

culated values that was made by Gelles and Pitzer¹ is unaffected.

The anharmonicity calculations are considered to be only approximations. Until more specific heat data and/or anharmonicity constants are experimentally determined, further significant refinements of anharmonicity contributions seem impossible.

We would like to thank Professor J. R. Nielsen of the University of Oklahoma, Dr. D. W. Scott of the Bureau of Mines, Professor W. H. Stockmayer of Massachusetts Institute of Technology and Dr. J. F. Masi of the Callery Chemical Company for advice and suggestions.

SCHOOL OF CHEMICAL ENGINEERING
DEPARTMENT OF CHEMISTRY
UNIV. OF OKLAHOMA
NORMAN, OKLA.

The Coefficient of Linear Thermal Expansion of Tridymite

By J. B. AUSTIN

RECEIVED JUNE 9, 1954

The occurrence of two "high-low" inversions in tridymite is well-established and the inversion temperatures have generally been accepted as close to 117 and 163°, respectively,¹ although there have been occasional suggestions that these temperatures may vary significantly.

Mosesman and Pitzer,² however, have reported heat content data which indicate the possible existence of a third transition at 223°. Since this transition had not been described previously, and since they were unable to explain it on the basis of possible impurities present in their sample or to interpret it in terms of present knowledge of the crystalline structure of tridymite, they suggested that final acceptance should await further verification. As such transitions are usually accompanied by a change in volume, measurements of thermal expansion offer a possible means of confirmation. Accordingly, a number of measurements of linear expansion, made some years ago during a study of the behavior of silica refractories, have been re-examined for indications of this third transition.

Samples.—Three different samples of silica were examined. Two were purified tridymite, one being the same material used by Mosesman and Pitzer. The third was a silica coke-oven liner which, after long service, had been converted almost entirely to tridymite.

The raw material for the purified tridymite was, in each case, a very pure sample of vein quartz from Lake Toxaway, North Carolina. This material was ground to pass a 60-mesh sieve, was repeatedly washed with hydrochloric acid, and then dried. Analysis with hydrofluoric acid gave 99.99% SiO₂. The residue, when tested with sodium thiocyanate, gave a red coloration indicating the presence of iron.

For the first preparation, this purified quartz was mixed with purified sodium tungstate in the proportion of 6 silica to 1 Na₂WO₄ by weight. The mixture was ground in an agate mortar to pass 200-mesh screen. It was then placed in a platinum cone, which was covered with platinum foil resting on two porcelain rods, set in a magnesia block into which a noble metal thermocouple had been inserted. This

assembly was then heated in a furnace provided with silicon carbide heating elements for 24 hours at 1250°. On removal from the furnace, a piece of the sintered mass was cut off for the preparation of specimens for the dilatometer. The remainder was washed repeatedly with hot water to remove the flux. A second set of interferometer specimens was then prepared from this material and was further treated successively with boiling water, hydrochloric acid, ammonium hydroxide and boiling water, and was then carefully dried. Analysis showed 98.7% silica and examination under the petrographic microscope indicated complete conversion to tridymite. The residual mass was ground in an agate mortar to pass through a 400-mesh screen and was given the same series of washings as before. It was this finely ground material which was used by Anderson³ and by Mosesman and Pitzer in their specific heat measurements.

Another sample was prepared by heating the purified quartz and sodium tungstate in the same proportions for 27 hours at 1300°. The cooled sinter was boiled in 1:1 HCl for 2 hours, was left overnight in a constant-boiling mixture of HCl, was then repeatedly washed in boiling distilled water and was finally dried. Specimens for the dilatometer were then prepared from the dried material. Examination under the microscope showed complete conversion to tridymite.

A fourth set of specimens was cut from the center of a silica coke-oven liner which, as a result of long service at high temperature, had been converted almost completely to tridymite. This liner has been described elsewhere.⁴

Apparatus.—The measurements were made by means of an interferometric dilatometer which has already been described.⁵ The specimens for each sample were in the form of three small pyramids, about 3 mm. in height, which were placed between the silica plates of the interferometer. The observations were plotted on a large scale as increase in length per unit length against temperature.

Since these measurements were made with the temperature increasing at a constant rate of 3° per minute, and since the specimens were not good thermal conductors and, moreover, were not of identical shape, there were inevitably small temperature differences among them. The evidence indicates that this difference was usually less than 0.3°. The specimens therefore transformed in succession at intervals of a few seconds, rather than simultaneously. This made it difficult to obtain precise measurements within a degree or so of the transition temperatures, with the result that the several length-temperature curves did not coincide but were displaced relative to each other. There was, however, substantial agreement in the slope of the curves, as read from the plot by means of an optical tangent meter. Accordingly, the results are reported in the form of instantaneous coefficients as a function of temperature.

Results

The composite data for all three types of specimens are presented in Fig. 1. For all specimens, the values of the coefficient, at or just above room temperature, clustered in the range 23 to 26 × 10⁻⁶, and then increased sharply to the inversion temperature. In all specimens, the first inversion appeared to be complete within a degree of 117°.

The coefficient for the intermediate form was, for all specimens, close to 45 × 10⁻⁶, and again increased rapidly as the inversion temperature was approached. The second inversion appeared to be complete within a degree of 163°.

Above the second transition, the coefficient for each set of samples was, within the error of measurement, constant over the range 163 to 210°. There was, however, some variation in the magnitude of the coefficient in this range. Thus, the specimens cut from the coke-oven brick gave 45 × 10⁻⁶, and a second run on the sample which still contained the flux gave 65 × 10⁻⁶, whereas for five

(3) C. T. Anderson, *ibid.*, **58**, 568 (1936).

(1) R. B. Sosman, "The Properties of Silica," Chemical Catalog Co., New York, N. Y., 1927, pp. 124, 125.

(2) A. Mosesman and K. S. Pitzer, *THIS JOURNAL*, **63**, 2348 (1941).

(4) J. B. Austin and R. H. H. Pierce, *J. Amer. Ceramic Soc.*, **16**, 102 (1933).

(5) J. B. Austin and R. H. H. Pierce, *THIS JOURNAL*, **55**, 661 (1933).

other runs on the purified specimens the coefficient was close to 55×10^{-6} . To indicate this variation, Fig. 1 shows a shaded band including the two extreme values but the curve is drawn to represent the results of the other concordant runs.

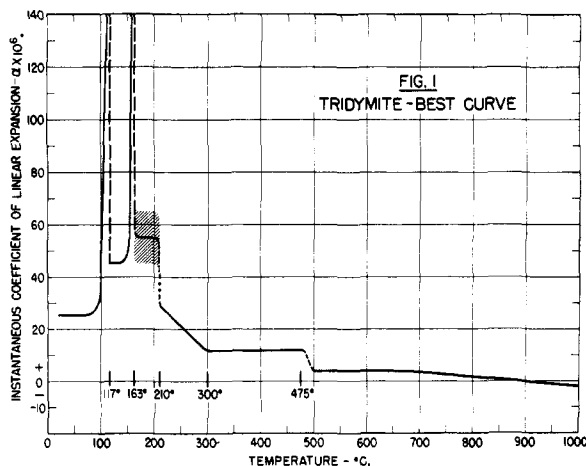


Fig. 1.—Instantaneous coefficient of linear thermal expansion of tridymite.

At about 210°, however, the coefficient for all specimens showed a virtually discontinuous decrease, after which there was a substantially linear decrease to about 300°. From this temperature to about 475° the coefficient was practically constant. At approximately 475° there was another small, though definite, break in the curve. Above 500° there is a continuous decrease in the coefficient until it becomes negative in the range above 900°.

Discussion

The marked change in the expansion coefficient at 210° is believed to correspond to the thermal effect reported by Mosesman and Pitzer, although it occurs at a temperature slightly lower than that which they observed. There is, likewise, a smaller change at 475°, but this is beyond the range of temperature investigated by these authors.

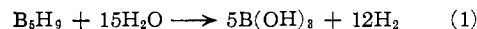
The extended transitions which occur at 117 and 163° are interpreted by Mosesman and Pitzer in terms of the rotation of oxygen atoms in the lattice structure. But they point out that this interpretation leaves no room for a third transition just over 200°. In line with this view, it is evident from the expansion data that the change which takes place at 210° must be of a totally different type. It is difficult to determine, however, just what its origin may be. Indeed, the whole course of the coefficient curve above 200° is puzzling. There appears, however, to be little hope of interpreting this behavior on the basis of expansion measurements alone. Additional data on lattice structure and thermal effects are needed. It should be noted, however, that these effects are presumably not due to the presence of impurity since they occur in careful purified samples as well as in relatively impure material.

RESEARCH LABORATORY
UNITED STATES STEEL CORPORATION
KEARNY, NEW JERSEY

Hydrolysis of Pentaborane

BY I. SHAPIRO¹ AND H. G. WEISS¹

The rate of hydrolysis of pentaborane had been reported² to be very slow at room temperature with prolonged heating with water at *ca.* 90° required to achieve complete hydrolysis. On the basis of hydrogen measurements the reaction is given as



In our laboratories we have found that the slowness of the rate of hydrolysis of pentaborane is only apparent, and can be attributed to the poor miscibility of pentaborane and water. Pentaborane can be shaken with water³ at room temperature with very little noticeable reaction. After cessation of shaking, the two liquids separate, and some gas bubbles and a white solid form at the interface. The situation is entirely different when one adds an inert mutually miscible solvent, such as dioxane, to the mixture. In this case the rate of reaction becomes too rapid to measure in glassware by the usual techniques of freezing with subsequent warming of the mixture, or by using break-off tubes to introduce one liquid into another liquid.

Several experiments on measuring the rate of hydrolysis have been attempted in metal equipment in which the pressure of the system was recorded by means of a statham gage connected to a brush oscillograph. In these experiments a vial containing known amounts of pentaborane (usually 15 cc. gas at S.C.) was crushed beneath the surface of a (50 ml.) solution of dioxane containing 20% water after the system had been evacuated of non-condensable gases and then brought to a constant temperature (30°). A perforated disk connected to a hand-operated plunger served as a means of crushing the vial and stirring the solution. After the crushing of the vial the pressure of the system increased rapidly (25% of maximum pressure rise in 7.2 sec.; 50%, in 16.3 sec.; 70%, in 41.5 sec.), and attained within several minutes a maximum pressure rise corresponding to that expected from Eq. 1.⁴ The rate of stirring has a profound effect on the rate of increase in pressure of the system. By alternately stirring and resting the solution during the course of the reaction, one obtains plateaus on the pressure-time trace. Consequently, better mixing will be necessary in order to distinguish the rate of hydrolysis of pentaborane from the rate of mixing of the reactants.

The use of an inert solvent in hydrolyzing pentaborane simplifies the time required for its analysis. In a typical experiment carried out in glassware, 31.2 cc. of B_5H_9 (gas at S.C.) shaken for five minutes with excess water in dioxane yielded 375 cc. of H_2 (gas at S.C.). Titration of the resulting boric acid with standard base after the addition

(1) Research Department, Olin Mathieson Chemical Corporation Pasadena, California.

(2) A. Stock, "Hydrides of Boron and Silicon," Cornell Univ. Press, Ithaca, N. Y., 1933, p. 71.

(3) In order to avoid ignition of pentaborane these experiments were carried out in the absence of air—the usual high-vacuum techniques were employed.

(4) Equation 1 has been found applicable for the case of excess water. Studies on the hydrolysis of pentaborane in the presence of excess pentaborane will be reported later.