[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Formation, Stability and Crystal Structure of Solid Silicon Monoxide[1,2]

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The formation of solid silicon monoxide from a mixture of silicon and silicon dioxide according to the reaction $Si + SiO_2 \rightarrow 2SiO$ was observed from X-ray diffraction patterns taken at 1250 and 1300°, during various time intervals. The crystal structure and lattice constants of Si and SiO were determined at 1300 and 25°. Results showed that Si has the same body-centered lattice at 1300° as an room temperature, with a lattice constant of a = 5.445 Å. at 1300° and a = 5.413 Å. at 25°. The lattice of SiO was found to be cubic, the lattice constants at 1300 and 25° being 7.135 and 7.09 Å., respectively.

Introduction

The existence of SiO has been established by Bonhoeffer[3] from measurements of the adsorption spectrum. Since then, several unsuccessful attempts have been made to obtain solid SiO. In attempts, by several investigators,[4-8] to produce this solid, SiO_2 was heated in vacuum to 1100–1500° in the presence of a reducing agent (mostly Si or C), and a high rate of evaporation was observed. The substances which condensed on the cold walls of the tube were found to be amorphous, and X-ray diffraction patterns taken of these substances indicated the presence of silicon and Crystobalite.[9] Very faint and unconvincing electron diffraction patterns of the distillate were obtained by H. de Wet Erasmus and Persson.[10] A description of the reactions of the distillation product is presented in a paper by Zintl.[4]

The vapor pressure of SiO from the reaction $SiO_2 + H_2 \rightarrow SiO + H_2O$ was measured at temperatures between 900 and 1500° by Grube and Speidel[5] and by Geld and Kochnev.[8] In addition, the partial pressure of SiO over a mixture of Si and SiO_2, between 1050 and 1200°, was measured by Schaefer and Hoernle[11] who concluded that in this temperature region no solid SiO exists and that the mixture consists only of SiO_2 and Si.

It appeared to us that the best method of observing the formation of SiO would be through the reaction $SiO_2 + Si \rightarrow 2SiO$ where only solid components are present, with X-ray diffraction patterns obtained during the reaction. If the reaction is slow, as is usually the case for solid reactions, so that two or more X-ray diffraction patterns can be taken during the reaction, then the consecutive patterns should show a decrease in intensity of the diffraction lines of the reactants and the appearance, with increasing intensity, of the diffraction lines of the products. It is, of course, necessary that the components do not undergo a change in crystal structure at the reaction temperature.

During the present investigation the crystal structures of Si and SiO_2 were studied at 1300°, and then the reaction between Si and SiO_2 was followed at this temperature using the method described above. The disappearance of the Si diffraction lines and the appearance of a new set of diffraction lines, together with the fact that upon cooling the sample to room temperature this new set of lines was found to disappear while the Si lines reappeared, constitute proof of the formation of solid SiO.

Materials and Experimental Procedure

The X-ray diffraction patterns were taken in our high temperature camera which has been described elsewhere.[12] A few changes were made in this apparatus in order to improve its performance. To avoid evaporation of the sample, the high temperature patterns were taken under a helium pressure of 800 mm. The temperature was measured with a Leeds and Northrup disappearing filament optical pyrometer which had been calibrated against a standard lamp obtained from the National Bureau of Standards. The temperature calibration of the camera was carried out by placing a "black body," made from a piece of tantalum tube, in place of the X-ray specimen. By taking account of the various calibration and correction factors, the uncertainty in the reading of the pyrometer, and the slight temperature variations during the runs, the temperature may be considered accurate to within 20°. Ni-filtered Cu $K\alpha$ radiation, obtained from a Machlett tube operated at 50 kv. and 20 ma., was used. The exposure time was three hours.

The silicon was in the form of a powder and was obtained from C. Hardy, Inc., New York; the SiO_2 was Baker analyzed and was in amorphous powder form. Rods of $^1/_{32}$ in. diameter were pressed from Si, from SiO_2 and from a stoichiometric mixture of Si and SiO_2, and were placed in the camera. After filling with helium, the camera was heated and the X-ray diffraction patterns were taken. After each picture the camera was cooled, a new film inserted, and the process repeated.

Experimental Results

Silicon was found to have the same crystal structure at 1300° as at room temperature. The lattice constant was determined, from the back reflection lines, to be a = 5.445 Å. at 1300°.

The SiO_2 was amorphous and heating it for 20 hours failed to crystallize it.

When heated to 1250°, the mixture of Si and SiO_2 reacted only slightly, if at all, since only the Si diffraction pattern could be obtained. At 1300°, the reaction took place slowly and was completed in about nine hours. Figure 1 shows the three patterns obtained during the reaction: pattern No. 1 still shows the Si diffraction lines, with very faint SiO lines; pattern No. 2 shows Si and SiO lines in about equal intensity; pattern No. 3 shows only SiO lines with faint Si diffraction lines. The diffraction lines of SiO were identified from pattern

(1) This work was supported in part by the Office of Naval Research under contract with The Ohio State University Research Foundation.

(2) Presented at the Los Angeles meeting of The American Chemical Society, March, 1953.

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(4) E. Zintl, *Z. anorg. allgem. Chem.*, **245**, 1 (1940).

(5) G. Grube and H. Speidel, *Z. Elektrochem.*, **53**, 339, 341 (1949).

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(8) P. V. Geld and M. I. Kochnev, *ibid.*, **61**, 649 (1948).

(9) H. N. Baumann, *Trans. Electrochem. Soc.*, **80**, 95 (1941).

(10) H. de Wet Erasmus and J. A. Persson, *ibid.*, **95**, 316 (1949).

(11) H. Schaefer and R. Hoernle, *Z. anorg. allgem. Chem.*, **263**, 261 (1950).

(12) J. W. Edwards, R. Speiser and H. L. Johnston, *Rev. Sci. Instr.*, **20**, 343 (1949).

No. 3 and found to be cubic (see Table I). The lattice constant of SiO at 1300°, obtained from back reflection lines, is a = 7.135 Å.

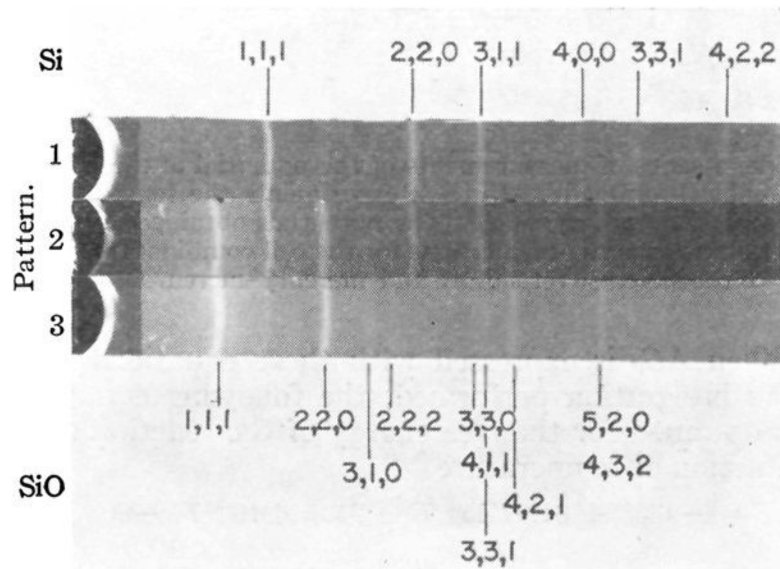

Fig. 1.—X-Ray diffraction patterns taken at 1300° showing the reaction Si + SiO_2 → 2SiO.

After pattern No. 3 of Fig. 1 was taken, the sample was rapidly quenched (from 1300 to 850° in 2 sec.) and an X-ray diffraction pattern at room temperature was obtained (shown in Fig. 2). Besides the SiO diffraction lines, Si lines appear, due to some disproportionation into Si and SiO_2. The pattern shown in Fig. 2 was used to determine the lattice constant of SiO at 25°, the result being a = 7.09 Å.

An attempt was made to obtain a larger quantity of SiO at room temperature in the following way. A mixture of 4 g. of Si and SiO_2 was heated to 1300° for nine hours in a tantalum container and then quenched. However, the quenching speed obtained was too slow (from 1300 to 850° in 10 sec.) and the X-ray diffraction pattern of the powder contained strong Si diffraction lines and two faint SiO lines. The same results were obtained when the X-ray sample was heated to 1300°, after taking the pattern of Fig. 2, and then slowly cooled.

TABLE I

X-RAY DIFFRACTION LINES OF SiO AT 1300°

Intensity	$\sin^2\theta$	Interplanar spacing, d(Å.)	Indices hkl
Strong	0.0348	4.13	1,1,1
Strong	.0924	2.53	2,2,0
Weak	.1238	2.18	3,1,0
Weak	.1409	2.05	2,2,2
Very weak	.2118	1.67	4,1,1 3,3,0
Very weak	.2197	1.64	3,3,1
Medium	.2477	1.54	4,2,1
Medium	.3389	1.32	5,2,0 4,3,2
Weak	.7429	0.89	8,0,0
Weak	.8352	0.84	8,2,2 6,6,0

From these measurements, we can draw the following conclusions regarding silicon monoxide. SiO is formed in the solid phase above 1250°, it has a cubic crystal structure with lattice constant of a = 7.135 Å. at 1300°, and it disproportionates into Si and SiO_2 upon cooling.

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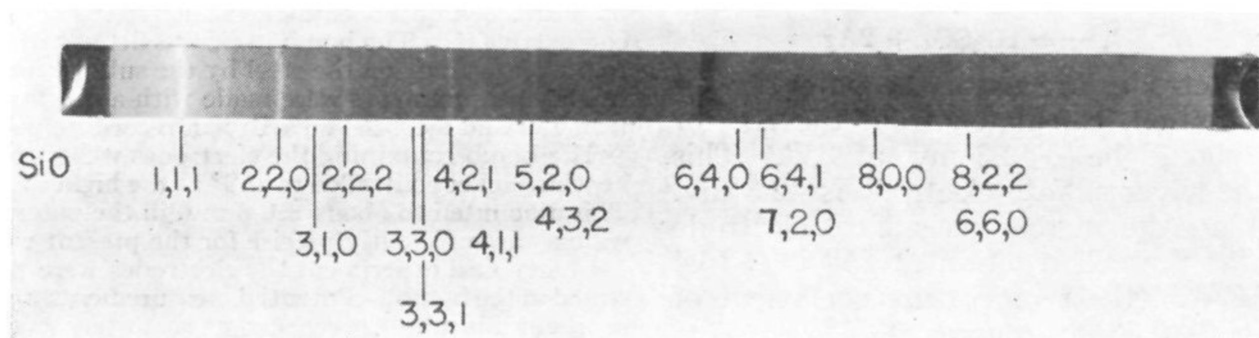

Fig. 2.—X-Ray diffraction pattern taken at room temperature of SiO quenched rapidly (1300—850° in 2 sec.).