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**Abstract**

**Full Text**

**CHEMISTRY**

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## EQUILIBRIUM WITH HYDROGEN AND THERMODYNAMIC CHARACTERISTICS OF $\text{BaMoO}_4$ AND $\text{BaMoO}_3$

In the present work, which is a continuation of a series of studies on the thermodynamics of tungstates and molybdates (<sup>1-4</sup>), the equilibrium of barium molybdate with hydrogen was investigated.  $\text{BaMoO}_4$  was prepared by precipitating sodium molybdate with an equivalent amount of  $\text{Ba}(\text{NO}_3)_2$  solution; the precipitate was thoroughly washed, dried, and calcined. The  $\text{BaMoO}_4$  obtained has a tetragonal structure; the lattice constants found by us agree well with literature data (<sup>5</sup>).

**Table 1**

I stage	I stage	II stage	II stage
T, °K	$K_{pI}$	T, °K	$K_{pI}$
1479	0.084	1521	0.0348
1521	0.092	1562	0.0434
1562	0.102	1604	0.0550
1604	0.113	1645	0.0672
1687	0.126		

The equilibrium of  $\text{BaMoO}_4$  with hydrogen in the temperature range 1200-1400°C was studied by the circulation method in the apparatus described in (<sup>4</sup>). An X-ray diffraction study showed that the reduction of  $\text{BaMoO}_4$  in this temperature range proceeds with the formation of the intermediate compound  $\text{BaMoO}_3$  (perovskite type,  $a = 4.03 \text{ \AA}$ ) (<sup>6</sup>); the final products of reduction are BaO and Mo. BaO remains at these temperatures in the solid phase; at 1400°C, according to (<sup>7,8</sup>), the saturated vapor pressure of BaO does not exceed 0.001 mm Hg.

Thus, analogously to the reductions of magnesium (<sup>9</sup>), calcium (<sup>1</sup>), and strontium (<sup>4</sup>) molybdates studied earlier by us, the reduction of  $\text{BaMoO}_4$  by hydrogen proceeds in two stages:

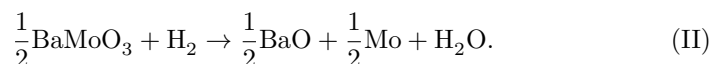
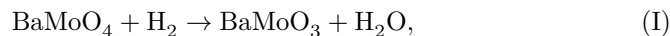
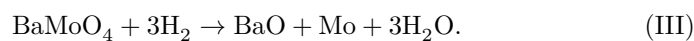


Table 1 gives the mean values of the equilibrium constants  $K_{p\text{I}} = p_{\text{IH}_2\text{O}}/p_{\text{IH}_2}$  and  $K_{p\text{II}} = p_{\text{IIH}_2\text{O}}/p_{\text{IIH}_2}$  for a number of temperatures of the I and II stages of reduction of  $\text{BaMoO}_4$ ; in Fig. 1 the dependence of  $\lg K_{p\text{I}}$  and  $\lg K_{p\text{II}}$  on  $\frac{1}{T}$  is presented graphically.

The logarithmic polynomials of the equilibrium constants for the two stages of reduction of  $\text{BaMoO}_4$  are described (with an accuracy of  $\pm 0.25\%$  for the first and  $\pm 0.2\%$  for the second) by the following equations:

$$\lg K_{p\text{I}} = -\frac{11155}{4.575T} + 0.5708, \quad \lg K_{p\text{II}} = -\frac{26610}{4.575T} + 2.3639.$$

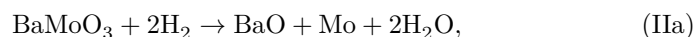
Combining reactions (I) and (II), we obtain the equation for the reaction of complete reduction of  $\text{BaMoO}_4$ :



For it

$$\begin{aligned} \lg K_{p\text{III}} &= \lg \frac{p_{\text{III H}_2\text{O}}^3}{p_{\text{III H}_2}^3} = \lg K_{p\text{I}} + 2 \lg K_{p\text{II}} = -\frac{64370}{4.575T} + 5.299, \quad \Delta Z_{\text{III}}^0 = \\ &= -RT \ln K_{p\text{III}} = 64370 - 24.24T. \end{aligned}$$

For the reaction of reduction of  $\text{BaMoO}_3$  by hydrogen



$$K_{p\text{IIa}} = K_{p\text{II}}^2; \quad \Delta Z_{\text{IIa}}^0 (\text{kcal}) = -4.575T \lg K_{p\text{II}}^2 = 5321Q - 21.63T.$$

The values of  $\Delta Z_{\text{IIa}}^0$ ,  $\Delta Z_{\text{III}}^0$ , as well as  $\Delta H_{\text{IIa}}$  and  $\Delta H_{\text{III}}$  for a number of temperatures are given in Table 2.

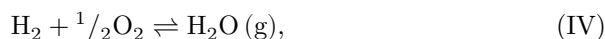
**Table 2**

Fig. 1

Figure 1: Fig. 1

T, °K	$\Delta Z_{\text{IIa}}^0$ , kcal	$\Delta H_{\text{IIa}}$ , kcal	$\Delta Z_{\text{III}}^0$ , kcal	$\Delta H_{\text{III}}$ , kcal	$\Delta Z_{\text{IV}}^0$ , kcal	$\Delta H_{\text{IV}}$ , kcal	$\Delta Z_{\text{V}}^0$ , kcal	$\Delta H_{\text{V}}$ , kcal	$\Delta Z_{\text{VI}}^0$ , kcal	$\Delta H_{\text{VI}}$ , kcal
1473	21.36		28.67		-39.75		-100.56		-147.47	
1523	20.27		27.45		-39.07		-98.10		-144.20	
1573	19.19	53.22	26.17	64.37	-38.38	-59.90	-95.64	-173.0	-140.87	-244.07
1643	17.68		24.54		-37.42		-92.20		-136.32	

Combining reactions IIa and III with the reaction of formation of water vapor

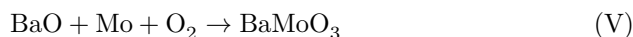


whose isobaric potential and enthalpy according to Chipman<sup>(10)</sup> are expressed by the equations

$$\Delta Z_{\text{IV}}^0 (\text{kcal}) = -59251 + 2.006T \lg T - 7.5 \cdot 10^{-5}T^2 + \frac{408000}{T} + 6.8085T,$$

$$\Delta H_{\text{IV}} (\text{kcal}) = -59251 - 0.871T + 7.5 \cdot 10^{-5}T^2,$$

one can calculate\*  $\Delta Z_{\text{V}}^0$  (respectively  $\Delta H_{\text{V}}$ ) and  $\Delta Z_{\text{VI}}^0$  (respectively  $\Delta H_{\text{VI}}$ ) for the formation of BaMoO<sub>3</sub> and BaMoO<sub>4</sub> according to the reactions:



The numerical values of  $\Delta Z_{\text{V}}^0$  and  $\Delta Z_{\text{VI}}^0$  are given in Table 2, and their temperature dependence in the temperature interval we studied is expressed by the equations:

**Fig. 1**

$$\Delta Z_{\text{V}}^0 (\text{kcal}) = -\Delta Z_{\text{IIa}}^0 + 2\Delta Z_{\text{IV}}^0 = -173020 + 49.19T,$$

$$\Delta Z_{\text{VI}}^0 (\text{kcal}) = -\Delta Z_{\text{III}}^0 + 3\Delta Z_{\text{IV}}^0 = -244070 + 65.58T.$$

It is not possible to calculate  $\Delta Z_V^0$  for 298°K because of the absence of heat-capacity data for BaMoO<sub>3</sub>. For BaO, Mo, and O<sub>2</sub>, according to <sup>(11)</sup>, and for

\* In the calculation we used the simpler equation  $\Delta Z_{IV}^0 = -59000 + 13.782T$ , which is obtained from Chipman's equation for the temperature interval 1473–1643°K.

For BaMoO<sub>4</sub>, according to (12), the following equations are available for the dependence of the true molar heat capacities of these compounds on temperature:

$$\text{Mo: } c_p = 5.48 + 1.30 \cdot 10^{-3}T;$$

$$\text{O}_2: c_p = 8.27 + 0.258 \cdot 10^{-3}T - 1.877 \cdot 10^5 T^{-2};$$

$$\text{BaO: } c_p = 12.74 + 1.04 \cdot 10^{-3}T - 1.984 \cdot 10^5 T^{-2};$$

$$\text{BaMoO}_4: c_p = 25.37 + 13.38 \cdot 10^{-3}T.$$

Using these equations and our data, we obtain the following equation for the dependence of  $\Delta Z_{VI}^0$  in the temperature interval 298–1643°K:

$$\Delta Z_{VI}^0 = -248520 + 5.255T \ln T - 5.325 \cdot 10^{-3}T^2 - \frac{2.4 \cdot 10^5}{T} + 38.21T,$$

whence, for 298.2°K:  $\Delta Z_{VI}^0 = -229.5$  kcal/mole;  $\Delta H_{VI}^0 = -251.2$  kcal/mole;  $\Delta S_{VI}^0 = -72.9$  e.u. Taking, according to (13), the standard molar entropies of BaO, Mo, and O<sub>2</sub> as equal, respectively, to 16.8, 6.83, and 49.00 e.u., we obtain (BaMoO<sub>4</sub>)  $S_{298.2} = 24.2$  e.u.

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*Note: Figure translations are in progress. See original paper for figures.*

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