

dication of crystallinity. Later Rinne [F Rinne, *Z. Krist.*, **60**, 55 (1924)] studied several samples of opals by means of x-rays and found them to be amorphous.

The results obtained in this Laboratory are quite different from these previous findings. Thus far fifteen samples of various types of opal have been investigated, all of which show definite crystallinity which is very pronounced in the majority of the cases. Also most of the samples give an identical pattern.

This pattern is of unusual interest since it does not correspond to either low-quartz, low-tridymite or low-cristobalite, which are the only modifications of silica ever definitely established to exist at room temperature. The pattern, is however, in perfect agreement with the one of high-temperature cristobalite as reported by Wyckoff [R. W. G. Wyckoff, *Am. J. Sci.*, **9**, 448 (1925)., *Z. Krist.*, **62**, 189 (1925)].

Comparison with a picture of the cubic high-temperature form prepared in this Laboratory confirms this identity. The unlikely possibility of a hydrate of similar structure is excluded by the fact that the diagram remains unchanged after heating of the sample for one hour at 1100°.

Two reports have been made suggesting that high temperature cristobalite might persist at room temperature for some time, but according to Sosman [R. B. Sosman, "The Properties of Silica," The Chemical Catalog Co., Inc., New York, 1927, p. 133] these claims, based on optical examination, are of doubtful validity; 200° is the lowest temperature at which high-cristobalite has been observed to exist according to reliable experiments (compare Sosman).

However, we have now provided definite proof of the existence of high-temperature cristobalite at room temperature for an indefinite period of time.

These investigations are being continued and a complete report will appear soon.

DEPARTMENT OF CHEMISTRY
THE JOHNS HOPKINS UNIVERSITY
BALTIMORE, MARYLAND
RECEIVED JANUARY 2, 1932
PUBLISHED FEBRUARY 5, 1932

ISADOR LEVIN
EMIL OTT

THE STARCH-IODIDE REACTION

Sir:

Remington, McClendon and von Kolnitz have recently reported [THIS JOURNAL, **53**, 1245 (1931)] that they could not confirm Turner's observations as to the reliability and stability of the color produced by the starch-iodide reaction. They state that if the blue solution is read against a blue glass instead of a starch-iodine solution, it will be found that the color is quite sensitive to temperature changes and varies with the time. These

conclusions were drawn apparently from a study of four standard solutions each containing 0.001 mg. of iodine. Their figures show an error of over 100% as read in the colorimeter against their blue glass.

Three years of careful study with the starch-iodide test indicate that the standard solutions prepared as described by Turner are reliable, stable and sufficiently uniform for clinical estimation of small amounts of iodine.

DEPARTMENT OF MEDICAL RESEARCH
DETROIT COLLEGE OF MEDICINE AND SURGERY
1516 ST. ANTOINE STREET
DETROIT, MICHIGAN

R. G. TURNER
MINNA Z. WEEKS

RECEIVED JANUARY 2, 1932
PUBLISHED FEBRUARY 5, 1932

THE ACTION OF HYDRIDIC ACID ON GLYCEROL

Sir:

The following seems reasonably good evidence for the mechanism involved in the formation of allyl iodide in the well-known reaction between glycerol and hydriodic acid.

When $\text{CH}_2\text{Br}-\text{CH}_2-\text{CH}_2\text{Br}$ is treated with zinc or sodium, cyclopropane is formed. However, when $\text{CH}_2\text{Br}-\text{CHOH}-\text{CH}_2\text{Br}$ [Aschan, *Ber.*, **23**, 1833 (1890)] or $\text{CH}_2\text{Cl}-\text{CHOH}-\text{CH}_2\text{Cl}$ is similarly treated [Hübner and Müller, *Ann.*, **159**, 168 (1871); Tornöe, *Ber.*, **24**, 2674 (1891)] allyl alcohol is formed and not cyclopropanol. Strange as it may seem, $\text{CH}_2\text{Br}-\text{CHOOR}-\text{CH}_2\text{Br}$ in absolute ether yields with sodium not cyclopropyl benzoate or acetate but allyl benzoate and allyl acetate, depending, of course, on the nature of the group R. Furthermore, in the action of nitrous acid on cyclopropyl amine, allyl alcohol is formed [Kishner, *Chem. Zentr.*, I, 1704 (1905)] and not cyclopropanol, while in the electrolysis of the potassium salt of cyclopropane monocarboxylic acid, the allyl ester of cyclopropane monocarboxylic acid was obtained [Fichter and Reeb, *Helv. Chim. Acta*, **6**, 454 (1923); Hofer and Moest, *Ann.*, **323**, 284 (1902)] and not the cyclopropyl ester of the cyclopropane monocarboxylic acid. Furthermore, allyl alcohol was obtained from diiodohydrin [Claus, *Ann.* **168**, 28 (1873); Swarts, *Z. Chem.*, 255 (1868)] when that compound was merely allowed to stand. The unstable nature of cyclopropanol offers a clue to the action of hydriodic acid on glycerol. In the light of the foregoing reactions, the following may be postulated

