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P-T-X PHASE DIAGRAM AND THERMODYNAMICS OF BARIUM-TUNGSTEN OXIDES

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ABSTRACT

P-T-X phase equilibria in the quasi-binary system $BaO-WO_3$ have been examined by the Knudsen-effusion technique with mass spectrometric analysis of the vapours. Thermodynamic functions of the crystalline and gaseous ternary oxides were derived.

Standard mass spectrometer, model MS 1301, was used in the experiments. The inner surfase of the tungsten effusion cells was coated with iridium metal. The ratio of the evaporation surface to the effusion-orifice cross-section was about 260. The temperature was measured by the standard optical pyrometer EOP-6. To obtain the thermodynamic functions of the ternary oxides the isothermal vaporization method was used.

Mass spectra of the principal ions, registered at different temperatures and $BaO-WO_3$ compositions, are given in table 1 for the ionizing potentials E_a=60-70 V. Analysis of the experimental results on isothermal vaporization of the $BaO-WO_3$ samples (90, 70, 50, and 10 mol.% BaO) together with the examination of the ionization-efficiency curves for the predominant ions made it possible to convert the ion intensities I to partial pressures P. It has been shown that the vapours consist of the following species: W_2O_6, W_3O_8, W_3O_9, W_4O_{12}, Ba, BaO, $(BaO)_2$, $BaWO_4$, Ba_2WO_5, $(BaWO_4)_2$, O_2.

The partial pressures were calculated from the correlation P = kIT. To estimate the values of k the Hertz-Knudsen equation and the relative ionization cross-sections were used for every species. The time dependences of the partial pressures were converted to the compositional dependences by means of both differential and intergal methods. The former is based on the Gibbs-Duhem equation written for the quasi-binary system with multicomponent vapour. In the range 64 to 50 mol.% BaO partial pressures of $BaWO_4$ and Ba_2WO_5 were taken as the independent components. In this case the form of the Gibbs-Duhem equation is:

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TABLE 1. **Mass spectrum of the saturated vapours for the BaO-WO_3 system (E_a= 60-70 V)**

Ion	Composition, mol.% BaO						
	90	70	60	50	30	20	10
	1825 K				1525 K		
Ba^+	100	53	64	121	50	40	37
BaO^+	100	100	100	100	100	100	100
$Ba_2O_2^+$	2	0,2	0,09	0,02	-	-	-
WO_2^+	-	0,06	0,2	0,9	1200	4166	4060
WO_3^+	-	0,01	0,03	0,23	230	800	690
$W_2O_6^+$	-	-	-	-	250	533	560
$W_3O_9^+$	-	-	-	-	520	1900	1900
$W_4O_{12}^+$	-	-	-	-	12	15	16
$W_3O_8^+$	-	-	-	-	200	700	700
$BaWO_4^+$	0,3	4,3	13,5	50	21	15	16
$Ba_2WO_5^+$	0,02	0,25	0,23	0,13	-	-	-
$(BaWO_4)_2^+$	-	0,003	0,01	0,03	-	-	-
$BaW_2O_7^+$	-	-	-	0,06	20	20	12,5
O_2^+	not measured						

$$\frac{d\ \ln P(BaWO_4)}{d\ \ln P(Ba_2WO_5)} = \frac{n(WO_3) - n(BaO)}{2n(WO_3) - n(BaO)}$$

To obtain the isothermal diagrams (partial pressures vs. composition) and (total vapour pressure vs. composition) the experimental results were recalculated to the corresponding constant temperatures. The necessary sublimation enthalpies of the vapour phase species were obtained from the temperature dependences of the principal ion currents: $W_4O_{12}^+$, $W_3O_9^+$, $W_2O_6^+$, Ba^+, $BaWO_4^+$, and and $BaW_2O_7^+$, for the following compositions: 15, 20, 25, 30, 40, and 50 mol.% BaO.

The molar enthalpies of formation of crystalline and gaseous barium-tungsten oxides were calculated from the second-law enthalpies of the following reactions:

$BaWO_4(s) = BaWO_4(g)$ (1)

$BaWO_4(g) + 1/3\ W_3O_9(g) = BaW_2O_7(g)$ (2)

$BaWO_4(g) + 0.5\ W_2O_6(g) = BaW_2O_7(g)$ (3)

$BaO(g) + BaWO_4(g) = Ba_2WO_5(g)$ (4)

$2\ BaWO_4(g) = (BaWO_4)_2(g)$ (5)

$Ba_3WO_6(s) = 2\ BaO(g) + BaWO_4(g)$ (6)

TABLE 2. Standard molar enthalpies of reactions (1)-(6) and formation of barium-tungsten oxides (kJ.mol^{-1})

Reaction	$\Delta_r H_m^\circ$(298 K)	Compound	$-\Delta_f H_m^\circ$(298 K)
(1)	594 ± 11	$BaWO_4(g)$	1088 ± 21
(2)	-285 ± 25	$BaW_2O_7(g)$	2042 ± 42
(3)	-393 ± 29	$BaW_2O_7(g)$	2046 ± 42
(4)	-418 ± 25	$Ba_2WO_5(g)$	1632 ± 33
(5)	-289 ± 38	$(BaWO_4)_2(g)$	2464 ± 46
(6)	1628 ± 17	$Ba_3WO_6(s)$	2983 ± 29

Table 2 lists the standard molar enthalpies of reactions (1)-(6) and the resulting enthalpies of formation of the ternary oxides converted to 298.15 K. Since no data on temperature dependences of the molar heat capacities is available for the gaseous barium-tungsten oxides these were taken equal to those reported in the literature for the corresponding barium-molybdenum oxides.