441.7	410.8
1738	2.04	0.40	0.59	1.35	0.49	457.4	418.5
1739	1.91	0.36	0.51	0.90	0.29	453.1	415.5
1735	1.72	0.22	0.36	0.75	0.20	452.9	420.3
1738	7.40	1.58	1.71	8.5	4.43	455.1	406.6
1754	5.71	1.59	1.83	4.29	2.98	456.3	404.1
1802	3.39	3.06	2.27	2.53	0.61	454.4	412.5
1768	4.27	1.98	2.15	7.58	1.85	454.8	416.8
1770	4.66	1.73	2.23	6.64	1.86	453.5	416.1
1772	4.48	0.75	0.76	2.47	1.55	467.8	415.0
1778	2.73	0.80	0.84	1.91	0.62	461.8	418.7
1851	4.07	2.94	2.18	3.47	0.97	457.4	419.1
					Average	410.8 ± 6.9	454.4 ± 7.0

Table 3. Partial pressures of vapor components over the systems Fe_3O_4–SrO and Fe_3O_4–BaO and enthalpies of reaction (4)

T, K	*p*, atm			$-\Delta_r H^0(0)$, kJ	*T*, K	*p*, atm			$-\Delta_r H^0(0)$, kJ
	FeO, $\times 10^6$	SrO, $\times 10^7$	$SrFeO_2$, $\times 10^8$			FeO, $\times 10^6$	BaO, $\times 10^6$	$BaFeO_2$, $\times 10^8$	
2027	5.91	13.06	4.7	411.3	1986	3.02	4.52	6.48	387.8
2030	4.58	8.92	3.14	415.8	1984	0.60	0.94	0.31	389.7
2041	1.51	5.98	0.63	416.5	1900	0.95	1.29	2.21	392.3
2050	1.72	5.73	0.65	417.2	1921	1.57	3.00	4.47	386.3
2058	0.90	2.51	0.19	423.6	1929	1.93	3.32	5.38	386.0
1982	1.34	4.76	0.70	411.9	1931	1.84	3.52	5.39	386.2
2028	4.25	13.54	5.72	419.7	1936	2.07	3.63	5.85	386.1
2026	3.19	11.36	4.29	422.3	1940	1.90	4.04	6.32	387.8
2032	2.89	8.68	2.15	418.1	1941	1.68	3.94	5.42	387.9
2034	1.52	7.6	0.72	413.0	1939	1.19	2.63	2.26	385.5
1983	2.11	8.79	3.98	423.1	1928	1.50	1.83	2.85	389.1
1988	2.59	10.07	5.32	423.4	1928	1.73	3.19	4.56	385.5
2002	2.61	9.89	5.02	425.6	1927	1.73	3.32	5.13	386.6
1994	1.38	8.59	3.00	428.2	1932	1.67	3.33	5.14	388.0
1994	1.00	6.57	1.67	428.4	1927	1.67	3.57	5.70	387.6
2012	0.50	6.12	0.67	429.7	1908	1.06	2.73	3.95	389.5
2054	0.58	9.11	0.69	429.6	1907	1.16	2.43	2.96	385.2
			Average	420.5 ± 5.9	1906	0.96	3.09	4.93	392.1
					1912	1.06	3.40	4.95	390.4
					1948	1.77	6.32	9.07	389.1
					1953	1.78	5.88	8.08	389.3
					1956	1.58	5.21	7.08	391.6
					1959	0.89	3.25	2.03	388.9
					1880	0.70	1.65	1.79	385.9
					1886	0.82	1.97	2.40	386.4
								Average	388.0 ± 2.1

Table 4. Normal mode frequencies (cm^{-1}) of gaseous iron salts $FeXO_4$ and their assignment

$FeMoO_4$	$FeWO_4$	Assignment[a]
112.0	104.3	$\tau(FeO_{cycl}O_{term})$
256.8	229.9	$\tau(O_{cycl}XO_{term}O_{term})$
279.3	284.5	$\delta_{as}(O_{cycl}XO_{cycl})$
297.1	289.7	$\delta_{s}(O_{term}XO_{cycl})$
349.1	343.5	$\delta(O_{term}XO_{term})$
391.9	368.6	$\delta(O_{term}XO_{term})$
477.9	469.4	$\delta(O_{cycl}FeO_{cycl})$
659.1	649.9	$\delta(O_{cycl}FeO_{cycl})$
704.9	698.0	$\delta(O_{cycl}FeO_{cycl})$
788.6	786.9	$\delta(O_{cycl}FeO_{cycl})$
1073.6	1228.4	$\nu_{as}(XO_{term})$
1108.4	1269.7	$\nu_{s}(XO_{term})$

[a] (τ) Torsion, (δ) bending, (ν) stretching, (as) antisymmetric, and (s) symmetric vibrations.

structed earlier for strontium and barium gaseous salts [28]. According to the criterion of thermal stability of gaseous salts suggested in [4], gaseous calcium ferrate $CaFeO_2$ should also be stable. We did not carry out the thermodynamic study of this molecule, as it was impossible to separate the intensities of CaO^+ and Fe^+ ion currents in the mass spectrum of vapor over the Fe_3O_4–CaO system. Linear equation (7) obtained previously [28] for gaseous calcium salts allowed us to estimate the enthalpies of atomization and formation of $CaFeO_2$ at 1305 and –213.7 kJ mol^{-1}, respectively.

The existence of gaseous salts in which FeO acts as both cation- and anion-forming oxide points to the amphoteric character of gaseous iron(II) oxide. The acid properties of FeO are more expressed than those of CrO and MnO, which results in the following facts: the relative content in the vapor of salts with iron as anion-forming element is higher compared to salts with iron as cation-forming element, and the content of $FeXO_3$ salts is insufficient for their reliable detection. These facts confirm the validity of the suggested criterion of the reactivity of gaseous oxides [3] and makes it possible to predict the behavior of oxides of other *d* elements in gas-phase synthesis reactions.

EXPERIMENTAL

This study was carried out on an MS-1301 mass spectrometer at the ionizing electron energy of 25 eV. Samples of Fe_3O_4 were evaporated from single molybdenum and tungsten effusion cells and also

Table 5. Normal mode frequencies (cm^{-1}) of gaseous iron salts $FePO_3$, $FePO_2$, and $CaFeO_2$ and their assignment

$FePO_3$		$FePO_2$		$CaFeO_2$	
frequency	assignment	frequency	assignment	frequency	assignment
132.7	$\tau(FeO_{cycl}PO_{term})$	236.9	$\nu_{as}(OFeO)$	216.4	$\tau(FeOOCa)$
209.6	$\nu_{as}(O_{cycl}Fe)$	264.4	$\tau(FeOOP)$	287.9	$\delta(OFeO)$
328.7	$\nu_{s}(O_{cycl}Fe)$	360.9	$\nu_{s}(OFeO)$	429.1	$\nu_{as}(OCaO)$
527.8	$\delta(O_{cycl}PO_{term})$	582.6	$\delta(OPO)$	545.0	$\nu_{s}(OCaO)$
528.9	$\tau(O_{term}PO_{cycl}O_{cycl})$	1057.5	$\nu_{as}(OPO)$	647.8	$\nu_{s}(OFeO)$
640.2	$\delta_{s}(O_{cycl}PO_{cycl})$	1090.7	$\nu_{s}(OPO)$	698.5	$\nu_{as}(OFeO)$
1110.6	$\nu_{s}(PO_{cycl})$				
1256.7	$\nu_{as}(PO_{cycl})$				
1553.6	$\nu(PO_{term})$				

Table 6. Geometric parameters and effective charge on Fe atoms (electron charge units) of gaseous salts formed by iron oxide

Molecule	r(Fe–O), Å	$r(X–O)_{cycl}$, Å	$r(X–O)_{term}$, Å	$\angle OXO_{cycl}$, deg	$\angle OXO_{term}$, deg	Effective charge on Fe
$FeMoO_4$	1.908	1.875	1.677	88.3	110.9	1.31
$FeWO_4$	1.918	1.867	1.696	88.5	111.9	1.39
$FePO_3$ (X = P)	2.063	1.493	1.430	105.1	–	0.63
$FePO_2$ (X = P)	2.061	1.536	–	106.2	–	0.58
$CaFeO_2$ (X = Ca)	1.764	2.209	–	109.7	–	1.53

Table 7. Standard entropies and enthalpies of formation and atomization of gaseous iron salts

Molecule	$-\Delta_f H^0(298)$, kJ mol^{-1}	$\Delta_{at} H^0(298)$, kJ mol^{-1}	$S^0(298)$, J mol K^{-1}
$FeWO_4$	543.3 ± 7.7	2766 ± 20	346.4
$FeMoO_4$	559.5 ± 7.3	2595 ± 25	341.1
$FePO_3$	470.1 ± 7.0	1957 ± 15	308.9
$FePO_2$	172.7 ± 6.9	1387 ± 17	296.4
$BaFeO_2$	245.6 ± 4.0	1338 ± 14	340.9
$SrFeO_2$	165.3 ± 5.9	1239 ± 18	330.2

from a double two-temperature molybdenum cell [15] providing the conditions for coexistence in vapor of oxides considerably differing in the volatility. The cells were heated by electron bombardment. The temperature was measured with an EOP-66 optical pyrometer. Partial pressures of vapor components were determined by the comparison of ion currents using gold as an internal reference of pressure [19]. The ionization cross sections were calculated by the additivity method [31]; the ionization cross sections of gaseous salts were multiplied by 0.7 [32]. To determine the molecular composition of vapor, we measured the appearance potentials of ions in the mass spectra by the method of vanishing ionic current, using the ionization potentials of gold as a reference [16]. The unit was preliminarily calibrated by the CaF_2 vapor pressure [17].

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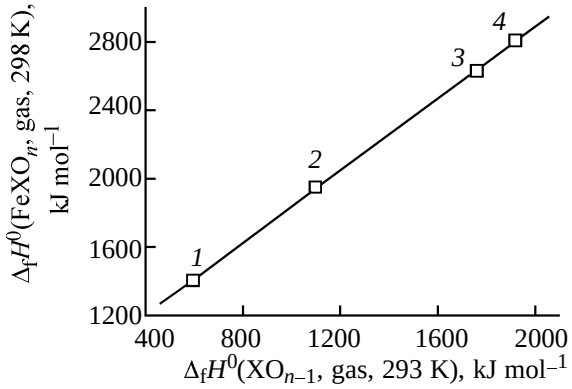

Correlation between the enthalpies of atomization of gaseous iron salts and gaseous anion-forming oxides: (*1*) $FePO_2$, (*2*) $FePO_3$, (*3*) $FeMoO_4$, and (*4*) $FeWO_4$.

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