Russian Journal of General Chemistry, Vol. 71, No. 6, 2001, pp. 828–832. Translated from Zhurnal Obshchei Khimii, Vol. 71, No. 6, 2001, pp. 884–888.

Thermochemical Study of Gaseous Salts of Oxygen-containing Acids: VII.[1] Alkaline-Earth Metal Niobates

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Received January 13, 2000

Abstract—The existence of gaseous alkaline-earth metal niobates was established by high-temperature mass spectrometry. The constants of equilibria involving the niobates and the corresponding oxides were calculated, and the standard enthalpies of formation and atomization of gaseous $BeNbO_3$, $CaNbO_3$, $SrNbO_3$, $BaNbO_2$, $BaNbO_3$ and $BaNb_2O_6$ were determined.

Knowledge of thermodynamic properties of gaseous alkaline-earth metal niobates is necessary for comprehension of vaporization processes in connection with the production of thin-film materials based on these compounds by gas-phase deposition and epitaxy. Tanke has shown [2] that barium and niobium can be simultaneously vaporized at high temperatures from uranium dioxide fresh irradiated with neutrons, though in unknown chemical form. In [3–5] we have studied thermochemical properties of gaseous alkaline-earth metal vanadates and tantalates, which are chemical analogs of niobates. Recently [5] we also reported the results of studies of vapor over the BaO–Nb_2O_5 system. An attempt was made to determine the standard enthalpy of formation of $BaNbO_3$ (g) but because of experimental and calculational errors the resulting data could only be considered as preliminary. The aim of the present research was to determine thermodynamic properties of alkaline-earth niobates Selected results of this work have been breifly reported in [6].

The typical mass spectra of vapor over the MO–Nb_2O_5 systems (M = Ca, Sr, Ba) at an ionizing electron energy of 25 eV, and also the appearance energies of ions are shown in Table 1. The intensities of ion currents are normalized, and corrections for isotope compositions and efficiency of the secondary electron multiplier are introduced. The WO_2^+, WO_3^+, MWO_3^+, and MWO_4^+ ions generated by interaction of the samples with the chamber material were also oberved but their intensities did not exceed 0.5% of the intensity of NbO_2^+. The mass spectrum of vapor over the BeO–Nb_2O_5 system at 2230–2450 K contains Be^+, $Be_nO_n^+$ (n = 1–4, $Be_3O_3^+$ is the base ion), NbO^+, NbO_2^+, and $BeNbO_3^+$ ions. The appearance energies of the $MNbO_3^+$ (M = Ca, Sr, Ba) and $BaNb_2O_6^+$ ions are low and compare with those of alkaline-earth metal vanadates [3] and tantalates [4], as well as europium niobates and tantalates [7, 8], implying direct ionization of the corresponding molecules. The low $BeNbO_3^+$ and $MNbO_2^+$ ion currents, and also the high level of noise on sensitive scales of the voltmeter allowed the appearance energies of these ions to be estimated to an accuracy of no higher than ±1 eV. The appearance energy of the $EuNbO_2^+$ ion of 6.5 eV, reported in [7], allowed us to suggest that $MNbO_2^+$ are for the most part molecular ions.

The partial pressures of vapor components were measured by differential mass spectrometry (the

Table 1. Mass spectra of vapor over MO–Nb_2O_5 systems (I^+ is ion current) and appearance energies (AE ± 0.3 eV) of ions

Ion	M = Ca, 2410 K		M = Sr, 2380 K		M = Ba, 2350 K	
	I^+	AE	I^+	AE	I^+	AE
M^+	10.5	6.0	53.5	6.0	25.0	5.8
MO^+	0.6	7.5	0.3	7.1	48.6	7.0
Nb^+	0.5	–	0.5	–	0.6	–
NbO^+	19.4	7.5	16.6	7.5	25.5	7.5
NbO_2^+	100	8.1	100	8.0	100	8.2
$MNbO_2^+$	0.01	–	0.06	–	0.12	–
$MNbO_3^+$	0.36	7.0	0.24	6.1	3.1	6.3
$MNb_2O_6^+$	0.05	–	0.06	–	0.14	10.7

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

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Table 2. Partial pressures of vapor components over the $BeO–Nb_2O_5$ system and calculated heats of reaction (10)

T, K	p, atm			$-\Delta_r H^0$, kJ
	Be_3O_3, $\times 10^7$	NbO_2, $\times 10^5$	$BeNbO_3$, $\times 10^8$	
2237	1.22	0.62	1.00	115
2320	3.08	1.08	2.37	118
2369	4.63	1.38	4.49	115
2358	4.79	1.33	4.82	113
2428	8.22	1.69	6.38	119
2428	12.65	1.80	6.73	122
2446	11.79	1.29	4.64	123
2443	7.00	1.05	4.99	114
Average value			117 ± 4	

Table 3. Partial pressures of vapor components over the $CaO–Nb_2O_5$ system and calculated heats of reaction (3)

T, K	p, atm			$-\Delta_r H^0$, kJ
	CaO, $\times 10^7$	NbO_2, $\times 10^5$	$CaNbO_3$, $\times 10^7$	
2376	3.03	4.84	2.37	528
2369	3.38	2.49	1.05	521
2298	1.41	1.05	0.51	526
2337	2.70	1.74	0.86	522
2386	4.15	2.46	1.32	525
2371	4.30	2.36	1.14	521
2275	0.14	0.54	0.02	531
2336	2.83	9.02	2.63	511
2415	5.88	3.59	1.79	524
Average value			524 ± 4	

method of comparison of ion currents), based on consequtive measurements of the ion currents of a standard with known vapor pressure and of the sample under study (the indices 1 and 2 refer to the sample and standard, respectively).

$$p_1 = p_2 I_1 T_1 \sigma_2 \gamma_2 a_2 / I_2 T_2 \sigma_1 \gamma_1 a_1. \qquad (1)$$

We used gold [9] and NbO_2As as the pressure standards. The ionization cross sections of molecules σ_i were calculated by the additive scheme, using the atomic ionization cross sections after Mann [10]; the ionization cross sections of the $MNbO_3$, NbO_2, $BaNb_2O_6$, and Be_3O_3 molecules were multiplied by 0.7 [11]. The effective conversion coefficient on the first electrode of the secondary electron multiplier γ_i was taken to be proportional to $M^{-0.5}$ [12] (M is the mass number of an ion). The measurements were carried out at ionizing electron energies 3 eV higher the appearance energies of molecular ions, assuming that under these conditions dissociative ionization is completely suppressed.

The vapor pressure of NbO_2 over niobium dioxide was measured by the method of full isothermal vaporization. The samples had the composition $NbO_{2.008}$ (determined by weight gain on calcination in air). The dependence of the NbO_2 vapor pressure over $NbO_{2\pm x}$ on the O/Nb ratio has been carefully measured by Matsui and Naito [13]. The partial pressures of NbO_2 over $NbO_{2.008}$, obtained by us, proved to be rather close to those obtained in [13] for the composition $NbO_{2.011}$. The partial pressures were corrected for the contents of NbO in the vapor. The vapor pressure of NbO_2 over the standard in the range 2012–2155 was further calculated by Eq. (2):

$$\log p(NbO_2,\ Pa) = -28640/T + 13.27. \qquad (2)$$

The partial pressures of vapor components over the $MO–Nb_2O_5$ systems were used for calculating the equilibrium constants of gas-phase synthesis reactions.

$$MO + NbO_2 = MNbO_3, \qquad (3)$$

$$Ba + NbO_2 = BaNbO_2, \qquad (4)$$

$$BaO + NbO = BaNbO_2, \qquad (5)$$

$$BaO + 3\ NbO_2 = BaNb_2O_6 + NbO, \qquad (6)$$

$$2BaO + 2NbO_2 = BaNb_2O_6 + Ba, \qquad (7)$$

$$2BaNbO_3 = BaNb_2O_6 + Ba, \qquad (8)$$

$$2BaNbO_3 + NbO_2 = BaNb_2O_6 + NbO + BaO, \qquad (9)$$

$$1/3Be_3O_3 + NbO_2 = BeNbO_3. \qquad (10)$$

The measured partial pressures of vapor components over the $MO–Nb_2O_5$ systems, the equilibrium constants, and the enthalpies of reactions (3)–(10) at 0, estimated by Eq. (11), are given in Tables 2–6.

$$\Delta_r H^0(0) = T[\Delta_r F^0(T) - R\ln K_e(T)]. \qquad (11)$$

The enthalpies of reactions (3)–(10) were calculated using the thermodynamic data for the MO, NbO, NbO_2, and Be_3O_3 molecules and atomic barium, taken from the handbook [14]. The thermodynamic functions of alkaline-earth metal niobates were calculated by statistical thermodynamics in the rigid rotator–harmonic oscillator approximation. For the $MNbO_3$ molecules we accepted a cyclic structure of C_{2v} symmetry, similar to the structures accepted in [7, 8] for the $EuNbO_3$ and $EuTaO_3$ molecules. The ONbO

Table 4. Partial pressures of vapor components over the $SrO–Nb_2O_5$ system and calculated heats of reaction (3)

T, K	p, atm SrO, $\times 10^7$	p, atm NbO_2, $\times 10^6$	p, atm $SrNbO_3$, $\times 10^7$	$-\Delta_r H^0$, kJ
2333	1.42	13.80	1.06	522
2381	1.97	18.20	1.59	528
2206	0.38	2.83	0.30	524
2185	0.25	2.00	0.19	526
2231	0.50	3.47	0.39	526
2285	0.89	5.09	0.65	530
2400	2.98	12.69	1.73	533
2272	0.80	10.30	0.77	519
2211	0.42	4.47	0.31	516
2237	0.44	5.43	0.42	523
2303	0.78	7.46	0.59	527
2411	3.04	13.87	1.60	533
Average value				526 ± 3

Table 5. Partial pressures of vapor components over the $BaO–Nb_2O_5$ system and calculated heats of reaction (3)

T, K	p, atm BaO, $\times 10^6$	p, atm NbO_2, $\times 10^6$	p, atm $BaNbO_3$, $\times 10^7$	$-\Delta_r H^0$, kJ
2028	0.27	0.27	0.07	451
2105	1.34	1.11	0.45	447
2102	1.06	0.71	0.45	454
2000	0.53	0.34	0.20	448
2068	1.28	0.96	0.49	445
2194	3.14	2.41	1.20	453
2202	3.76	3.12	1.60	453
2263	5.31	4.10	2.20	459
2299	6.72	5.54	2.74	460
2415	18.45	27.20	8.84	457
2351	8.84	21.30	4.96	454
1989	0.60	0.29	0.24	449
2363	12.48	11.30	5.63	460
2198	0.40	5.30	0.26	454
2265	0.89	11.80	0.78	457
Average value				454 ± 4

angle in the cycle was taken to be 120° and the lengths of the bridging bond r(Nb–O) and the terminal bond r(Nb–O), 1.91 and 1.77 Å, respectively. The metal–oxygen interatomic distances r(M–O) were accepted as sums of the ionic radii of oxygen and the corresponding metals [15], Å: r(Be–O) 1.63, r(Ca–O) 2.19, r(Sr–O) 2.35, and r(Ba–O) 2.53. The only available experimental Ba–O bond length is that in the $BaMoO_4$ molecule [16]: r(Ba–O) 2.54 Å, which almost coincide with the value we accepted for

Table 6. Partial pressures of vapor components over the $BaO–Nb_2O_5$ system and calculated heats of reactions (4–9)

T, K	p, atm Ba, $\times 10^6$	BaO, $\times 10^6$	NbO, $\times 10^6$	NbO_2, $\times 10^6$	$BaNbO_2$, $\times 10^8$	$BaNbO_3$, $\times 10^7$	$BaNb_2O_6$, $\times 10^8$	$\Delta_r H^0$, kJ, for reactions (4)	(5)	(6)	(7)	(8)	(9)
2305	3.37	3.71	2.91	15.6	0.93	2.62	0.53	291	395	903	1008	96	–9
2321	3.40	3.74	2.93	15.7	0.93	2.64	0.54	293	398	908	1027	96	–9
2363	8.06	8.91	4.19	19.3	1.91	5.16	0.82	291	395	909	1013	96	–8
2351	8.02	8.87	4.17	19.2	1.90	5.13	0.82	289	393	905	1008	96	–8
2415	19.6	18.5	6.96	24.5	2.93	8.82	3.37	283	387	937	1040	122	18
2483	23.6	22.5	7.02	19.4	2.67	11.0	7.21	290	391	987	1088	135	33
2151	1.78	2.83	0.24	1.04	–	0.81	0.36	–	–	945	1033	114	27
2102	0.65	1.25	0.08	0.44	–	0.39	0.18	–	–	953	1040	109	22
2433	23.9	23.3	6.10	21.6	1.35	9.90	5.56	268	372	953	1057	134	28
2451	28.8	27.6	8.35	27.2	2.89	12.6	8.29	277	380	957	1050	137	31
2493	42.0	34.8	13.9	40.4	4.68	18.1	17.6	275	381	968	1074	145	39
2117	5.43	7.08	–	3.52	–	2.84	1.10	–	–	–	982	108	–
2365	7.02	7.15	1.11	5.98	–	3.05	0.70	–	–	935	1014	110	3
Average value								284 ± 9	388 ± 9	938 ± 26	1033 ± 29	115 ± 18	14 ± 19

Table 7. Enthalpies of reactions (4)–(10) and standard enthalpies of formation and atomization of underlined gaseous alkaline-earth metal niobates

Reaction	$-\Delta_r H^0_{298}$, kJ	$-\Delta_f H^0_{298}$, kJ/mol	$\Delta_{at} H^0_{298}$, kJ/mol
1/3 BeO + NbO_2 = $\underline{BeNbO_3}$	116±4	658±4	2453±7
CaO + NbO_2 = $\underline{CaNbO_3}$	524±4	682±4	2330±7
SrO + NbO_2 = $\underline{SrNbO_2}$	526±3	741±3	2372±6
BaO + NbO_2 = $\underline{BaNbO_3}$			
equation (10)	454±4	783±4	2433±7
equation (12)	456±20	785±20	2435±21
Recommended value	455±20	784±20	2434±21
Ba + NbO_2 = $\underline{BaNbO_2}$	284±9	303±10	1704±12
BaO + NbO = $\underline{BaNbO_2}$	388±6	305±7	1706±10
Recommended value		304±10	1705±12
BaO + $3NbO_2$ = $\underline{BaNb_2O_6}$ + NbO	935±26	1877±27	4997±30
2BaO + $2NbO_2$ = $\underline{BaNb_2O_6}$ + Ba	1031±29	1868±30	5006±32
2BaNbO3 + NbO_2 = $\underline{BaNb_2O_6}$ + NbO + BaO	11±19	1864±20	5002±23
Recommended value		1867±24	5001±27

our calculations. The vibration frequencies for the NbO_3 group were taken from [7]: 918, 863, 736, 333, 317, and 264 cm^{-1}. The remaining three frequencies were estimated at 550, 350, and 150 cm^{-1} for $BeNbO_3$, 250, 150, and 120 cm^{-1} for $CaNbO_3$, 130, 95, and 80 cm^{-1} for $SrNbO_3$, and 112, 75, and 65 cm^{-1} for $BaNbO_3$. By analogy with $EuNbO_2$ [7], for the $BaNbO_2$ molecule we accepted a rhombic structure of C_{2v} symmetry with the bond lengths r(Ba–O) 2.53 and r(Nb–O) 1.91 Å, the angle $\angle$ONbO 120°, and the vibration frequencies 668, 660, 292, 112, 75 and 65 cm^{-1}. The thermodynamic functions of the $BaNb_2O_6$ molecule were calculated on the assumption that its structure is similar to the structure of the CuN_2O_6 molecule experimentally studied by gas-phase electron diffraction [17, 18]. It is a bicyclic structure of D_{2D} symmetry with two planar rhombic NO_3 fragments residing in planes turned by 90° to each other. The interatomic distances were taken the same as for the $BaNbO_3$ molecule, and the vibration frequencies were 918(2), 813(2), 736(2), 333(2), 317(2), 246(2), 112(4), 75(2), and 65(3) cm^{-1}.

The average enthalpies for all the gas-phase reactions studied, and the standard enthalpies of formation and atomization of gaseous niobates are given in Table 7.

Reaction (12) was the only for which we could study the temperature dependence of the equilibrium constant in a sufficiently wide temperature range (1990–2365 K) and to estimate by Eq. (13) the $\Delta_r H^0$(2078 K) value (434.3±20.0 kJ/mol).

$$BaNbO_3 = BaO + NbO_2, \tag{12}$$

$$\Delta_r H^0(T) = -R\,\frac{\partial \ln K_p(T)}{\partial(1/T)}. \tag{13}$$

Examining the tendencies in the enthalpies of atomization of gaseous salts of oxygen-containing acids along isocationic series one can see that the enthalpy of atomization of a salt is linearly related to the enthalpy of atomization of the gaseous anion-forming oxide [19]. Such plots constructed on the basis of available published data allowed us to obtain the following estimates for the standard enthalpies of atomization and formation of the niobates $MgNbO_3$, $MNbO_2$, and MNb_2O_6 (M = Be, Mg, Ca, Sr), kJ/mol: 172 and 1717 ($BeNbO_2$), –1830 and 5095 ($BeNb_2O_6$), –336 and 1705 ($MgNbO_2$), –734 and 2352 (MgNbO3), –1700 and 4789 ($MgNb_2O_6$), –311 and 1711 ($CaNbO_2$), –1773 and 4892 ($CaNb_2O_6$), –373 and 1755 ($SrNbO_2$), and –1803 and 4905 ($SrNb_2O_6$).

The enthalpies of atomization gaseous NbO, NbO_2, and Nb_2O_5 were taken from [14, 20].

The reliability of the resulting enthalpies of formation and atomization of gaseous alkaline-earth metal niobates is confirmed by their correlation with similar values for gaseous vanadates and tantalates, as wel as for europium niobates.

EXPERIMENTAL

Measurements were carried out on an MS-1301 mass spectrometer by the differential mass spectrometry technique. Samples were vaporized from a double Knudsen tungsten effusion chamber heated by electron impact. The temperature was measured with an EOP-66 optical pyrometer; correction for brightness attenuation by the pyrometric window glass was introduced. The apparatus was calibrated by gold and CaF_2 vapor pressure; therewith, the difference between the calibration results and published data [9, 14, 21] did not exceed ±10%. The scale of appearance energies was corrected by the Au^+ ionization energy of 9.22 eV [22]. The samples were mixtures of Nb_2O_5 and carbonates of the corresponding alkaline-earth metals in a 1 : 1 molar ratio.

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