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# Topotactic Oxidation of Valentinite $Sb_2O_3$ to Cervantite $Sb_2O_4$: Kinetics and Mechanism

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It has been shown earlier by the authors (*Pramana* 3, 277 (1974)) that the oxidation of orthorhombic valentinite $Sb_2O_3$ to orthorhombic cervantite $Sb_2O_4$, as well as the reverse reduction, is a topotactic reaction, where the structure of valentinite is completely preserved in cervantite. Kinetic studies of the oxidation have now been done in a polycrystalline sample as well as in single crystals. The latter studies using hot-stage microscopy have enabled the rates of the reaction along different crystallographic directions to be determined. On the basis of structural and kinetic studies, a mechanism for the diffusion of oxygen atoms involving the making and breaking of bonds between (pentavalent) antimony and these oxygen atoms has been proposed. The results show that the oxidation of valentinite to cervantite is an interesting example of a solid–state reaction where the diffusion process for the oxidation is governed by structural considerations.

## Introduction

We have recently shown (*1*) that the oxidation of valentinite $Sb_2O_3$ to cervantite $Sb_2O_4$ as well as the reverse reduction process is a topotactic reaction. With the help of a "hybrid" crystal of the two oxides, the three-dimensional orientation relationships between the lattices and the close relationship between the structures were established. The crystallographic axes in the two orthorhombic crystals were observed to be individually parallel. It was shown that the oxidation involves very little change in the structure of valentinite, the additional oxygen atoms in cervantite merely occupying positions along the empty channels present in the former. Consequently, an understanding of the mechanism by which the oxygen atoms enter the lattice of valentinite acquires interest. Kinetic studies of the oxidation in a polycrystalline sample as well as in a single crystal have therefore been done and are reported in this paper.

## Kinetic Studies in a Polycrystalline Sample

### *Experimental*

The kinetic studies were done using valentinite crystallites of fairly uniform size, about 2 × 0.1 × 0.02 mm. They were prepared (*1*) from semiconductor purity $Sb_2O_3$ powder supplied by Koch–Light Laboratories. The principle of the method adopted was to measure the volume of oxygen taken up by a known weight of the sample at constant temperature and pressure. A diagram of the apparatus used for the study is shown in Fig. 1. The temperature of the reaction zone is maintained accurate to ±1°C using an electronic proportional temperature controller. The volume of oxygen taken up with time is measured using the gas burette (B). Six temperatures at intervals of 10°, between 470 and 520°C, were chosen for the kinetic studies. The oxygen pressure was, however,

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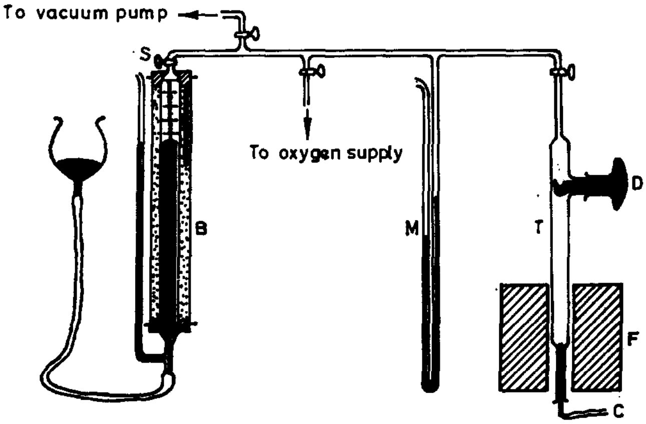

FIG. 1. Apparatus used for the kinetic study of the oxidation of $Sb_2O_3$ to $Sb_2O_4$. B, gas burette; M, manometer; T reaction tube; F, furnace; D, device for dropping specimen; and C, thermocouple.

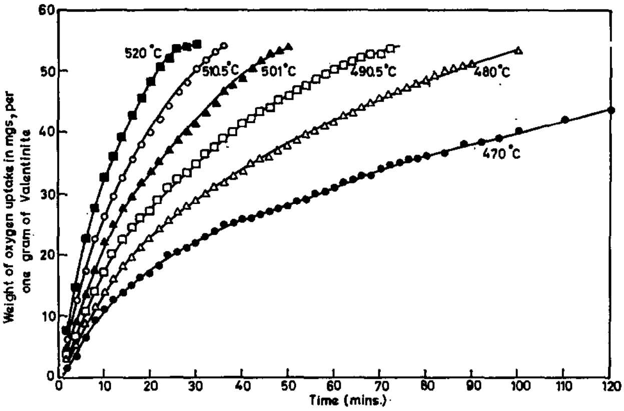

FIG. 2. Kinetic data for the oxidation of polycrystalline $Sb_2O_3$ to $Sb_2O_4$.

kept constant throughout at 140 mm/Hg, which is approximately the partial pressure of oxygen in air under laboratory conditions. The accuracy of the measurements is of the order of 0.1 %.

The results of the investigations are shown in Fig. 2, where the fraction of valentinite oxidized with time is plotted for different temperatures. An analysis of the data shows that the amount of oxidation is proportional to the square root of time. This is seen in Fig. 3. This suggests that the oxidation is diffusion controlled. Further evidence for this conclusion is obtained from kinetic studies on single crystals described below. Rate constants were obtained from Fig. 3 and were used to calculate the activation energy for the overall process using the Arrhenius equation. The straight line obtained in the Arrhenius plot (Fig. 4) has a slope corresponding to an activation energy of 41.6 kcal/mole.

## Kinetic Study in Single Crystals

This section reports a kinetic study on single crystals of valentinite using a hot-stage polarizing microscope. This was feasible because valentinite crystals are fairly transparent to light whereas cervantite crystals are opaque.

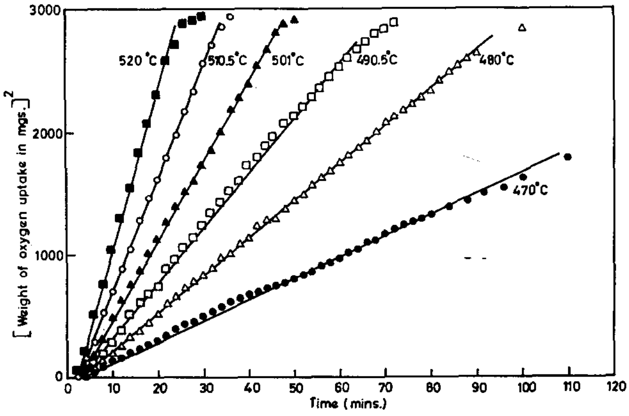

FIG. 3. Oxidation of polycrystalline $Sb_2O_3$ to $Sb_2O_4$. Plots of square of oxygen uptake versus time.

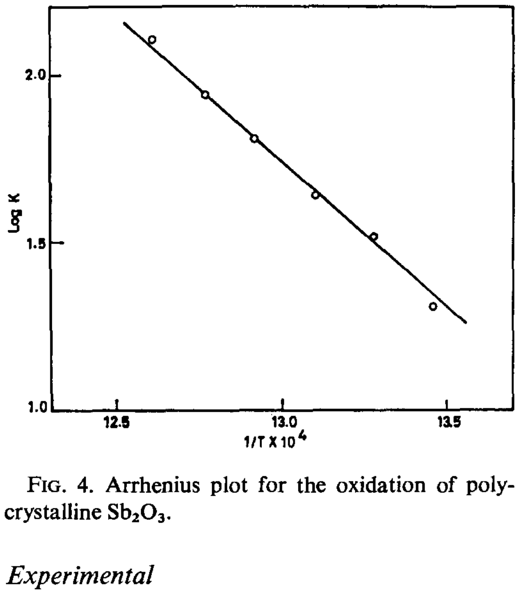

FIG. 4. Arrhenius plot for the oxidation of polycrystalline $Sb_2O_3$.

## Experimental

For this study, a hot-stage attachment to an ordinary microscope was fabricated. The hot stage is shown in Fig. 5, which is self explanatory. The overall dimensions of the hot stage are 1.5 in. in length and 2 in. in diameter.

The thermocouple of the hot stage was calibrated by observing through the microscope melting points of standard substances such as potassium dichromate (mp, 394°C) and barium nitrate (mp, 593°C). The temperature on the stage was maintained at the desired value accurate to ±2°C using a low-voltage high-amperage autotransformer coupled to a voltage stabilizer. This temperature control unit formed part of the Unicam high temperature X-ray powder camera.

Crystals of valentinite of fairly uniform size, about 4 × 0.5 × 0.05 mm, were employed in this study. These crystals, as reported earlier (*1*), were in the form of long thin plates, with the *c*-axis coinciding with the length of the plate (needle axis), *a* being perpendicular to the plate and *b* in the plane of the plate. A good single crystal was placed on the specimen stage on its (100) face, simultaneously noting the time, and it was observed through the microscope. It was found that the reaction starts at the surface of the crystal and proceeds inwards. This is seen as the movement of the boundary which is fairly sharp and straight, between the transparent and opaque regions. The movements of the boundary perpendicular to the *b*- and *c*-axes were measured at intervals of time using a calibrated micrometer eyepiece with an accuracy of 0.01 mm. The studies were done at 10° intervals of temperatures between 470 and 520°C. It should be stated here that high accuracy cannot be claimed for measurements perpendicular to the *b*-axis, in view of the very small movements involved in this direction. Since there is free access of air to the crystal, the pressure of oxygen over the crystal will be the partial pressure of oxygen in air, viz., approximately 140 mm/Hg under laboratory conditions.

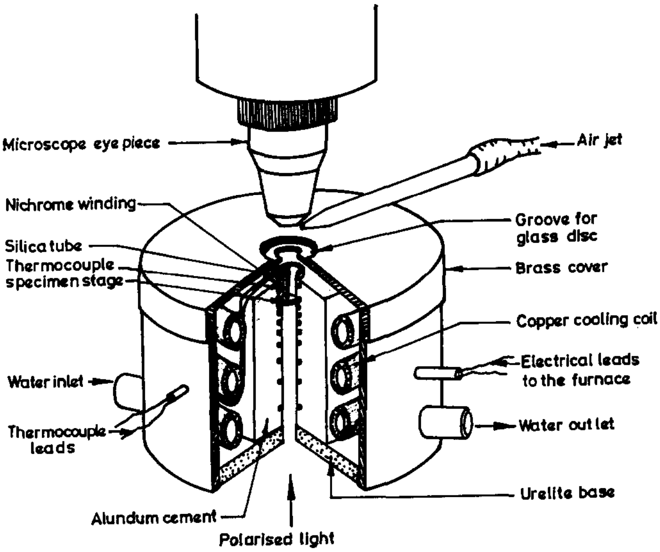

FIG. 5. Diagram of hot stage.

*Results*

It was found that the rate of the reaction was fastest along the needle axis (the common $c$-axis) and most of the reaction occurred this way. There was a small amount of reaction along the $b$-axis but practically none along the $a$-axis. The latter fact was indeed advantageous in following the kinetics because the crystals could be conveniently viewed only down the $a$-axis. Photographs of partly oxidized crystals have been taken after cooling to room temperature. One such photograph is shown in Fig. 6. The reaction front can be seen between the transparent and opaque regions.

The results obtained in these studies are shown in the form of graphs in Figs. 7 and 8, where the square of the thickness of the product layer has been plotted against time. These straight-line graphs can be explained in terms of a diffusion mechanism. As in the previous study, rate constants and activation energies for the oxidation along the two crystallographic directions have been determined. The two Arrhenius plots are shown in Fig. 9. The activation energies obtained are 55.5 and 36 kcal/mole along the $b$- and $c$-axes of valentinite, respectively.

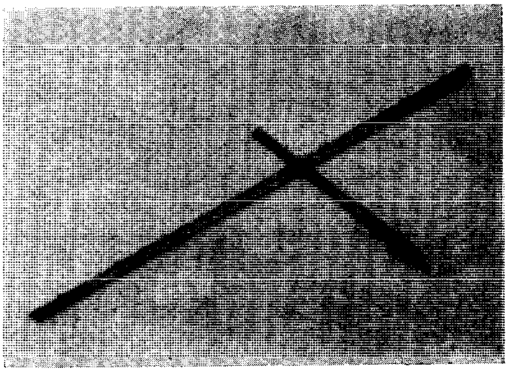

FIG. 6. Crystals of valentinate partly oxidized at 500°C. The reacted (dark) and the unreacted (transparent) regions can be seen. Magnification, ×20.

## Discussion

In attempting to postulate a mechanism for the oxidation of valentinite to cervantite the following points have to be taken into consideration.

(1) It has been clearly established from the two types of kinetic studies that the oxidation is a diffusion-controlled process.

(2) From the structural point of view, the reaction involves very little disturbance to

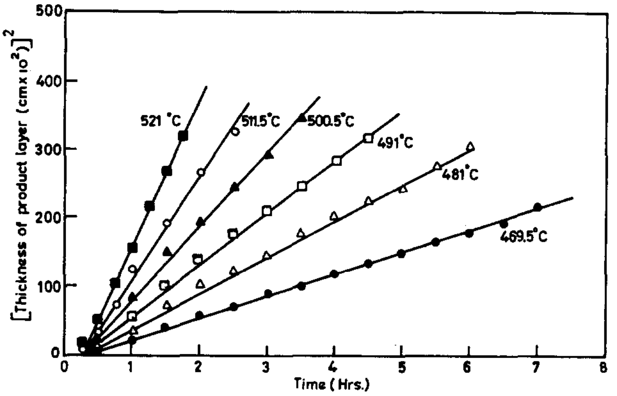

FIG. 7. Plots of square of product layer thickness against time for the oxidation along *c*-axis of $Sb_2O_3$.

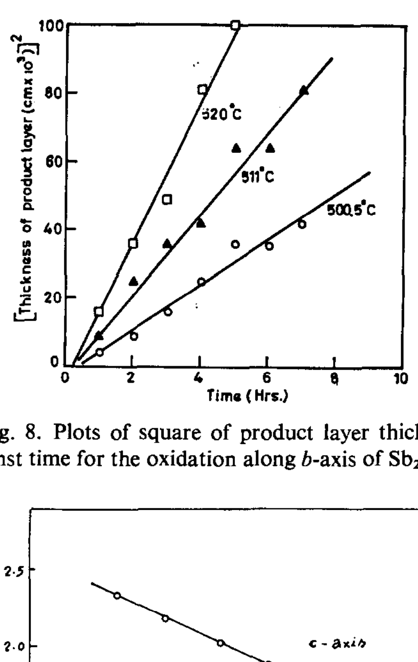

Fig. 8. Plots of square of product layer thickness against time for the oxidation along *b*-axis of $Sb_2O_3$.

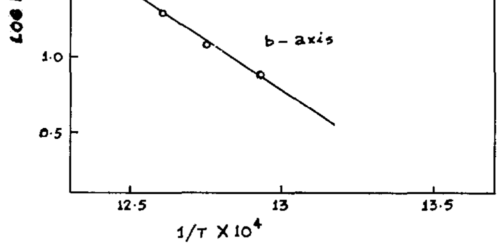

FIG. 9. Arrhenius plots for the oxidation along the *b*- and *c*-axes.

the valentinite structure. We have shown (*1*) that the additional oxygen atoms in cervantite occupy positions along the empty channels available in the structure of valentinite and bridge the $(Sb_2O_3)_\infty$ chains in the direction *a* perpendicular to the length of the channels. Because of this fact, any diffusion mechanism involving a breakup of the valentinite lattice is untenable. For the same reason, movement of the antimony atoms toward the cervantite–oxygen interface also must be ruled out.

(3) Assuming covalent radii of 1.41 and 0.74 Å for antimony and oxygen, respectively (*2*), one finds that the channels present in the valentinite structure have an approximate diameter of only 1.5 Å. Hence, molecular diffusion of oxygen through the structure cannot be expected. Further, the fact that strongly directional bonds are formed by the diffusing oxygens with the antimony atoms in the product cervantite also precludes this possibility.

(4) The observation (*1*) that the reduction of cervantite to valentinite in a hydrogen atmosphere takes place topotactically has an important bearing on the mechanism. This implies that the oxygen atoms in cervantite are removed from the same sites, such as O(11) and O(12), (Fig. 1, *1*) which they occupied during the oxidation. The removal of oxygen atoms from any other atomic positions during the reduction would have left the product polycrystalline. Therefore, it may be concluded that only the bonds

between antimony and these oxygens are broken during the reduction process.

In the light of the above arguments, it appears that the breakage of these same bonds between oxygens O(11), O(12), etc., and antimony atoms Sb(1), Sb(3), etc., is energetically favored during the oxidation as well. Therefore, a jumping of oxygen atoms, occupying positions such as O(11) and O(12), from site to site by the making and breaking of bonds between these oxygens and the antimony atoms could constitute the diffusion process for the oxidation. This not only accounts satisfactorily for the points made earlier, but also explains the faster rate of oxidation along the needle (*c*) axis of valentinite crystal, i.e., in the direction of the channels. The mechanism of diffusion along the *b*-axis, however, may be different.

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## References

1. P. S. Gopalakrishnan and H. Manohar, *Pramana* 3, 277 (1974).
2. L. Pauling, "Nature of the Chemical Bond," 3rd ed., Cornell Univ. Press, Ithaca, N.Y. (1960).