

$\pm 0.025$  and  $0.051 \pm 0.01$ , at 420, 444, 460 and  $525^\circ$ , respectively. From these constants, together with the equilibrium constants for the  $N_2-H_2-NH_3$  system, the dissociation pressures of  $Fe_4N$  according to the reaction  $2Fe_4N = 8Fe + N_2$  have been calculated to be 4250, 4300, 5400 and 5600 atmospheres, respectively, at the above temperatures. The solid phases were identified as  $Fe_4N$  and Fe by means of x-ray powder photographs. They give no indication of any distortion of the iron lattice as might possibly result if under the condition of our experiments appreciable solution of nitrogen in the iron samples were to occur. The results explain many but not all of the phenomena observed in the nitriding of steels.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY,  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 2]

## A STUDY OF THE REACTION OF HYDROGEN BROMIDE WITH SILICON

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Although the facts concerning the reaction of hydrogen bromide upon silicon at elevated temperatures have long been known in a general way, and the similarity of this reaction to that of hydrogen chloride upon silicon has been pointed out, especially by the work of such investigators as Buff and Wöhler,<sup>1</sup> Gattermann,<sup>2</sup> Besson and Fournier,<sup>3</sup> and Combes,<sup>4</sup> no very precise data concerning the necessary conditions, the purity of the materials used, the yields of the various products and the mechanism of this reaction appear to have been laid down; the present investigation was undertaken with the object of throwing further light upon these and allied matters. Inasmuch as a mixture of products is inevitably obtained, and the separation by fractionation of the crude product by the usual methods of distillation is not particularly clean-cut, the boiling points of the bromine derivatives of silane given by the different earlier observers mentioned do not agree closely, so that more recently Stock and his co-workers,<sup>5</sup> starting with silane, have prepared these compounds and determined their constants with greater accuracy.

The apparatus used in the present study of the reaction of gaseous hydrogen bromide with crystalline silicon is shown in Fig. 1.

Electrolytic hydrogen was passed through three towers (two of which appear in the figure) containing fused flakes of potassium hydroxide, thence it could be passed directly

<sup>1</sup> Buff and Wöhler, *Ann.*, **104**, 99 (1857).

<sup>2</sup> Gattermann, *Ber.*, **22**, 193 (1889).

<sup>3</sup> Besson, *Compt. rend.*, **112**, 530 (1891); Besson and Fournier, *ibid.*, **151**, 1055 (1910).

<sup>4</sup> Combes, *ibid.*, **122**, 531 (1896).

<sup>5</sup> Stock and Somiesky, *Ber.*, **50**, 1739 (1917).

through the rest of the apparatus in order to sweep out the air, or it could be caused to bubble through liquid bromine at 45° and a mixture of hydrogen and bromine vapor in nearly equimolar proportions thereby obtained. This mixture passed through a pyrex tube containing platinized asbestos which was heated electrically to 200°. The gas passing beyond this catalyst tube showed no color of free bromine, but was nevertheless allowed to pass through a tower containing ferrous bromide, which had been partly dehydrated at 100°, to absorb any traces of the halogen, and finally through two towers

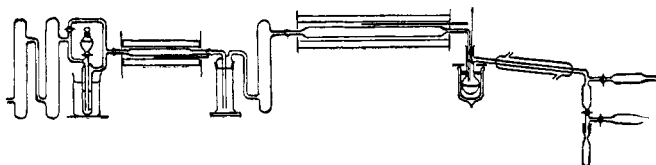


Fig. 1.

(one of which is shown) of freshly fused calcium bromide, before entering the reaction tube containing pulverized commercial silicon (averaging 97.5% Si), which was heated electrically to the desired temperature (usually 360°). The calcium bromide and ferrous bromide towers were frequently refilled. The gaseous products were condensed in a flask deeply immersed in alcohol, which was cooled by addition of solid carbon dioxide to a temperature of about -30°—below this temperature solidification of silicon tetrabromide caused clogging of the tube entering the receiver—and the unchanged hydrogen bromide passing through the remaining portion of the apparatus was vented through a drying tube into the hood.

The crude product condensed in the flask was twice distilled, the first distillation being directly from the flask, the fractions collected being (a) up to 125° and (b) from 125 to 154°. The device indicated in the diagram permitted the evacuation of the receiver, the sealing off of each fraction as collected, and the replacement of a second receiver, which in turn could be evacuated. These precautions were necessary not only because of the danger of hydrolysis of the products, but also because tribromosilane (silicobromoform) is spontaneously inflammable in the air. As a rule, the hydrogen passed at such a rate through the bromine that about 60 g. of the latter was vaporized in a run of five hours, yielding about 57 g. of mixed halides. Variations of this procedure are discussed below.

The first distillation of the mixture of halides obtained in one series of ten runs gave a fraction, representing about 60% of the total, boiling below 125°, the remainder distilling up to 154°. These proportions, however, were somewhat variable, even when conditions of temperature, rate of flow, fineness of subdivision of the silicon, etc., were kept as nearly constant as possible.

The crude fractions obtained in the first distillation as above described were finally fractionated in the apparatus shown in Fig. 2, the principal features of which were the means of transferring the liquid in an atmosphere of dry nitrogen and the spiral fractionating column, which enabled a remarkably sharp separation of the mixture. This type of column has been found exceptionally satisfactory in the distillation of

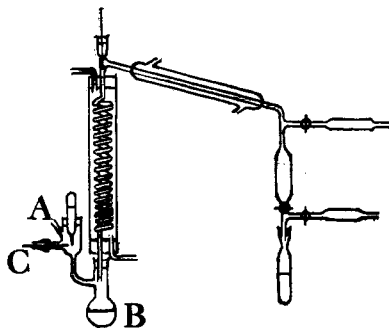


Fig. 2.

various mixtures of organic liquids by Professor H. S. Davis,<sup>6</sup> to whom we are indebted for the use of the spiral employed by us. The pyrex spiral was surrounded by a glass air-jacket, through which compressed air, preheated to a few degrees below the boiling point of the fraction being collected, was passed. Variation in the rate of flow of this air through an electrically heated tube enabled rather close adjustment of the temperature of the air-jacket.

In carrying out a fractionation, the sealed tube containing the crude sample was inserted, point downward, into the funnel (A); the whole apparatus was filled with dry, oxygen-free nitrogen; the tip of the sample tube was broken by the glass plunger (C), thus permitting the liquid to run down into the distilling flask (B). By means of this apparatus the crude fractions were separated quite sharply into three, possessing very definite boiling points: 64.0, 111.8, and 153.4° (corrected). These correspond to di-, tri- and tetrabromosilane, respectively. The lowest value, 64.0°, is somewhat lower than that given by Stock and Somiesky (66.0°), but their result was obtained indirectly by a rather long extrapolation of the vapor pressure curve for this substance and may be slightly in error.

The freezing point of silicobromoform is given in the literature as below -60°. Our product was found to freeze at  $-73 \pm 1^\circ$ , and showed a very decided tendency to undercool.

In one series of experiments the quantities of the fractions obtained were as follows: 64°, 7 g. or 2.8%; 111.8°, 166 g. or 66.1%; 153.4°, 78 g. or 31.1%. We were unable to obtain any evidence of the formation of monobromosilane,  $\text{SiH}_2\text{Br}$ , and we feel that if formed it must have been present in only minute quantities. A very small residue of material boiling above 153.4° was left in the distilling flask.

In studying the influence of varying conditions upon the reaction of hydrogen bromide on silicon, it was decided to observe the effect of the following variables: (a) the temperature, *i. e.*, to note the lowest temperature at which the formation of reaction products can be detected in a reasonable length of time, and to observe any change in the composition of the products obtained at increasingly elevated temperatures; (b) the rate of flow of the hydrogen bromide gas through the system; (c) the fineness of subdivision of the silicon; (d) the presence of alloying metals with the silicon, such as copper. The results in each case will be briefly indicated.

It was noted that below 340° the speed of reaction becomes so slow as to be imperceptible, but that above this temperature reaction becomes apparent, and at 360° progresses very readily. This is, of course, far below a visible red heat. In most of the work aimed at the preparation of silicobromoform, the temperature was kept close to 360°. To observe the effect of still higher temperatures the reaction tube was heated to 470° and later to 700° (as measured by a Hoskins pyrometer), at which temperature the pyrex tube softened slightly. It was found with rising temperature that the proportion of silicon tetrabromide was increased, and that of silicobromoform was decreased: Thus at 470° the reaction product consisted of approximately 55%  $\text{SiBr}_4$  and 45%  $\text{SiHBr}_3$ ; while

<sup>6</sup> H. S. Davis, *Ind. Eng. Chem., Anal. Ed.*, **1**, 61 (1929).

at 700° approximately 80% SiBr<sub>4</sub> was found, as compared with 31% obtained at 360°. <sup>7</sup>

The rate of flow of the gaseous hydrogen bromide was varied over a wide range, as is shown by the fact that whereas in a normal run 60 g. of bromine was consumed in a five-hour period, in other runs the same quantity of bromine was consumed in periods varying from two and one-half to fifteen hours. Examination of the products formed showed that the variation in the rate of flow of the hydrogen bromide over the range indicated was without noticeable effect upon the nature of the products formed, although a variation was noted in the percentage composition of the products, the fast runs yielding, in general, a greater proportion of silicon tetrabromide than the slowest runs. The significance of this fact will be discussed later.

The particle size of the silicon used was varied from 40-mesh to 150-mesh in successive runs, and in one case an alloy of copper and silicon (90% Cu, 10% Si) was substituted for the silicon; no difference in the nature of the products was detected by these changes. However, it was noted that, using the finely divided silicon, as the quantity of the element in the reaction tube diminished, the proportion of silicon tetrabromide found in the products tended to increase.

As concerns the mechanism of the reaction of gaseous hydrogen bromide on silicon, of several hypotheses which suggest themselves, we believe the following is the most probable. The primary product is silicon tetrabromide, formed by the reaction  $\text{Si} + 4\text{HBr} \rightarrow \text{SiBr}_4 + 2\text{H}_2$ , and the other compounds are produced either by side reactions, such as  $\text{Si} + 3\text{HBr} \rightarrow \text{SiHBr}_3 + \text{H}_2$  and  $\text{Si} + 2\text{HBr} \rightarrow \text{SiH}_2\text{Br}_2$ , or by consecutive reactions,  $\text{SiBr}_4 + \text{H}_2 \rightarrow \text{SiHBr}_3 + \text{HBr}$  and  $\text{SiHBr}_3 + \text{H}_2 \rightarrow \text{SiH}_2\text{Br}_2 + \text{HBr}$ . We are led to this conclusion through consideration of the following experimental facts.

(1) At 360°, hydrogen reduces silicon tetrabromide to a slight extent to silicobromoform. This was observed when a mixture of the vapor of purified silicon tetrabromide (b. p. 153.4°) and hydrogen was passed through a hard glass tube heated to this temperature and the resulting products were condensed; a very small proportion of material boiling below 150°

<sup>7</sup> This result does not agree with the observations of Gattermann in the study of the reaction of hydrogen chloride with silicon; he found the greater proportion of silicochloroform to be formed at 450–500°, while *lower* temperatures (300–310°) favored the formation of silicon tetrachloride. His silicon had been prepared from silica by reduction with magnesium powder, and its purity was not definitely stated.

In the preparation of silicobromoform, Gattermann used hydrogen bromide prepared from potassium bromide and concentrated sulfuric acid and dried the gas by passage through sulfuric acid, so that his gas must have contained free bromine, as well as sulfur dioxide; furthermore, his reaction product was colored reddish and doubtless contained free bromine. It is not surprising, therefore, to note that Gattermann found the product to consist mainly of silicon tetrabromide, with a small percentage of silicobromoform.

was obtained on distillation of this condensate. When the experiment was repeated at  $600^{\circ}$ , a similar result was obtained, and when another trial was made at  $600^{\circ}$ , the heated tube now being filled with powdered silicon, the products, when fractionated with a small spiral column of the type above described, yielded a small quantity of silicobromoform, (b. p.  $111.8^{\circ}$ ).<sup>8</sup>

(2) Silicobromoform is not converted, at  $360^{\circ}$ , into silicon tetrabromide by hydrogen bromide. When a mixture of gaseous hydrogen bromide and the vapor of silicobromoform was passed through a glass tube heated to  $360^{\circ}$ , no evidence of material boiling above  $111-112^{\circ}$  was obtained.

(3) It is improbable that dibromosilane reacts with hydrogen bromide to form silicobromoform, inasmuch as the di-halogen substitution products of methane,  $\text{CH}_2\text{Br}_2$ , and of monogermane,  $\text{GeH}_2\text{Br}_2$ , are known not to react with hydrogen bromide.<sup>9</sup> When this is considered in conjunction with the preceding fact, (2), it may be concluded that silicon tetrabromide cannot be formed from the less highly brominated compounds by the action of hydrogen bromide, but must rather be a primary product of the reaction.

(4) At higher temperatures, as at  $700^{\circ}$ , silicobromoform is decomposed almost completely into silicon tetrabromide, silicon and hydrogen (together with a very small proportion of hydrogen bromide). In our experiments the proportions of products obtained indicate that the decomposition progresses almost entirely according to the equation  $4\text{SiHBr}_3 \rightarrow 3\text{SiBr}_4 + \text{Si} + 2\text{H}_2$ . This fact accounts for the decreasing yield of silicobromoform and increasing proportions of the tetrabromide noted above in the reaction of hydrogen bromide on silicon at elevated temperatures.

### Summary

The reaction of gaseous hydrogen bromide with pulverized crystalline silicon has been studied with the object of determining the effect of varying conditions upon the nature and the percentage composition of the products. It was found that reaction becomes perceptible at about  $340^{\circ}$ , and progresses readily at  $360^{\circ}$ . The proportion of silicon tetrabromide formed increases with rising temperature, while that of silicobromoform decreases. Increase in the rate of flow of hydrogen bromide and decrease in the quantity of silicon in the reaction tube likewise favor increasing proportions of silicon tetrabromide formed. A small proportion of dibromosilane was obtained at the lowest temperatures, but monobromosilane, if formed, must be present in only very minute quantity.

<sup>8</sup> In this connection Friedel and Ladenburg [*Bull. soc. chim.*, [2] **12**, 92 (1869)] noted that when a mixture of silicon tetrachloride and hydrogen is heated to redness, a little silicochloroform is produced.

<sup>9</sup> Compare, for example, Dennis and Judy, *THIS JOURNAL*, **51**, 2321 (1929).

It is pointed out that at  $700^{\circ}$  silicobromoform is almost wholly decomposed into silicon tetrabromide, silicon and hydrogen.

The corrected boiling points of the products were:  $\text{SiBr}_4$ ,  $153.4^{\circ}$ ;  $\text{SiHBr}_3$ ,  $111.8^{\circ}$ ;  $\text{SiH}_2\text{Br}_2$ ,  $64.0^{\circ}$ . The freezing point of silicobromoform was fixed at  $-73 \pm 1^{\circ}$ .

As concerns the mechanism of the reaction, it is believed that the primary products are silicon tetrabromide and hydrogen and that the former is reduced in part by the hydrogen to form the other products. Experimental evidence in favor of this hypothesis is given.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NORTH CAROLINA]

## A STUDY OF THE QUANTITATIVE PRECIPITATION OF CALCIUM OXALATE IN THE PRESENCE OF THE PHOSPHATE ION

BY J. T. DOBBINS AND W. M. MEBANE

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In the course of the analytical work involved in a previous problem,<sup>1</sup> the authors found it necessary to make calcium determinations on a large number of solutions containing an excess of phosphoric acid. To avoid the long and tedious process of removing the phosphate ion as the ferric salt, a short method was devised whereby the calcium oxalate precipitation was made in the presence of the phosphate ion. Consistent results were obtained by the method, and on the completion of the previous problem a study was made to determine the general applicability of the method.

The method is based on the assumption that the so-called tertiary calcium phosphate, which forms on the addition of ammonium hydroxide to the solution, having a much greater solubility product than calcium oxalate, would go into solution and the calcium oxalate form. Consequently, if the solution be allowed to stand long enough for this metathesis to be complete, it would be possible to precipitate calcium oxalate in the presence of the phosphate ion. In order to determine the most favorable conditions under which to carry out the precipitation, several series of analyses were made to determine the time required for a complete transformation of calcium phosphate into calcium oxalate and the effect of temperature and alkalinity of solution at time of precipitation.

After first having found the minimum time necessary for the complete precipitation, series of analyses were made to determine the difference in results, if any, caused by adding the precipitating agent before and after the solutions were made alkaline with ammonium hydroxide. These series were run both at  $20^{\circ}$  and at  $100^{\circ}$ . Some preliminary experiments indicated

<sup>1</sup> Mebane, Dobbins and Cameron, *J. Phys. Chem.*, **33**, 961 (1929).