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Kinetics and Mechanism of the Transformation in Antimony Trioxide from Orthorhombic Valentinite to Cubic Senarmontite

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The kinetics of the polymorphic transformation in antimony trioxide from metastable orthorhombic valentinite to cubic senarmontite has been studied in polycrystalline material between 490 and 530°C. Quantitative analysis of the mixtures was done using infrared spectrophotometry. The kinetic data was analyzed and the activation energy for the process was obtained: (i) On the basis of Avrami's equation, which is derived on the basis of a nucleation and growth mechanism; and (ii) from the time required for a constant fraction of the transformation to take place. The values obtained were 50.8 and 46.0 kcal/mole. Observations have also been made on partly transformed single crystals of valentinite using a polarizing microscope. The latter studies and the value of the activation energy suggest that a better understanding of the transformation could be obtained on the basis of a vapor phase mechanism.

Introduction

Antimony trioxide, Sb_2O_3, exists in two crystalline modifications. The cubic form, senarmontite, is stable up to 570°C, while the orthorhombic form, valentinite, is stable between 570°C and its melting point, 650°C (*1*). However, valentinite can exist as a metastable phase even at room temperature.

The crystal structures of the two polymorphs are known. In senarmontite (*2*) the structure consists of molecular Sb_4O_6 groups, while in valentinite (*3*) it is made up of infinitely long chains of Sb_4O_6 groups. In both structures, each antimony atom is bonded to three oxygen atoms and each oxygen is bonded to two antimony atoms. Weak Sb–O bonds hold the groups or chains, as the case may be, together in the crystal. It may be added that the structure of antimony trioxide in the vapor phase below 1000°C has been shown (*4*, *5*) from electron diffraction studies to be that of senarmontite. Structurally, the transformation involves the destruction of one molecular type and formation of another. Buerger (*3*) classifies this as a reconstructive transformation of secondary coordination that is expected to require considerable activation energy. Apart from this suggestion, no other information on the mechanism of the transformation is available. The present studies are directed toward throwing more light on this aspect of the problem. The studies include detailed kinetics of the transformation of metastable valentinite to senarmontite in a polycrystalline sample and microscopic studies in partly transformed single crystals of valentinite.

Experimental

Materials Used

Antimony trioxide of semiconductor grade purity (supplied by Koch-Light Laboratories Ltd.) was used in these studies. X-ray powder patterns and infrared spectra showed that the oxide supplied was pure valentinite and

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therefore it was used as such. The valentinite powder used for the kinetic studies was of particle sizes between −300 and +350 mesh. Its surface area as measured by the B.E.T. method was 1.1 m^2/g. Senarmontite was also needed to draw the calibration curve used in the quantitative analysis of the two polymorphs (*vide infra*). This was prepared by subliming valentinite at 520°C in an atmosphere of nitrogen and condensing the vapor at room temperature. That the condensate was pure senarmontite was confirmed by X-ray and ir methods.

The valentinite crystals used for the microscopic studies were prepared by heating Sb_2O_3 powder in platinum-lined evacuated and sealed silica tubes at 640°C in a tubular furnace for about 10 hr. This heat treatment yielded a cluster of colorless long platy crystals of dimensions of the order $4 \times 0.5 \times 0.1$ mm.

Kinetic Studies

A nichrome wire-wound tubular furnace, 2 in. in diameter and placed vertically, was used for the kinetic studies. The thermal stability of the furnace was increased by placing an alloy steel cylindrical block in the uniform temperature zone. Holes 8 mm in diameter were drilled into the steel block extending to its center. The holes were to be used to place the silica tubes, which were closed at one end and into which capsules containing the specimen could be dropped. A chromel–alumel thermocouple was accommodated in the central hole of the block. Temperature was determined by measuring the potential developed at the thermocouple junction using a Tinsley potentiometer. The temperature of the furnace was maintained constant to an accuracy better than ±1°C using an electronic proportional controller supplied by the National Aeronautical Laboratory, Bangalore.

For the kinetic studies 15 mg of valentinite were loosely packed into a capsule made of platinum foil. This capsule was placed inside a snugly fitting pyrex glass tube closed at one end. The tube was evacuated to a pressure of 0.1 mm and sealed to get a capsule about 2 cm in length and 4 mm in diameter. Blank experiments showed that no detectable transformation of Sb_2O_3 occurred during the sealing. The experiment was started by dropping these capsules into the silica tubes placed in the furnace, the temperature of which was maintained at the desired value. After predetermined time intervals the silica tubes were withdrawn from the furnace and quenched in water at room temperature. The capsules were then broken open, all the material was taken out and powdered, and then it was analyzed for the two modifications. Preliminary experiments showed that powdering the heat-treated samples for 5 min in an agate mortar does not cause any transformation. Note that the transformation of senarmontite to valentinite has been found to take place by grinding in a mechanical mortar for several hours (*6*).

Senarmontite and valentinite exhibit characteristic infrared absorption peaks at 745 and 690 cm^{-1}, respectively (*7*, *8*). Therefore the ir technique could be employed conveniently for the analysis of the mixture. A calibration curve was prepared by plotting the ratio of the absorbance of senarmontite at 745 cm^{-1} to that of valentinite at 690 cm^{-1} against the percentage (by weight) of valentinite. For drawing the curve, standard mixtures of senarmontite and valentinite were prepared in steps of 10% senarmontite covering the range 10–90% of senarmontite by weight. The infrared spectra of these mixtures as well as those of pure valentinite and senarmontite were recorded in the range 600–1000 cm^{-1} using a Carl Zeiss U.R.-10 double-beam infrared spectrophotometer. All the spectra were taken using KBr pellets. The composition of the unknown mixture could be read off from the calibration curve by determining the absorbances of the mixture at 690 and 745 cm^{-1}, respectively. The accuracy obtained by this technique was better than 5%.

Microscopic Studies

These studies involved the observation under a polarizing microscope of single crystals of valentinite that had been heated at 520°C for different lengths of time (up to about 10 hr) and cooled to room temperature. The crystals had been heated in platinum containers placed inside evacuated and sealed pyrex capsules using the furnace assembly described earlier. Note that different crystals were used for the heat treatment for different lengths of time. It was not possible to use the same crystal for all the observations due to the difficulties involved in handling them.

Results

Preliminary results on the transformation showed that below 490°C the rate was extremely slow, while above 530°C the results obtained were not consistent and indicated a reduction in the reaction rate. Therefore, the kinetic studies were confined to the temperature range between 490 and 530°C at intervals of about 10°C.

The fraction of valentinite transformed at different temperatures for different intervals of time is shown graphically in Fig. 1. The plots are characterized by a long induction period and an acceleratory period followed by a deceleratory period. Such a sigmoidal shape of the curves suggests that the transformation takes place by a nucleation and growth process. Avrami's equation (*9–11*), which has been successful in explaining the kinetics of many polymorphic transformations (*12*, *13*) and which makes use of this model, was therefore employed for analyzing the kinetic data. The Avrami equation

$$\alpha = 1 - \exp(-Kt^n)$$

where α is the fraction transformed in time t, n is a constant that depends on the nucleation rate and the nature of the growth, and K is the rate constant, was fairly satisfactory in explaining the data with a value of 2.6 for n. (2.6 is the average value of the slopes of the straight line graphs obtained by plotting log $\log[1/(1-\alpha)]$ against log t. These plots are shown in Fig. 2). The graphs obtained by plotting $[-\log(1-\alpha)]^{1/2.6}$ against t were fairly linear, as seen in Fig. 3, and were used for evaluating the rate constants. The Arrhenius plot, Fig. 4, shows the dependence of the rate constants on temperature and this has a slope corresponding to an activation energy of 50.8 kcal/mole. However, the Avrami model was not pursued further since direct observations on single crystals made later suggested that a different model was more suitable for explaining the transformation.

The activation energy could be obtained, at least approximately, without assuming any specific model, from the time required for a

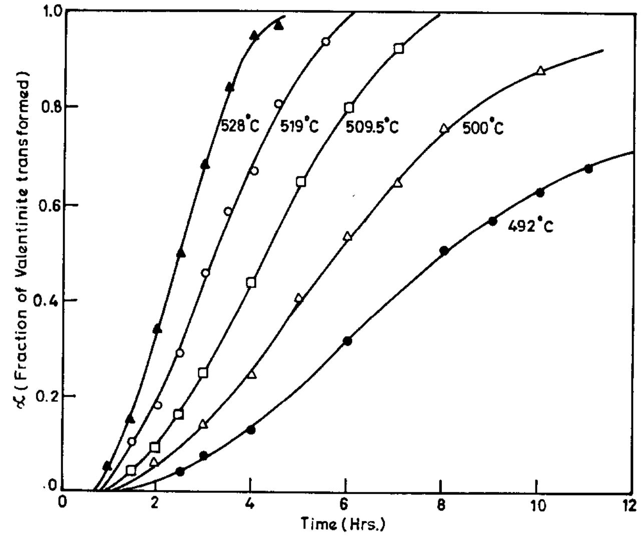

FIG. 1. Plots of fraction of valentinite transformed versus time.

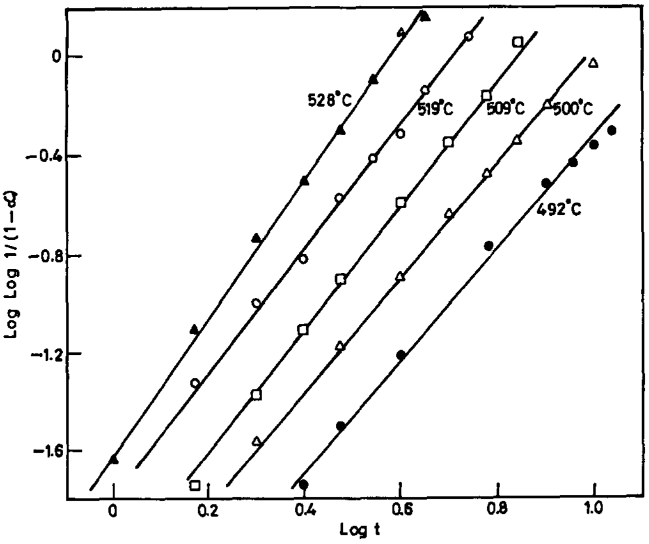

FIG. 2. Plots of log log $[1/(1-\alpha)]$ versus log t.

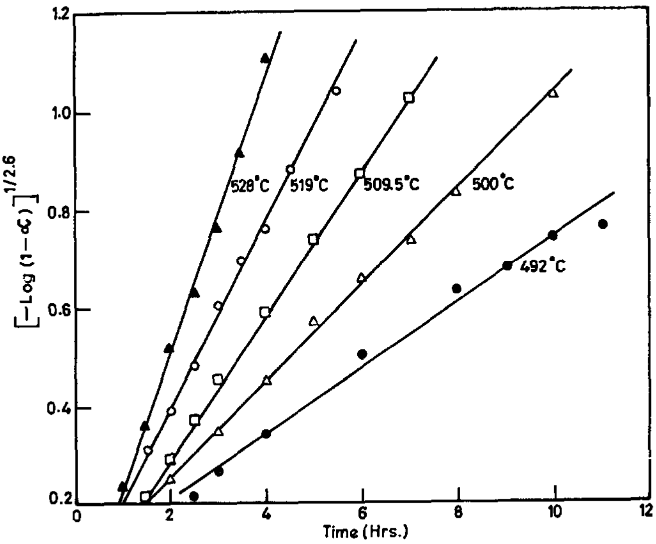

FIG. 3. Plots of $[-\log(1-\alpha)]^{1/2.6}$ versus t.

constant fraction of the transformation to take place. This method has also been employed in the present case, the time required for 50% transformation excluding the induction period being used for the calculation. Fig. 5 shows the Arrhenius plot where the reciprocal of the time required for 50% transformation has been plotted against reciprocal temperature. This gives a slope corresponding to an activation energy of 46 kcal/mole, in reasonably good agreement with the earlier figure.

A significant observation made at this stage was that the value of activation energy obtained for the overall process was close to the value of the heat of sublimation of valentinite, which is 43.6 kcal/mole (*14*, *15*). This seems to suggest that if the reaction

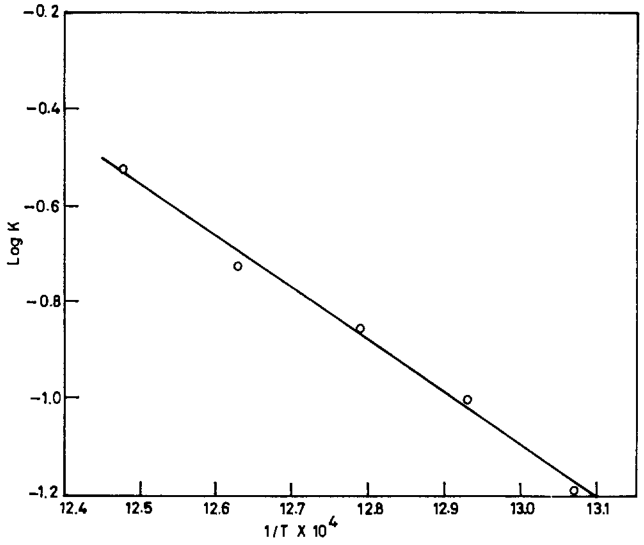

FIG. 4. Arrhenius plot of log K versus $1/T$.

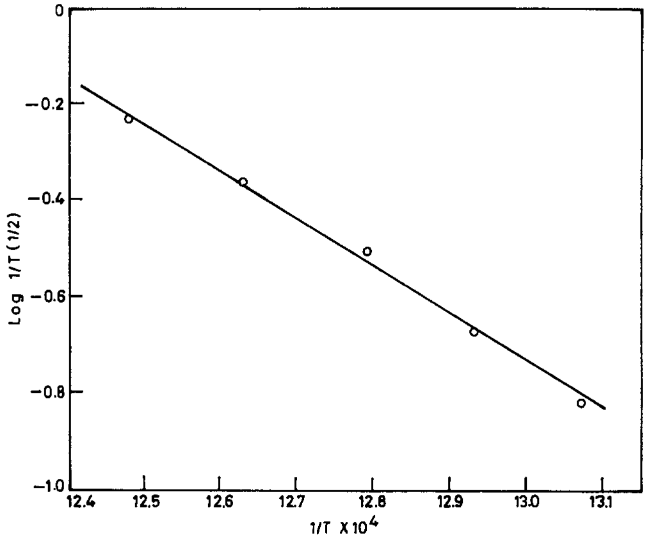

FIG. 5. Arrhenius plot making use of the time for 50% transformation.

were taking place by a true solid state nucleation and growth process, the interface between the senarmontite nuclei and the valentinite matrix would be highly disordered and, in the words of Tompkins (*16*), have a "psuedo-gaseous structure." One could go further and even visualize a true vapor phase between the two polymorphs in the process of transformation. In fact, Buerger has suggested (*17*) that "if the material undergoing transformation has a substantial vapor pressure, the metastable phase could distil into the more stable form." Such a process appeared likely in the present case since the two modifications of Sb_2O_3 have a fairly high vapor pressure at the temperatures of the experiment (*14*, *15*).

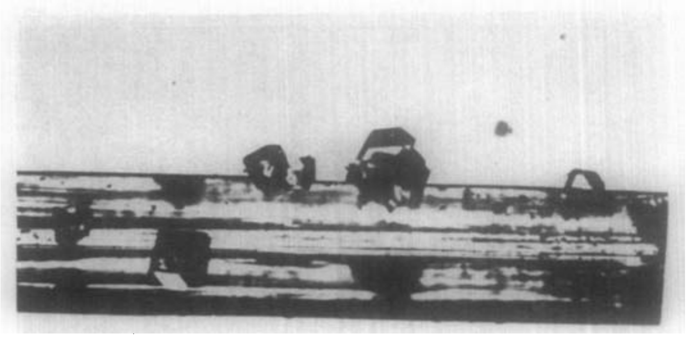

FIG. 6. Photomicrograph of a partly transformed crystal of valentinite. Note the octahedral crystals of senarmontite growing on the surface of the needle-shaped crystal of valentinite. (×40).

The metastable valentinite, of course, has a higher vapor pressure than senarmontite. The microscopic studies reported above (see Experimental) were done to verify this possibility and, as indicated later, appear to confirm it.

The first observation made from the microscopic study was that it takes more time for the first formation of the stable phase in single crystals than in polycrystalline material. For example, at 520°C the formation of senarmontite could be observed only after a time interval of 5 hr. The second, and more important, observation was that the senarmontite phase always appears on the surface of the needle-shaped valentinite crystal in the form of small pyramids which then grow outward at the expense of the latter into the familiar octahedral shapes. A photograph of a transforming crystal of valentinite is shown in Fig. 6. In addition to visual observation, confirmation that the product was indeed senarmontite was obtained from X ray diffraction patterns.

Discussion

The formation of the stable phase senarmontite, in the manner described, on the surface of the metastable phase valentinite, suggests that the nucleation is heterogeneous and takes place by condensation of vapor molecules. The growth of the senarmontite crystals outward from the surface is difficult to explain in terms of propagation of the transformation by reaction at the interface between the two phases. It can only be understood either in terms of direct impingement of molecules from the vapor on to the nuclei or by surface diffusion of adsorbed molecules to the growth centers. From the numerous studies done on the growth of crystals from the vapor (*18–20*), it has been established that surface diffusion, because of the low activation energy needed, plays a predominant role in the growth. Thus, it appears that the probable mechanism of the transformation involves the following steps: (i) vaporization of valentinite, (ii) nucleation of senarmontite on some suitable sites on the surface by condensation of vapor, (iii) growth of these nuclei by surface diffusion of the adsorbed molecules to the growth centers, and (iv) completion of the transformation when the vapor pressure becomes equal to the equilibrium vapor pressure of senarmontite. However, it has not been possible to derive a kinetic equation for this model of the transformation and explain the kinetic data using such an equation. The authors are also not aware of any transformation where such a mechanism has been experimentally observed.

On the basis of the mechanism suggested, the two important steps in the transformation are the evaporation of valentinite and condensation of senarmontite. It has been pointed out earlier that the structure of antimony trioxide in the vapor phase is that of senarmontite. Therefore, it appears that the rate-controlling step in the transformation is the vaporization of valentinite, which readily accounts for the experimental observation that the activation energy for the process has a value close to the heat of sublimation of valentinite.

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