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Abstract

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EQUILIBRIUM WITH HYDROGEN AND THERMODYNAMIC CHARACTERISTICS OF $BaMoO_4$ AND $BaMoO_3$

In the present work, which is a continuation of a series of studies on the thermodynamics of tungstates and molybdates ([1–4]), the equilibrium of barium molybdate with hydrogen was investigated. $BaMoO_4$ was prepared by precipitating sodium molybdate with an equivalent amount of $Ba(NO_3)_2$ solution; the precipitate was thoroughly washed, dried, and calcined. The $BaMoO_4$ obtained has a tetragonal structure; the lattice constants found by us agree well with literature data ([5]).

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 $BaMoO_4$ with hydrogen in the temperature range 1200–1400°C was studied by the circulation method in the apparatus described in ([4]). An X-ray diffraction study showed that the reduction of $BaMoO_4$ in this temperature range proceeds with the formation of the intermediate compound $BaMoO_3$ (perovskite type, $a = 4.03$ Å) ([6]); the final products of reduction are BaO and Mo. BaO remains at these temperatures in the solid phase; at 1400°C, according to ([7,8]), the saturated vapor pressure of BaO does not exceed 0.001 mm Hg.

Thus, analogously to the reductions of magnesium ([9]), calcium ([1]), and strontium ([4]) molybdates studied earlier by us, the reduction of $BaMoO_4$ by hydrogen proceeds in two stages:

$$BaMoO_4 + H_2 \rightarrow BaMoO_3 + H_2O, \qquad \text{(I)}$$

$$\frac{1}{2}BaMoO_3 + H_2 \rightarrow \frac{1}{2}BaO + \frac{1}{2}Mo + H_2O. \qquad \text{(II)}$$

Table 1 gives the mean values of the equilibrium constants $K_{p\mathrm{I}} = p_{\mathrm{I}H_2O}/p_{\mathrm{I}H_2}$ and $K_{p\mathrm{II}} = p_{\mathrm{II}H_2O}/p_{\mathrm{II}H_2}$ for a number of temperatures of the I and II stages of reduction of $BaMoO_4$; in Fig. 1 the dependence of $\lg K_{p\mathrm{I}}$ and $\lg K_{p\mathrm{II}}$ on $\frac{1}{T}$ is presented graphically.

The logarithmic polynomials of the equilibrium constants for the two stages of reduction of $BaMoO_4$ are described (with an accuracy of $\pm 0.25\%$ for the first and $\pm 0.2\%$ for the second) by the following equations:

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

Combining reactions (I) and (II), we obtain the equation for the reaction of complete reduction of $BaMoO_4$:

$$BaMoO_4 + 3H_2 \rightarrow BaO + Mo + 3H_2O. \qquad \text{(III)}$$

For it

$$\lg K_{p\mathrm{III}} = \lg \frac{p^3_{\mathrm{III}\ H_2O}}{p^3_{\mathrm{III}\ H_2}} = \lg K_{p\mathrm{I}} + 2\lg K_{p\mathrm{II}} = -\frac{64370}{4.575T} + 5.299, \quad \Delta Z^0_{\mathrm{III}} =$$

$$= -RT \ln K_{p\mathrm{III}} = 64370 - 24.24T.$$

For the reaction of reduction of $BaMoO_3$ by hydrogen

$$BaMoO_3 + 2H_2 \rightarrow BaO + Mo + 2H_2O, \qquad \text{(IIa)}$$

$$K_{p\mathrm{IIa}} = K^2_{p\mathrm{II}}; \qquad \Delta Z^0_{\mathrm{IIa}}\,(\mathrm{kcal}) = -4.575T \lg K^2_{p\mathrm{II}} = 5321Q - 21.63T.$$

The values of $\Delta Z^0_{\mathrm{IIa}}$, $\Delta Z^0_{\mathrm{III}}$, as well as ΔH_{IIa} and ΔH_{III} for a number of temperatures are given in Table 2.

Table 2

Fig. 1

Figure 1: Fig. 1

T, °K	ΔZ^0_{IIa}, kcal	ΔH_{IIa}, kcal	ΔZ^0_{III}, kcal	ΔH_{III}, kcal	ΔZ^0_{IV}, kcal	ΔH_{IV}, kcal	ΔZ^0_{V}, kcal	ΔH_{V}, kcal	ΔZ^0_{VI}, kcal	ΔH_{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

$$H_2 + {}^1/_2O_2 \rightleftharpoons H_2O\,(g), \qquad \text{(IV)}$$

whose isobaric potential and enthalpy according to Chipman [10] are expressed by the equations

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

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

one can calculate* ΔZ^0_{V} (respectively ΔH_{V}) and ΔZ^0_{VI} (respectively ΔH_{VI}) for the formation of $BaMoO_3$ and $BaMoO_4$ according to the reactions:

$$BaO + Mo + O_2 \rightarrow BaMoO_3 \qquad \text{(V)}$$

$$BaO + Mo + {}^3/_2O_2 \rightarrow BaMoO_4. \qquad \text{(VI)}$$

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

Fig. 1

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

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

It is not possible to calculate ΔZ^0_{V} for 298°K because of the absence of heat-capacity data for $BaMoO_3$. For BaO, Mo, and O_2, according to [11], and for

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

For $BaMoO_4$, according to (12), the following equations are available for the dependence of the true molar heat capacities of these compounds on temperature:

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

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

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

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

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

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

whence, for 298.2°K: $\Delta Z^0_{\text{VI}} = -229.5$ kcal/mole; $\Delta H^0_{\text{VI}} = -251.2$ kcal/mole; $\Delta S^0_{\text{VI}} = -72.9$ e.u. Taking, according to (13), the standard molar entropies of BaO, Mo, and O_2 as equal, respectively, to 16.8, 6.83, and 49.00 e.u., we obtain ($BaMoO_4$) $S_{298.2} = 24.2$ e.u.

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