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Abstract

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EQUILIBRIUM OF STRONTIUM MOLYBDATE WITH HYDROGEN AND THERMODYNAMIC CHARACTERISTICS OF $SrMoO_4$

The equilibrium of the reduction of strontium molybdate by hydrogen was studied in the temperature range 950–1392° C. We used a circulation method, which makes it possible to avoid the influence of thermal diffusion and at the same time accelerates the attainment of equilibrium. Our apparatus had two variants: in the first variant measurements were carried out up to 1122°, and in the second from 1122° and above. Apparatuses analogous to the first variant have been described in earlier works ([1]–[6]). In the second variant a small molybdenum short-circuit heater H was used (Fig. 1), placed inside a quartz reactor P. On the outside the reactor was washed with water, and during operation of the heater it remained cold. The heater was supplied by a low-voltage current (5–15 V), which was fed through brass electrodes E, cooled internally by water. The boat was fastened to a platinum capillary K_1, through which the gas mixture $H_2 + H_2O$ entered the reaction zone. The boat and thermocouple T were introduced into the heater through side ground joint Sh_1, the hot junction of the thermocouple touching the wall of the boat. From the opposite side, through ground joint Sh_2, a semipermeable palladium membrane M was introduced into the heater, making it possible to measure the partial pressure of hydrogen in the hot zone. The membrane consisted of a palladium plate 0.1 mm thick, forming the bottom of a platinum tube K_2, 3 mm in diameter. The membrane had first been tested for tightness and for the rate of diffusion of hydrogen at $t = 1200°$ K. The method of introducing the current leads was borrowed by us from work ([7]).

Fig. 1. Diagram of the apparatus

The temperature of the furnace was maintained constant to an accuracy of +1–3°. The platinum–platinum-rhodium thermocouple had previously been

Fig. 2

Figure 2: Fig. 2

calibrated against the melting temperatures of chemically pure metals and salts. The hydrogen for reduction was obtained by electrolysis of a 20% NaOH solution on nickel electrodes, purified from oxygen over palladized silica gel, and dried over $CaCl_2$ and P_2O_5. In both variants the water-vapor pressure was set by the temperature of a saturator with water placed in a Dewar vessel with finely crushed ice. The equilibrium constant was calculated from the formula

$$K_p = \frac{p_{H_2O}}{p_{H_2}}.$$

The total pressure in the system was measured with a mercury manometer to an accuracy of ± 0.1 mm.

Strontium molybdate was prepared by precipitating a Na_2MoO_4 solution with a $Sr(NO_3)_2$ solution in stoichiometric proportions. The starting salts, reagent grade, were preliminarily purified by recrystallization. The resulting $SrMoO_4$ was thoroughly washed, dried, and calcined at 1000–1100°. Analysis of the preparation, carried out by the Hillebrand and Lundell method ([8]) with an accuracy of 0.5%, confirmed the composition corresponding to the formula $SrMoO_4$. The gross composition of the reduction products was determined from the loss in weight of the preparation. To determine the phase composition, an X-ray diffraction study was carried out by the Debye method in a camera with $D = 86$ mm on an iron anode.

Fig. 2. Reduction isotherms of $SrMoO_4$ for temperatures: *a*–994°, *b*–1037°

It should be noted that the high-temperature apparatus described in the present work, in comparison with the original variant described in work ([9]), is more advanced. The need to improve the apparatus (semipermeable membrane, inlet platinum capillary) was caused by the lack of agreement between the data obtained on the high-temperature apparatus in the original variant (without an inlet capillary and membrane) and on an apparatus with an ordinary furnace. In addition, there are reports in the literature ([10]) that, with a small heating zone and a large temperature gradient with the surroundings, distortion of the results is possible owing to thermal diffusion, despite the presence of circulation. Preliminary heating of the gas mixture reduces cooling of the boat with the substance by a stream of colder gas. Experiments carried out with a semipermeable palladium membrane allowed us to draw the following conclusions. In the absence of an inlet platinum capillary, thermal diffusion takes place, and the data obtained without the capillary are too high, as is clearly seen from Fig. 3. The presence of an inlet platinum capillary provides preliminary heating of the gas mixture

Fig. 3

Figure 3: Fig. 3

Fig. 3. Polytherms of reduction of $SrMoO_4$:
I–first stage of reduction, II–second stage of reduction. Experimental points: *a* –obtained on an ordinary apparatus, *b*–on a high-temperature apparatus with an inlet platinum capillary, *c*–on a high-temperature apparatus without a capillary.

and completely eliminates thermal diffusion. The data obtained on the high-temperature apparatus with an inlet platinum capillary are in good agreement with the data obtained on the ordinary apparatus (up to 1100°).

Reduction of strontium molybdate proceeds in two stages:

$$SrMoO_4 + H_2 = SrMoO_3 + H_2O, \qquad \text{(I)}$$

$$^1\!/_2\, SrMoO_3 + H_2 = {}^1\!/_2\, SrO + {}^1\!/_2\, Mo + H_2O. \qquad \text{(II)}$$

In the first stage of reduction a compound of tetravalent molybdenum, $SrMoO_3$, having the perovskite structure, is obtained. We determined

Table 1

Gross chemical composition of the specimen	$K_p = 994°$	$K_p = 1037°$	Gross chemical composition of the specimen	$K_p = 994°$	$K_p = 1037°$
$SrMoO_{3.9}$	0.157		$SrMoO_3$	0.0314	
$SrMoO_{3.8}$	0.156	0.180	$SrMoO_{2.95}$	0.0123	0.0168
$SrMoO_{3.5}$	0.148		$SrMoO_{2.9}$	0.0117	
$SrMoO_{3.05}$	0.147	0.175	$SrMoO_{1.5}$	0.0116	
$SrMoO_3$	0.111	0.0279	$SrMoO_{1.1}$		0.0169
$SrMoO_3$	0.0763	0.0186			

the lattice constant of this compound, $a = 3.968$ Å, which agrees well with the data of Sholder and Brixner ([11]). Table 1 and Fig. 2 give the dependence of the equilibrium constant on the gross composition of the reduction products.

Table 2 and Fig. 3 give the dependence of the equilibrium constant on temperature for the first and second stages of reduction of $SrMoO_4$.

Table 2

First stage	First stage	Second stage	Second stage
t, °C	K_p av.	t, °C	K_p av.
950	0.131		
994	0.150	994	0.0119
1015	0.168		
1037	0.177	1037	0.0169
1164	0.318	1080	0.0194
1248	0.405	1122	0.0236
		1284	0.0423
		1392	0.0575

By the method of least squares the equations obtained were:

$$\lg K_{p\mathrm{I}} = -\frac{3152.3}{T} + 1.6770 \ (\pm 3\%),$$

$$\lg K_{p\mathrm{II}} = -\frac{3506.5}{T} + 0.8762 \ (\pm 3\%).$$

Combining these equations, we obtain for the reaction of complete reduction of $SrMoO_4$:

$$SrMoO_4 + 3H_2 = SrO + Mo + 3H_2O, \qquad \text{(III)}$$

$$\lg K_{p\mathrm{III}} = \lg K_{p\mathrm{I}} + 2\lg K_{p\mathrm{II}} = -\frac{10165.3}{T} + 3.4293,$$

whence

$$\Delta Z^0_{\mathrm{III}} = 46516 - 15.6925\,T.$$

Using for the reaction of formation of water vapor

$$H_2 + {}^1\!/_2 O_2 = H_2O \qquad \text{(IV)}$$

the equation, equivalent to Chipman' s equation ([12]) in the temperature interval 1000-1600°K,

$$\Delta Z^0_{\mathrm{IV}} = -59564 + 13.44\,T,$$

we obtain for the reaction of formation of $SrMoO_4$:

$$SrO + Mo + {}^3/_2O = SrMoO_4, \tag{V}$$

$$\Delta Z_V^0 = 3\Delta Z_{IV}^0 - \Delta Z_{III}^0.$$

The calculated values of ΔZ_{III}^0, ΔZ_V^0, and the mean thermal effect of reaction (V) for the experimental temperatures are given in Table 3. Taking into account the temperature dependence of the heat capacities of the participants in reaction (V),

$$C_{p\mathrm{SrMoO4}} = 25.2086 + 14.3195 \cdot 10^{-3}T, \tag{13}$$

$$C_{p\mathrm{SrO}} = 10.49 + 3.2 \cdot 10^{-3}T, \tag{14}$$

$$C_{p\mathrm{Mo}} = 5.81 + 1.15 \cdot 10^{-3}T - \frac{0.347}{T^2} \cdot 10^5, \tag{15}$$

$$C_{p\mathrm{O2}} = 7.52 + 0.81 \cdot 10^{-3}T - \frac{0.9}{T^2} \cdot 10^5, \tag{15}$$

Table 3

$T_{\mathrm{av.}}$, °K	ΔZ_{III}^0, cal/mole	ΔZ_V^0, cal/mole	ΔH_V^0, cal/mole
1200	27680	158010	225210
1300	26120	152410	225210
1400	24550	146975	225210
1500	22980	141190	225210
1600	21410	135590	225210

by the method of Temkin and Shvartsman[16] we obtain for ΔZ_T^0 the following equation:

$$\Delta Z_T^0 = -231138 + 62.86\,T - T(M_0\Delta a + M_1\Delta b + M_{-2}\Delta c'),$$

whence $\Delta H_{298}^0 = -231.14$ kcal/mole; $\Delta S_{298}^0 = -62.86$ cal/mole · deg; $\Delta Z_{298}^0 = -212.39$ kcal/mole.

The maximum error in the calculation of ΔZ_V^0 does not exceed 0.13% in comparison with the data of Table 3.

Taking the entropies of the reaction participants as follows: SrO: $S^0_{298} = 12.5$[16]; Mo: $S^0_{298} = 6.83$[15]; $^3/_2O_2$: $S^0_{298} = 75.50$[15], and ΔH^0_{298} and ΔZ^0_{298} for SrO according to [18], respectively equal to −141.1 kcal/mole and −133.8 kcal/mole, we obtain for $SrMoO_4$: $S^0_{298} = 29.97$ cal/mole · deg, $\Delta Z^0_{298} = -346.2$ kcal/mole, and $\Delta H^0_{298} = -372.2$ kcal/mole. In view of the absence of heat-capacity data for $SrMoO_3$, we had to confine ourselves to calculating the thermodynamic characteristics of $SrMoO_3$ at 1273°K: $\Delta Z^0_{1273} = -211.8$ kcal/mole; $\Delta H^0_{1273} = -279.6$ kcal/mole; $S^0_{1273} = 72.65$ cal/mole · deg.

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