may explain, at least in part, the presence of a heavy sulfur compound isolated with dibenzyl.

In Fig. 1 the points corresponding to experiments 34, 35, 36, 54 and 55 fall below the Arrhenius line. By increasing the ratio of toluene to sulfide (runs 33 and 56), the rate constant in this temperature range, where the extent of decomposition was rather high (in the region of 75%), returned to the expected value. This is interpreted as being due to either a recombination of the SCH_3 with benzyl radicals or to a dimerization of the SCH_3 radicals, when the concentration of those radicals is exceedingly high.

In accordance with the foregoing interpretation of the mechanism of the thermal decomposition of benzyl methyl sulfide, the activation energy of 51.5 ± 2 kcal./mole, derived from the Arrhenius line of Fig. 1, is considered to represent the activation energy of reaction (1). The frequency factor for reaction (1) is calculated to be 3×10^{13} sec.$^{-1}$ within a factor of 3. Assuming that the activation energy of the reverse recombination reaction of the CH_3S and benzyl radicals is equal to zero, it follows that D ($C_6H_5 \cdot CH_2$—$S \cdot CH_3$) is equal to 51.5 ± 2 kcal./mole. Unfortunately the heat of formation of benzyl methyl sulfide has not yet been determined. When this becomes known, one will be able to calculate the heat of formation of the CH_3S radical on the basis of the value proposed here for D($C_6H_5 \cdot CH_2$—SCH_3).

Dimethyl Sulfide and Dimethyl Disulfide

Only preliminary results on the thermal decomposition of these compounds have been obtained.

In the pyrolysis of dimethyl sulfide in a stream of toluene between 931 and 982°K. the products of the reactions were CH_4, CH_3SH, H_2S and dibenzyl. The formation of dibenzyl indicated that, at least in part, the thermal decomposition of dimethyl sulfide proceeded *via* a radical mechanism. The reaction was not studied sufficiently thoroughly to determine either the order of the reaction or the activation energy.

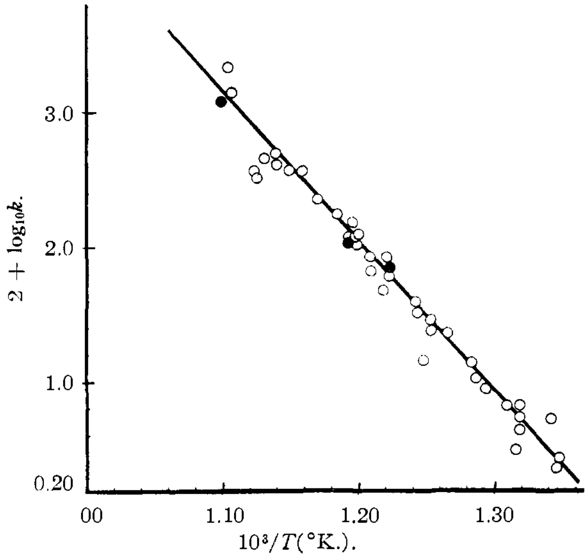

Fig. 1.—The thermal decomposition of methyl benzyl sulfide Arrhenius plot. Filled points denote experiments in packed vessel.

The thermal decomposition of dimethyl disulfide proceeded fairly vigorously at a much lower temperature, *viz.*, 735 to 833°K., with a time of contact of about 0.4 second. Only traces of dibenzyl were detected which indicated that dimethyl disulfide decomposes thermally by a molecular mechanism and not *via* radicals. The products were CH_3SH, H_2S, CH_4, H_2, $CH_2{=}CH_2$, CH_3CH_3 and heavier sulfur compounds.

OTTAWA, CANADA

[CONTRIBUTION FROM BELL TELEPHONE LABORATORIES]

On the Question of the Existence of a Crystalline SiO

BY S. GELLER AND C. D. THURMOND

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In a recent paper by Hoch and Johnston titled "Formation, Stability and Crystal Structure of Solid Silicon Monoxide,"[1] the existence of crystalline SiO is inferred from X-ray diffraction patterns obtained from mixtures of Si and SiO_2 heated in a high temperature camera. Some interesting features of the data published by Hoch and Johnston are pointed out and an alternative explanation of their data is presented. In addition, some experiments are described which substantiate the conclusion that crystalline SiO has not yet been identified, and that the pattern found by Hoch and Johnston and ascribed to SiO is actually from a mixture of β-cristobalite (high temp. form) and β-silicon carbide (cubic form).

Introduction

In a recent paper by Hoch and Johnston titled "Formation, Stability and Crystal Structure of Solid Silicon Monoxide"[1] the existence of crystalline SiO is inferred from X-ray diffraction patterns obtained from mixtures of Si and SiO_2 heated in a high temperature camera. We wish to point out some interesting features of the data published by Hoch and Johnston and then suggest an alternative explanation for these patterns. In addition, some experiments we have performed will be described which substantiate our conclusion that crystalline SiO has not yet been identified, and that the pattern found by Hoch and Johnston, and ascribed to SiO is due to a mixture of β-cristobalite (high temperature form) and β-silicon carbide (cubic form).

Hoch and Johnston assert that they have studied the reaction of Si and vitreous SiO_2 at 1300° in a powder diffraction camera. 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

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[1] M. Hoch and H. L. Johnston, THIS JOURNAL, 75, 5224 (1953).

while the Si lines reappeared, constitute proof of the formation of solid SiO."

Experiments and Discussion

As is well known the silicon–oxygen system is complex. However, there are some fairly well established phase relations among the various SiO_2 phases. A good summary of these relations is given by Hall and Insley.[2] It is well known that between 1100 and 1470°, vitreous silica transforms very sluggishly into β-cristobalite. Above 1470°, the transformation is much more rapid, although not as rapid as the α-β transitions of the silica minerals. Although other authors[3] who have worked on the SiO problem found evidence of the existence of Si, α-cristobalite and some α-quartz resulting from heating of Si plus SiO_2, Hoch and Johnston apparently did not consider seriously the possibility of such a transition in their case. A look at the X-ray data strongly suggests that such a transition should have been considered.

The pertinent data given by Hoch and Johnston are listed in the first two columns of Tables II and III. In the third column of Table III we have given the lattice constants derived from the spacings and indices given by them. Even if (310) is changed to (311), one obtains 7.23 Å., for a_0 derived from that value. The authors claim this to be a cubic cell with a_0 = 7.135 Å. The rather wide variation in a_0 calculated from each line considerably weakens this conclusion. Various amounts of stretching and contracting in the right places would be necessary before this cell could be called cubic.

As a consequence of these questions concerning the results of Hoch and Johnston, a series of experiments was performed in an effort to reproduce some of their results. Mixtures of Si and SiO_2 (1:1) were made from high purity Si and vitreous SiO_2. Small samples of these (50 to 300 mg.) were sealed into silica tubes under vacuum and heated to 1300° for from 4 to 19 hours then rapidly quenched (2–5 seconds) by plunging the tubes into water. No new lines appeared in the X-ray photographs of these samples. Silicon lines and the diffuse band from vitreous silica were observed. It was felt that the trouble was not that the quenching was too slow, but rather that there was actually no reaction other than perhaps the formation of a small amount of amorphous SiO.

We learned in private communication from Hoch that the pressed pellets that these authors studied were made using "radio cement" as a binder. The pellet so made was baked out at 500° in air and a sintered rod remained. We have performed similar experiments, *i.e.*, adding an organic base cement to the mixture of Si and SiO_2, baking out at 500° and heating to 1300°. This was done with various organic cements the bases of which were usually polystyrene or cellulose acetate. The very first trial gave a conversion from the vitreous silica to cristobalite. In several of the trials, it appeared that conversion did not occur but β-SiC was produced. In a few cases some quartz was produced.

The results of our experiments are summarized in Table I.

TABLE I

SUMMARY OF EXPERIMENTS AND RESULTS

	Sample description	No. of trials	Heating time, hr.	Results as given by X-ray photographs
1	SiO_2 only	1	4	No change
2	Si + SiO_2 (1:1)	5	4–19	No change
3	Si + SiO_2 (1:1) + organic cement (baked out at 500°)	10	4-7	1. Usually vitreous silica converted to cristobalite; β-SiC present, sometimes α-quartz was also present 2. In some cases conversion of vitreous silica did not occur but β-SiC was produced

Shown in Table II is a comparison of the data of Hoch and Johnston with those from β-cristobalite and β-SiC. The data for β-cristobalite and β-SiC were obtained using a Norelco diffractometer on which was mounted a hot stage sample holder devised by E. A. Wood of these Laboratories.[4] The temperature was held at 300°. Reflection intensities were recorded on charts and the relative integrated intensities obtained with the use of a Keuffel and Esser compensating polar planimeter. The radiation used was Ni filtered Cu Kα. The intensities are put on a relative basis with respect to the (111) intensity of β-cristobalite taken as 100. It is seen that all the lines in the photograph of Hoch and Johnston are accounted for except those with d-values of 1.67 and 2.05 Å. The intensities also compare quite well and the indication is that there is roughly a 3 to 1 ratio of β-cristobalite to β-SiC in their sample.

TABLE II

COMPARISON OF DATA OF H. AND J. WITH THOSE FROM β-CRISTOBALITE AND β-SiC

The β-cristobalite and β-SiC data were taken at 300°.

Data of H. and J.		β-Cristobalite		β-SiC	
d	I/I_0	d	I/I_0	d	I/I_0
4.13	s	4.125	100		
2.53	s	2.523	26	2.515	69
2.18	w			2.177	17
2.05	w	2.059	9		
1.67	vw				
1.64	vw	1.636	13		
1.54	m			1.542	46
		1.456	10		
		1.373	3		
1.32	m			1.315	32
		1.260	2	1.259	6
		1.206	5		
		1.128	3		
				1.090	8
0.99[a]	vw			1.000	16
.98[a]	vw			0.9753	8
.89	w			.8899	24
.84	w			.8394	24

[a] These are not from Table I of H. and J.'s paper but are interpolated from their Fig. 2.

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(2) F. P. Hall and H. Insley, "Phase Diagrams for Ceramists," The American Ceramic Society, 1947, p. 19.

(3) L. Brewer and R. K. Edwards, *J. Phys. Chem.*, **58**, 351 (1954).

(4) E. A. Wood, *Rev. Sci. Inst.*, to be published.

In Table III, the lines on the photograph of Hoch and Johnston are indexed on the β-cristobalite and β-SiC basis and it is seen that quite accurate results are obtained for the β-cristobalite and β-SiC lattice constants. The a_0 value obtained from the (111) β-SiC reflection is a little large because of overlapping with the (220) β-cristobalite line.

TABLE III

THE INDEXING OF THE DATA OF H. AND J. AS β-CRISTOBALITE + β-SiC

Data of H. and J.			β-Cristobalite		β-SiC	
d, Å.	(hkl)	a_0, Å.	(hkl)	a_0, Å.	(hkl)	a_0, Å.
4.13	111	7.15	111	7.15		
2.53	220	7.16	220	7.16	111	4.39
2.18	310	6.89			200	4.36
2.05[a]	222	7.10				
1.67[a]	411,330	7.08				
1.64	331	7.15	331	7.15		
1.54	421	7.06			220	4.36
1.32	520,432	7.11			311	4.37
0.89	800	7.12			422	4.36
0.84	822,660	7.13			333	4.36

[a] These lines apparently come from still another phase.

We have not been able, by the procedure mentioned earlier, to obtain β-cristobalite with the β-silicon carbide. One would not ordinarily expect to see β-cristobalite at room temperature because the transitions from β to α and α to β are extremely rapid. However, there have been several cases in which β-cristobalite has been seen at room temperature. Usually it has been seen in opals.[5–7] J. W. Greig has observed β-cristobalite at room temperature as a decomposition product of $Al_2O_3 \cdot SiO_2$.[8] Furthermore, Pundsack of the Johns-Manville Research Center has found[9] that when certain samples of naturally occurring α-cristobalite are heated to temperatures above the transition, and then cooled to room temperature the β-cristobalite remains and appears to be stable.

Some authors have noted that amorphous silica can be converted to cristobalite in the range 1200–1400° by a variety of additives[9] other than Si (but see ref. 3). Birks and Schulman[10] also have studied the effects of various impurities on the crystallization of silicic acid. These authors obtained conversion to either quartz or cristobalite or both at temperatures of 1200 to 1300° by adding alkaline earth carbonates, $MnCO_3$, Al_2O_3, Bi_2O_3, Li_2CO_3, Na_2CO_3 and $NiCO_3$ to amorphous silicic acid.

Conclusions

It is believed that Hoch and Johnston obtained a mixture of β-cristobalite and β-SiC. The conversion of vitreous silica to cristobalite at 1300° is probably catalyzed by the presence of highly active and finely divided carbon which is present as the result of the degradation and cracking of the organic polymer used as a cement for holding their X-ray samples together.

The disappearance of Si lines, which never really seems to be complete could come about from the conversion to β-SiC and to SiO, the vapor pressure of which is such that it can be expected to diffuse at appreciable rate to the cooler parts of the camera.[11]

The conclusion reached by Hoch and Johnston that the heating of a 4-g. mixture of Si and vitreous SiO_2 to 1300° for nine hours did not yield the new phase because quenching speed was too slow is contradictory to our observations. It should be pointed out that they were not able to observe what happened to that particular sample at 1300°. We would say that perhaps some amorphous SiO was formed in the sample and perhaps there was conversion of a small amount of vitreous SiO_2 to cristobalite. Finally, it should be pointed out that in terms of our observations, we are not able to explain the statement on p. 5225[1]: "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." This would be the only evidence presented which could not be immediately attributed to a mixture of β-cristobalite and β-SiC.

Brewer and Edwards have presented evidence for the existence of stable solid SiO above approximately 1180°. Their results lead to the conclusion that the rates of both formation and disproportionation of SiO are quite rapid above 1180°. The results of Hoch and Johnston would require that SiO form very slowly but disproportionate very rapidly. In addition, Hoch and Johnston were not able to observe a reaction at 1250° although Brewer and Edwards would predict the formation of SiO at that temperature.[3]

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The examination of the results of our work and suggestions made by Dr. F. L. Pundsack are also gratefully acknowledged.

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