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Abstract

Full Text

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Thermal Dissociation of Molybdenum Disulfide in Vacuum

(Presented by Academician I. V. Tananaev on 16 I 1965)

Chemistry

There are few and contradictory data on the behavior of molybdenum dichalcogenides when heated in vacuum. According to works (1-3), the thermal dissociation of molybdenum disulfide begins already at a temperature of about 1000° and proceeds with decomposition of MoS_2 into the elements, without formation of intermediate compounds. Moretto (4) established that molybdenum ditelluride, when heated in vacuum within a certain temperature interval, dissociates with formation of Mo_2Te_3. It is also known that the decomposition, for example, of uranium disulfide gives an entire series of lower sulfides (5, 6).

Thus, the question of the thermal stability of molybdenum disulfide at present remains open.

The present article considers the thermal dissociation of molybdenum disulfide in vacuum.

Experimental Part

The thermal decomposition of molybdenum disulfide was carried out as follows. Into a well-cleaned and preliminarily degassed quartz ampoule about 250 mm long and 20-25 mm in diameter, 3-4 g of substance was loaded. The ampoule was evacuated to a residual pressure of $1 \cdot 10^{-5}$ mm Hg and sealed. To carry out the reaction, the ampoule was placed in a tube furnace in such a way that one end (with the substance) was in the furnace, while the other extended from the furnace and could be cooled. The furnace was given a slight inclination so that the cooled end of the ampoule was slightly raised. The substance was heated to a specified temperature and held for several hours. The distilled-off chalcogen condensed in the cold end of the ampoule.

The thermal dissociation of MoS_2 proceeds as follows. When molybdenum disulfide is heated to a temperature of about 1000°, only a slight deposit of free sulfur is observed at the cooled end of the ampoule. Even prolonged holding at this temperature does not lead to further decomposition of the substance. Intensive distillation of sulfur occurs at higher temperatures.

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Heating molybdenum disulfide at a temperature of 1280–1300° is accompanied by the formation of a gray-steel-colored substance with a strong metallic luster. Chemical analysis of the products obtained in this way corresponds to the formula MoS_{2-x} or, correspondingly, $Mo_{1+x}S_2$, where "x" has a variable value depending on the holding time.

Microscopic and X-ray diffraction study of products obtained at different holding times showed their homogeneity and the absence of metallic molybdenum in the substance. The crystal lattice of the phase of variable composition $Mo_{1+x}S_2$ is based on hexagonal MoS_2. In this case, a slight distortion is observed in the "c" direction, while the parameter "a" remains unchanged.

It is known that, for sulfides of transition metals, phases of the type $M_{1+x}S_2$ ($0 < x \leq 1$) are characteristic; these are obtained from layered lattices of the MS_2 type by "inserting" additional metal atoms between the MS_2 layers ([7]). Such phases have been found, for example, for sulfides of niobium, tantalum, and other elements. According to Jellinek ([7]), the existence of $M_{1+x}S_2$ phases based on the original lattice of hexagonal MoS_2 is unlikely. However, for WS_2, which belongs to the structural type of MoS_2, similar phases are known. Thus Ehrlich ([8]) prepared, from the elements, tungsten disulfide preparations homogeneous over a small range of compositions, approximately from $WS_{1.95}$ to $WS_{2.00}$. Samoilov and Rubinshtein ([9]) obtained homogeneous samples with compositions in the range $WS_{1.862}$–$WS_{2.30}$.

Our data confirm the possibility of forming homogeneous phases of the $M_{1+x}S_2$ type based on hexagonal molybdenum disulfide.

The process of thermal decomposition of molybdenum disulfide is usually accompanied by sintering of the product and the associated slowing of the reaction. Therefore, the ampoule containing the substance obtained during thermal decomposition of MoS_2 for 10–12 h was opened, the product was thoroughly ground, again placed in the ampoule, and subjected to a second thermal treatment under the same conditions. As a result, a gray crystalline powder was obtained; chemical and X-ray diffraction analysis showed the formation of Mo_2S_3. The calculated interplanar spacings for the product obtained agree well with the data of ([10]).

Thus, decomposition of molybdenum disulfide on heating in vacuum proceeds with the formation of molybdenum sesquisulfide.

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