

## High-pressure polymorphism of $\text{As}_2\text{O}_3$ and $\text{Sb}_2\text{O}_3$

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*Dedicated to Prof. Dr. G. Menzer on the occasion of his 70th birthday*

(Received April 17, 1967)

### Auszug

Die polymorphen Umwandlungen von  $\text{Sb}_2\text{O}_3$  und  $\text{As}_2\text{O}_3$  wurden hydrothermal und bei hohen Drucken untersucht. Die Umwandlung Senarmontit  $\rightleftharpoons$  Valentinit des  $\text{Sb}_2\text{O}_3$  tritt im hydrothermalen Gebiet bei der Temperatur von  $606^\circ\text{C}$  ein; die  $\text{As}_2\text{O}_3$ -Reaktion Arsenolith  $\rightleftharpoons$  Claudetit erwies sich als reversibel bei einer Umwandlungstemperatur von  $110^\circ\text{C}$ ; beide Umwandlungen erfolgen bei 1 atm.

### Abstract

The polymorphic transitions in  $\text{Sb}_2\text{O}_3$  and  $\text{As}_2\text{O}_3$  have been examined, utilizing hydrothermal and opposed-anvil high-pressure techniques. The  $\text{Sb}_2\text{O}_3$  senarmontite  $\rightleftharpoons$  valentinite reaction occurs in the hydrothermal range with a transition temperature of  $606^\circ\text{C}$ ; the  $\text{As}_2\text{O}_3$  arsenolite  $\rightleftharpoons$  claudetite reaction has been shown to be reversible with a transition temperature of  $110^\circ\text{C}$ ; both at 1 atm.

### Introduction

Arsenic and antimony oxides are known to exist in two polymorphic forms: a cubic molecular structure of  $\text{As}_4\text{O}_6$  (arsenolite) or  $\text{Sb}_4\text{O}_6$  (senarmontite) molecules, and a structure stable at higher temperatures. The high-temperature form is monoclinic in the claudetite form of  $\text{As}_2\text{O}_3$  and orthorhombic in the valentinite form of  $\text{Sb}_2\text{O}_3$  (BECKER, PLETH and STRANSKI, 1962). Although the structures of these compounds are fairly well settled, there is little agreement concerning the transition temperature between the low and high temperature forms. The transition in  $\text{Sb}_2\text{O}_3$  occurs at about  $575^\circ\text{C}$  at one atmosphere according to ROBERTS and FENWICK (1928); the transition

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temperature of arsenolite to claudetite in  $\text{As}_2\text{O}_3$  is highly uncertain, and BECKER, PLIETH and STRANSKI (1962) have reported values ranging from  $-35^\circ\text{C}$  to  $233^\circ\text{C}$ . The reverse reaction of claudetite to arsenolite has not been observed and this system is said by some to be monotropic.

Indeed the  $\text{As}_2\text{O}_3$  polymorphism has its greatest interest in the fact that it is said to violate two of the classical "rules" of polymorphic behavior. Namely:

- (i) The crystals cannot be superheated above the transition temperature.
- (ii) In accordance with the Ostwald step rule, the high-temperature polymorph should have the highest nucleation frequency.

This paper describes a series of experiments in which both the  $\text{As}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_3$  transitions have been observed under controlled conditions in a reversible manner. Application of displacive shear or use of a mineralizer at high pressures is sufficient to provide activation energy for bond breakage and brings these reactions into the normal behavior of polymorphic transitions.

### Experimental

All polymorphic reactions were conducted by the quench method in which specified starting materials were held at the desired pressure and temperature for a run of usually 24 hours followed by a rapid temperature quench. Reagent grade  $\text{As}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_3$  were used as starting materials on all runs, including a pure arsenolite, a pure senarmontite, a mixture of senarmontite and valentinite and a synthetic claudetite prepared by reacting arsenolite in large anvils on a 100-ton uniaxial high-pressure unit.

The data on the atmospheric-pressure transition between senarmontite and valentinite were obtained using dry starting materials in welded gold capsules. A pure-valentinite starting material was obtained by reacting reagent grade  $\text{Sb}_2\text{O}_3$  hydrothermally at  $600^\circ\text{C}$  and 700 bars water pressure.

Most of the data on the senarmontite-valentinite equilibrium curve were obtained from hydrothermal runs in welded gold capsules. The hydrothermal high-pressure apparatus and techniques are well established and need not be discussed further (ROY and OSBORN, 1952).

The high-pressure runs on  $\text{As}_2\text{O}_3$  were conducted in a uniaxial-type high-pressure apparatus described by DACHILLE and ROY (1962). Such devices utilize the force developed on two opposed anvils driven

by a hydraulic ram. The sample was contained as a wafer pressed into a nickel ring and sandwiched between platinum-20% rhodium discs between the anvils. The devices used in this work had 20 ton rams and were capable of achieving pressures up to 60 kilobars on 0.25 inch-diameter single-stage anvils at temperatures up to 500°C. The calibration of these devices has been discussed by MYERS, DACHILLE and ROY (1963).

DACHILLE and ROY (1960) have also described the modification of the opposed-anvil apparatus which permits the application of shearing stress to the specimen under controlled  $P$ - $T$  conditions. The lower-anvil thrust bar is attached by a long lever to a motor-driven eccentric so that the lower anvil oscillates through an angle of 2° (or less if desired) at two revolutions per minute, thus shearing the sample against the upper anvil. Very slow shearing rates are used to prevent undue temperature rise. In the experiments described here, the platinum discs and nickel retaining rings used in the static anvil runs were omitted. At the pressures used, the anvils were not deformed and generally the sample was well-contained.

Identifications of the products of all runs were by x-ray powder diffraction and binocular microscope. Reliable powder-diffraction data for the four oxides under consideration are available in the National Bureau of Standards Publications (SWANSON *et al.*, 1953).

#### The senarmontite-valentinite reaction

Data for the results of 25 hydrothermal experiments are given in Fig. 1. In general, the products of a given run are quite conclusive. In a 24 hour period either a senarmontite or a valentinite starting material in the presence of a mineralizer reacted completely to the phase stable under the given  $P$ - $T$  conditions. Reactions conducted on dry starting materials were sluggish but lead to the same conclusions as the mineralizer-containing runs. The reaction products were usually well crystallized; senarmontite frequently appearing as clear octahedrons about one millimeter in diameter, while valentinite had a prismatic habit yielding prisms one to three millimeters in length.

A  $P$ - $T$  univariant curve for the senarmontite  $\rightleftharpoons$  valentinite phase reaction has been fitted to the data in Fig. 1. The slope of this curve is negative indicating the high-temperature phase is also the high-density phase, an observation which is validated by a comparison of the theoretical densities. A second observation is that the univariant

line exhibits a change in slope at pressures between 0.5–1.5 kilobars. This sort of feature is highly unusual on a solid-solid reaction between simple oxides, and indeed, of the S–S univariant curves so far determined (ROY and WHITE, 1964), no such feature has been observed. The curvature could arise either from a change in enthalpy of reaction with pressure, or from a pronounced change in molar volume of one

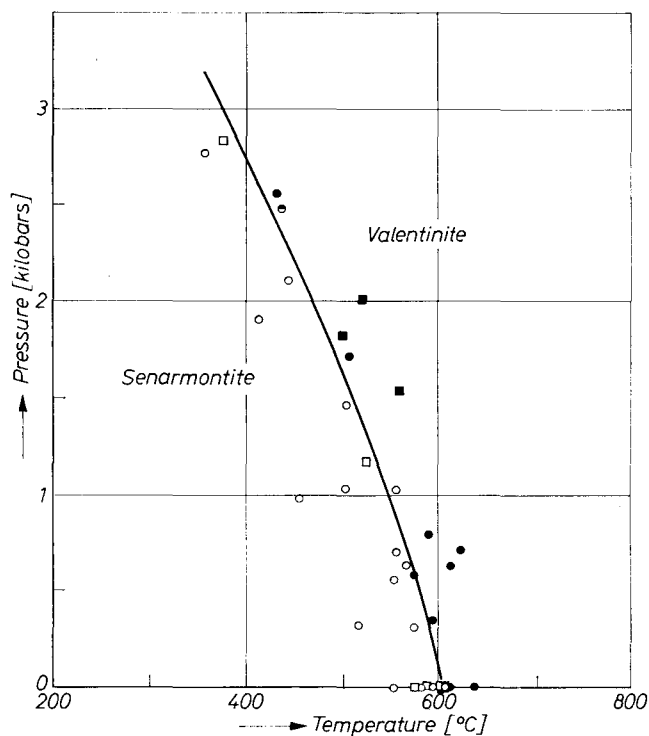


Fig. 1. Univariant curve for  $\text{senarmontite} \rightleftharpoons \text{valentinite}$  transition. ○ Starting material: mixed senarmontite and valentinite; Product: senarmonite. ● Starting material: mixed senarmontite and valentinite; Product: valentinite. □ Starting material: senarmontite; Product: senarmonite. ■ Starting material: senarmontite; Product: valentinite

of the reactants. Since senarmontite has a loosely packed molecular structure it does not seem unlikely that an expected change in compressibility of senarmontite above 0.5 kbar is responsible.

The intersection of the univariant curve with the temperature axis was determined by a series of runs made at atmospheric pressure using dry starting materials in sealed gold tubes. The results of these

Table 1  
*Results of atmospheric-pressure experiments on senarmontite $\rightleftharpoons$ valentinite transition*

Temperature of run	Starting material	
	Senarmontite	Valentinite
577°		100% senarmontite
587°		80% sen., 20% val.
597°	100% senarmontite	
600°		5% sen., 95% val.
606°	100% senarmontite	
607°		100% valentinite
611°	90% sen., 10% val.	
617°	60% sen., 40% val.	

runs are shown in Table 1. Senarmontite does not invert at all below 606°C. Above this temperature, laths of valentinite appear in the product in varying proportions, although temperatures of 640°C are necessary to drive the inversion to completion in 24 hours. Valentinite transforms to clear octahedrons of senarmontite below 606°C, but also recrystallizes into much larger laths of valentinite. Above 606°C valentinite merely recrystallizes and no senarmontite appears. The transition temperature of 606°C is higher than the 573°C value of ROBERTS and FENWICK but fits reasonably well with the extrapolation of our univariant curve.

One can calculate the heat of transition from the univariant curve using the Clapeyron relation if the volume change is known. The low-pressure part of the curve in Fig. 1 has a slope of  $-0.022$  kbar/°C. The molar volumes calculated from the x-ray theoretical densities are  $52.216$  cm<sup>3</sup> for senarmontite, and  $50.021$  cm<sup>3</sup> for valentinite.  $\Delta V$  is  $-2.195$  cm<sup>3</sup>. Using the above slope and a transition temperature of 606°C,  $\Delta H_R$  is calculated to be 1000 cal/mole, which may be compared with the value of 1800 cal/mole obtained by ROBERTS and FENWICK, or the value of 1390 cal/mole reported by COUGHLIN (1954).

#### The arsenolite-claudetite reaction

The results of 30 selected opposed-anvil runs of various kinds are given in Fig. 2. A best-fit univariant curve separating the stability fields of arsenolite and claudetite has been drawn.

The interpretation of these data is complex and may be summarized as follows:

- (i) Arsenolite when reacted statically (i.e. without application of displacive shearing) with a water mineralizer in the claudetite

field will invert to well-crystallized claudetite. Only 10% conversion is obtained at temperatures just above the transition temperature, but the amount of reaction increases as the temperature is increased, and complete conversion is obtained in

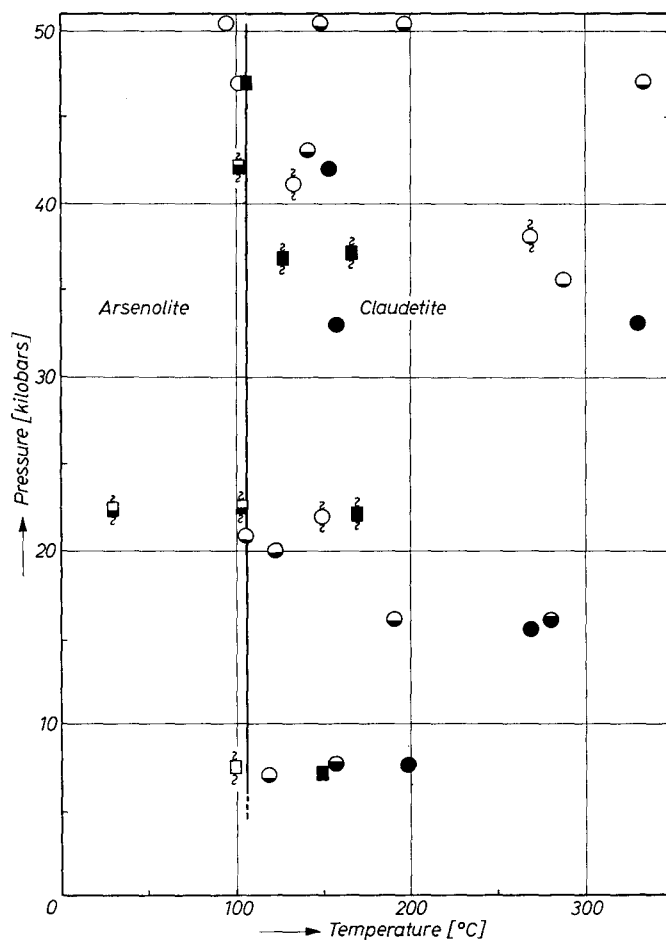


Fig. 2. Unvariant curve for arsenolite  $\rightleftharpoons$  claudetite transition.  $\circ$  Starting material: arsenolite; Product: arsenolite.  $\bullet$  Starting material: arsenolite; Product: claudetite.  $\square$  Starting material: claudetite; Product: arsenolite.  $\blacksquare$  Starting material: claudetite; Product: claudetite.  $\odot$  Runs in which shear was utilized

24 hours at temperatures  $200^\circ\text{C}$  above the transition temperature. The reaction will also proceed without the mineralizer but the rates are still more sluggish.

- (ii) Arsenolite, when heated in the arsenolite stability field, remains arsenolite regardless of presence of mineralizers or length of time of run.
- (iii) Claudetite, when reacted statically, remains claudetite regardless of the stability field in which the run is made. Thus the same irreversibility noted at atmospheric pressure is also observed in the high pressure static runs.
- (iv) Claudetite, when reacted in the shearing-anvil apparatus, transforms to arsenolite in the arsenolite field, but remains claudetite in the claudetite field. Although the x-ray peaks are broadened, the arsenolite powder pattern is easily recognized, and up to 100% transformation has been obtained in 24 hours.
- (v) A peculiar and unexplained result is that, when an arsenolite starting material is reacted in the shearing-anvil apparatus in the claudetite stability field, no inversion is observed.

The univariant curve in Fig. 2 is located between the lowest-temperature static runs which transform arsenolite to claudetite, and the highest-temperature shearing runs which transform claudetite to arsenolite.

One possible general criticism of the shearing-anvil apparatus is that it operates by local heating rather than by mechanical bond breakage. These experiments provide an answer to the criticism. The arsenolite  $\rightleftharpoons$  claudetite transition is almost independent of pressure. If local heating played any important role, one would expect the univariant curve determined in the shearing experiments to be displaced to lower temperatures from the one determined in the static experiments, since the actual sample temperature would be the sum of the measured anvil temperature and the temperature rise from local heating. No such displacement is observed, and we conclude that local heating due to shear cannot amount to more than 10°C.

The univariant curve of Fig. 2, when extrapolated to atmospheric pressure, yields a transition temperature of  $110 \pm 10^\circ\text{C}$ . Of the various transition temperatures proposed in the literature, this agrees best with the value of WELCH and DUSCHAK (1915) [ $100^\circ\text{C}$ ].

An analysis of Fig. 2 by the Clapeyron equation is not very rewarding. As in the case of the antimony oxides, the high-temperature form of  $\text{As}_2\text{O}_3$  is also the high-density form.  $\Delta V$  is thus a negative  $3.92 \text{ cm}^3/\text{mole}$  based on the x-ray densities, and the slope of the univariant curve is required to also be negative. The experimental slope is very

steep and has been drawn as a vertical line. Such a steep slope implies either a very high value of the transition enthalpy, or a vanishingly small value of the change in volume. The volume change is known from the x-ray measurements, and is quite finite. Slopes calculated from any of the transition enthalpies given in the literature, which range from 600 to 8000 cal/mole, have values ranging from 0.017 to 0.23 kbar/ $^{\circ}\text{C}$ . These are all much smaller than the near-vertical slope obtained (slope greater than 5 kbar/ $^{\circ}\text{C}$ ). No explanation of this peculiar behaviour is offered here.

### Summary

The polymorphic transitions in  $\text{Sb}_2\text{O}_3$  and  $\text{As}_2\text{O}_3$  have been examined, using hydrothermal and opposed-anvil high-pressure experiments.

The  $\text{Sb}_2\text{O}_3$  senarmontite  $\rightleftharpoons$  valentinite transition has been observed reversibly over the range of 0 to 3 kilobars, and from 300 to 600  $^{\circ}\text{C}$ . The transition temperature at one atmosphere is  $606 \pm 5^{\circ}\text{C}$ , with a heat of reaction of 1000 cal/mole.

The  $\text{As}_2\text{O}_3$  arsenolite  $\rightleftharpoons$  claudetite transition has been reversed for the first time, utilizing a shearing-anvil technique. This transition may now be regarded as reversible. The transition temperature at one atmosphere is  $110 \pm 10^{\circ}\text{C}$ . Grave problems remain in attempting to apply the Clapeyron equation to this transition.

### Acknowledgment

This work was supported by the Office of Naval Research, Ceramics and Metallurgy Branch.

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