

X-Ray Studies on the System Molybdenum Trioxide — Tungsten Trioxide

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The system molybdenum trioxide — tungsten trioxide has been previously studied by Rieck¹, who particularly examined preparations rich in molybdenum trioxide by thermal analysis and noticed that no «mixed crystals» were formed. The observations were controlled by means of X-ray powder photographs.

The starting materials for the present investigation were molybdenum trioxide

lich werden. Da sich zeigen liess, dass mit steigendem Sulfittierungsgrad der Lignosulfonsäure nicht nur die Vanillinausbeute⁹, sondern auch die Ausbeute an Acetaldehyd steigt, ist anzunehmen, dass auch dieser Typus von aldehydliefernden Gruppen «maskierte» Coniferylaldehydgruppen darstellt; sie müssen allerdings eine andere Struktur besitzen als der Typus der Formel I.

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(Kahlbaum *puriss*), which had been heated at 200° C for 15 hours and tungstic acid (Kahlbaum *purum*), which had been dehydrated at about 500° C. The preparations were obtained by heating weighed mixtures of the trioxides in evacuated silica tubes placed in an electric furnace, giving a rather long range of homogeneous temperature. For heating temperatures exceeding 700° C equilibrium was not reached (*v. infra*)*. Because of this the investigation was confined to a study of the products formed at 700° C. At the latter temperature the heating time was generally about 100 hours.

The preparations were examined by taking X-ray powder photographs with focusing cameras using Cr-K radiation. The phase analysis showed three phases to occur in the system. Preparations $\text{Mo}_{0.75}\text{W}_{0.25}\text{O}_3$ contain reflections of molybdenum trioxide and another phase, while preparations $\text{Mo}_{0.4}\text{W}_{0.6}\text{O}_3$ consist of tungsten trioxide and the same intermediary phase. Samples of $\text{Mo}_{0.6}\text{W}_{0.4}\text{O}_3$ and $\text{Mo}_{0.5}\text{W}_{0.5}\text{O}_3$ do not show any reflections belonging to the trioxides and thus represent fairly pure specimens of the double oxide, the composition of which for this reason may be MoW_2O_6 or approximately such a formula. However, due to the difficulty of detecting small amounts of accompanying contaminations from the powder photographs no further conclusions as to the composition of the intermediary phase can be drawn for the present.

* The silica tubes were strongly attacked when mixtures rich in molybdenum trioxide were heated at 1000° C. Powder photographs showed the tube content to be highly contaminated by cristobalite. Molybdenum trioxide evidently has a pronounced crystallizing effect on silica glass at high temperatures. In fact the white residue mentioned in ², obtained by dissolving molybdenum trioxide in ammonia after it had been heated in a silica tube at 1050° C for 35 hours, was also found to be cristobalite.

The unit cell dimensions of molybdenum trioxide have been determined at this Institute². The dimensions $a = 3.966 \text{ \AA}^*$, $b = 13.85 \text{ \AA}$, and $c = 3.696 \text{ \AA}$ of the orthorhombic unit cell are in good agreement with the figures previously reported by Bräkken³ and Wooster⁴. The structure of tungsten trioxide has been determined by Bräkken³ as well. He found it to be triclinic (pseudomonoclinic) and belonging to the space-group $C_2^1 - P \bar{1}$ with the unit cell dimensions $a = 7.28 \text{ \AA}$, $b = 7.48 \text{ \AA}$, $c = 3.82 \text{ \AA}$, $\alpha = \gamma = \frac{\pi}{2}$ and $\beta \sim \frac{\pi}{2}$. It has now been possible to evaluate powder photographs of this oxide heated in oxygen stream for 20 hours at 870°C . The following dimensions were obtained in good agreement with Bräkken's values:

$$\begin{aligned} a &= 7.29 \text{ \AA}^{**}, \quad b = 7.54 \text{ \AA}, \quad c = 3.85 \text{ \AA} \\ \alpha &= \gamma = 90^\circ, \quad \beta = 90^\circ 9'. \end{aligned}$$

Powder photographs of the preparations $\text{Mo}_{0.75}\text{W}_{0.25}\text{O}_3$ and $\text{Mo}_{0.4}\text{W}_{0.6}\text{O}_3$ do not show any displacements of the reflections of the trioxides in comparison with the positions of the lines in photographs of the pure trioxides. This is in agreement with Rieck's observations¹. However, due to the equality of the radii of the metal ions, limited solubilities might naturally cause very slight or even hardly detectable displacements of the lines. (Cf. for instance the small dimensional differences connected with a complete interchange of the two metals in $\text{MoO}_2\text{—WO}_2$ ⁵, and in molybdates and tungstates with the Scheelite structure⁶.) It is thus scarcely possible to confirm Rieck's thermal data from these powder photographs.

The intermediary phase, occurring in preparations $\text{Mo}_{0.6}\text{W}_{0.4}\text{O}_3$ and $\text{Mo}_{0.5}\text{W}_{0.5}\text{O}_3$,

forms a yellowish green powder. The powder photographs are rather complicated. No displacements of the lines are detectable in photographs of the preparations containing this phase together with either of the trioxides. The phase is decomposed at higher temperatures as is obvious from powder photographs of preparations heated at 850°C .

In a preparation $\text{Mo}_{0.5}\text{W}_{0.5}\text{O}_3$, heated at 700°C for 45 days, rather long and extremely thin, needle-shaped, green crystals occur. They are often somewhat bent and very fragile. They do not give reflections with hard X-rays so it was not possible to get Laue patterns or single crystal photographs with Mo- K radiation. Cu- K radiation, however, gave good photographs after long exposure. Rotation and Weissenberg photographs with this radiation were taken with rotation around the needle axis. The identity period parallel to this axis was found to be 3.99 \AA . The Weissenberg photographs, resembling those of β -tungsten oxide², show doublets or triplets of reflections lying rather close to points corresponding to a fairly simple reciprocal lattice. The Laue symmetry of the sublattice approximates $D_{4h} - 4/mmm$, while that of the real lattice is $C_{2h} - 2/m$. The a axis of the sublattice is about 5.35 \AA . It has not yet been possible to determine the corresponding dimensions of the real structure.

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* Referred to the wave length of Cr- $K\alpha$ = 2.2909 \AA . The dimensions given in ² are in fact expressed in kX units.

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