[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Thermal Decomposition of Silane

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As early as 1880 Ogier[1] noted that silane is completely decomposed into hydrogen and silicon when heated at 400° for several hours. Von Wartenburg[2] determined the extent of the decomposition of silane in the presence of finely divided nickel at temperatures ranging from 180 to 260°. He found the decomposition to be practically complete at 380° and his results led him to assume an equilibrium between silane, silicon and hydrogen

$$SiH_4 = Si + 2H_2 \qquad (1)$$

The kinetics of the thermal decomposition of both methane[3] and germane[4] have been recently studied. The methane reaction was found to be homogeneous and of the first order. In the latter study the reaction was shown to be heterogeneous with the rate of decomposition at the higher temperatures proportional to the one-third power of the undissociated germane. In the case of both germane and methane the hydrogen formed during the reaction exerted an inhibiting effect upon the rate of decomposition. The work of Ogier and Von Wartenburg indicated that a study of the kinetics of the decomposition of silane would be entirely feasible and this we have undertaken to complete the series, methane, silane and germane.

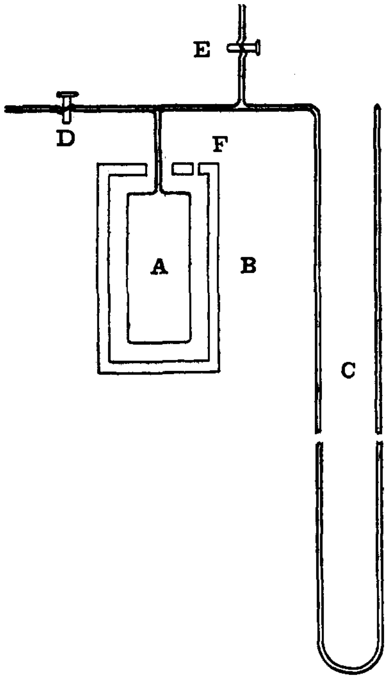

Fig. 1.

Experimental

Preparation of Silane.—The silane was prepared by allowing magnesium silicide, Mg_2Si, to drop into a solution of ammonium bromide in liquid ammonia.[5] The gas was carefully dried over phosphorus pentoxide and then separated from disilane and higher homologs by a series of fractional distillations and condensations. Analyses of the gas showed it to be of a very high purity.

Apparatus and Procedure.—Silane is very stable thermally at room temperature and decomposes very slowly even at temperatures in the neighborhood of 370°. At 500° and above its rate of decomposition is very high: too high to follow with the apparatus employed in the present study. Accordingly, all experiments were confined to the intermediate temperature range, 380–490°.

The rate of decomposition of silane was followed by observing the total pressure at different intervals of time. Since silane and hydrogen are the only gases present, the pressure of the undissociated silane may be determined readily at any time when the original pressure of silane is known.

The apparatus used in the experiments is shown in Fig. 1. The reaction vessel A, capacity of about 250 cc., was surrounded by a copper jacket which served to reduce any thermal gradients. The reaction vessel and jacket was heated by an electric furnace, not shown in the sketch, the temperature of which was determined by a Chromel-X-Copel thermocouple inserted in the well at F. In the experiments carried out at the higher temperatures, the temperature of the furnace was controlled with a manually operated variable resistance; at the lower temperatures, where the rate of decomposition is low, the temperature was controlled with U. V. 876 Ballast Tubes[6] to 1° over a period of at least ten hours. A was connected to a closed-end capillary manometer C and to stopcocks D and E by means of 2-mm. capillary tubing. The "dead" space in the external system was about 2% of the total volume. Stopcock E led to a one-liter auxiliary storage bulb containing silane, while D led to the external system and vacuum pumps. The mercury in the manometer was agitated with a small door bell buzzer.

Before each series of experiments the reaction vessel A was thoroughly evacuated and then, with stopcock D closed, E was opened for about ten seconds to allow the silane to enter A. The moment at which E was opened was taken as zero time. As the silane dissociated pres-

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(1) Ogier, *Ann. chim.*, [5] **20**, 37 (1880).

(2) Von Wartenburg, *Z. anorg. Chem.*, **79**, 71 (1912).

(3) Kassel, THIS JOURNAL, **54**, 3949 (1932).

(4) Hogness and Johnson, *ibid.*, **54**, 3583 (1932).

(5) Johnson and Isenberg, *ibid.*, **57**, 1349 (1935).

(6) Jones, *Gen. Elec. Rev.*, **28**, 329 (1925).

sure readings were taken on the manometer at fixed intervals of time.

The uncertainty in the time interval was of the order of two to three seconds, while that in the height of the mercury column was about 0.5 mm. At high temperatures and at low pressures these errors become appreciable but not serious. The pressure of the undecomposed silane at zero time was obtained in three ways. At the higher temperatures, above 450°, the reaction was allowed to go to completion and the initial pressure was taken as one-half the final pressure. At the lower temperatures, due to the presence of an induction period, it was possible to observe the initial pressure directly. In a few cases where it was not desirable to allow the reaction to proceed to completion (due to the inhibiting effect of the hydrogen the reaction was not complete in twenty-four hours), the initial pressure was found by the extrapolation to zero time of the pressure values measured in the first minute of decomposition. The last method was used in only a few cases as it is apt to give slightly high values for the initial pressure.

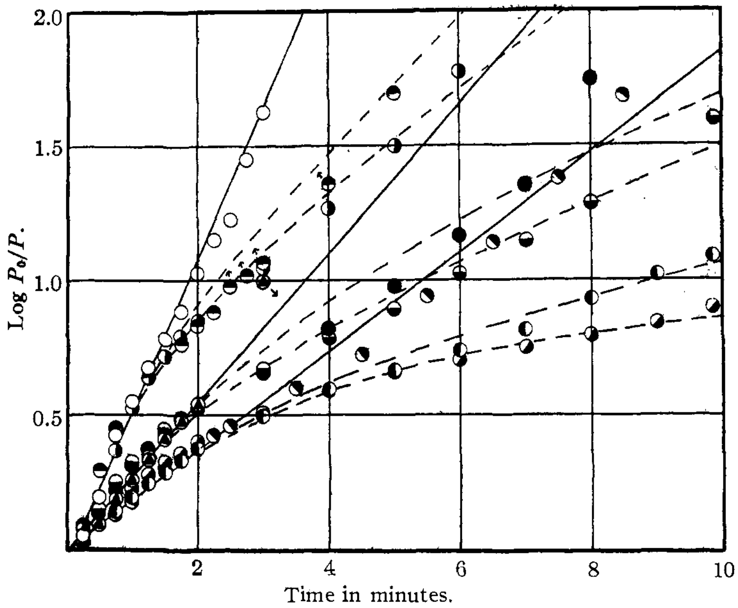

Fig. 2.

Results

The results of the measurements of the decomposition of silane at several different temperatures and pressures are shown in Figs. 2, 3 and 4, in which the logarithm of the ratio $P_0(SiH_4)/P(SiH_4)$ is plotted against the time in minutes. P_0 represents the initial pressure of silane and P, the pressure of silane at any specified time. In Fig. 2, the curves having the greatest slopes represent measurements at 488°, while those with the least slopes are at 461° and those with intermediate slopes, at 469°. Following the same order in Fig. 3, the temperatures are 440, 416 and 425°, respectively. In Fig. 4, all four experiments were carried out at 380°.

The Order of the Reaction.—The linear relationship between the logarithm of P_0/P and the time for the early part of each experiment indicates that for this pressure interval the reaction is of the first order. This first order relationship is particularly corroborated in Fig. 4 which more clearly shows that the rate is independent of the initial pressure. The experiments represented in this figure were carried out at initial pressures of silane of 14.2 (surface increased sixfold), 25.4, 31.8 and 39.5 cm. of mercury, respectively (reading in a clockwise direction). This same general effect is also shown in Figs. 2 and 3. All experiments at the same temperature approach the limiting first order line as the amount of decomposition becomes smaller. Reading clock-wise in Fig. 2 the initial pressures are 8.5, 19.7, 48.1, 8.7, 27.6, 44.4, 9.5, 29.1 and 55.7 cm. In a like manner the initial pressures for the series represented in Fig. 3 are 25.2, 39.8 (surface increased sixfold), 51.7, 4.3, 27.2 (surface increased sixfold), 8.5 and 20.3 cm., respectively.

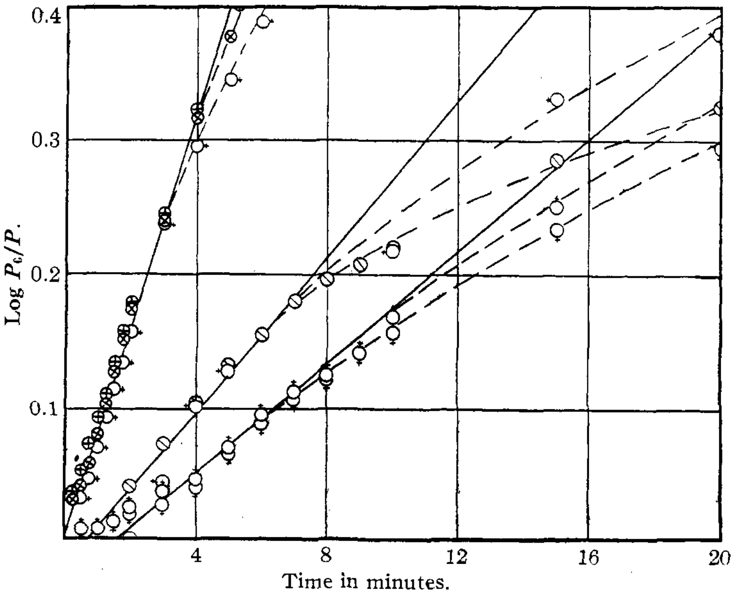

Fig. 3.

In plotting these same data appropriately for reaction orders of $^1/_2$, $^3/_2$, and 2, no consistent agreement was obtained. We were therefore forced to the conclusion that the principal factor in the rate of decomposition of silane was a first order reaction.

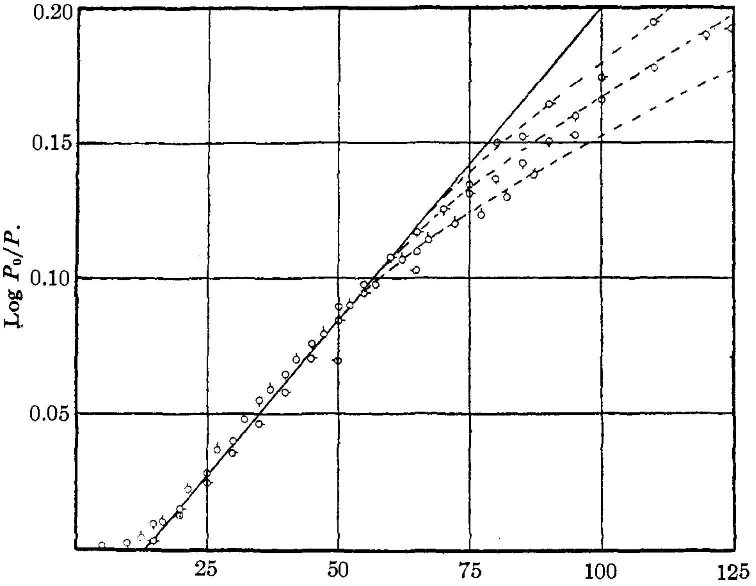

Fig. 4.

The Temperature Coefficient of the Reaction.—The rate constant K for the equation

$$-\mathrm{d}P/\mathrm{d}t_{(\mathrm{SiH_4})} = KP_{(\mathrm{SiH_4})} \qquad (2)$$

was determined at each temperature from the limiting straight line. The values of these constants so determined are given in Table I.

TABLE I

DATA FOR THE DECOMPOSITION OF SILANE AT DIFFERENT TEMPERATURES

Expts.	T, °K.	$1/T \times 10^3$	K sec.$^{-1}$ average	Log K
3	761	1.314	2.20×10^{-2}	−1.652
3	742	1.344	1.06×10^{-2}	−1.976
3	734	1.362	7.10×10^{-3}	−2.148
3	713	1.402	3.20×10^{-3}	−2.492
2	698	1.433	1.03×10^{-4}	−2.988
2	689	1.451	6.18×10^{-4}	−3.210
4	653	1.531	8.35×10^{-5}	−4.084

Figure 5 shows a plot of the logarithm of the rate constant against the reciprocal of the absolute temperature. The heat of activation for the thermal decomposition of silane was obtained from the slope of this line (Fig. 5) and from the equation $-\Delta H = R\ \mathrm{d} \ln K/\mathrm{d}(1/T)$, and was found to have a value of 51.7 ± 2 kcal. per mole. Thus it is possible to express the rate of the reaction as follows

$$w = 2 \times 10^{13} e^{-51,700/RT}\, p \text{ (cm. Hg) sec.}^{-1} \qquad (3)$$

where w represents the rate.

The Effect of Hydrogen.—As in the case of the thermal decomposition of both methane and germane, the hydrogen formed in the decomposition of silane acts as an inhibitor. At high temperatures and low initial pressures of silane this inhibition is not appreciable. At lower temperatures and high hydrogen pressures the hydrogen inhibition becomes quite marked, as can be seen from the curves in Figs. 2, 3 and 4.

In order to determine whether adsorbed hydrogen played any part in the reaction mechanism, adsorption measurements were made over the temperature range, −195 to 480°. Several liters of silane were allowed to decompose at high temperatures in order to obtain about 10 g. of finely divided silicon. This was placed in the usual adsorption apparatus, the free space of the system was determined with helium and then pure hydrogen gas was introduced. The measurements showed that, over the temperature range specified above, no hydrogen was adsorbed by the silicon. Even at pressures of hydrogen as high as 1 atm. no adsorption effect was observed within the limits of experimental error.

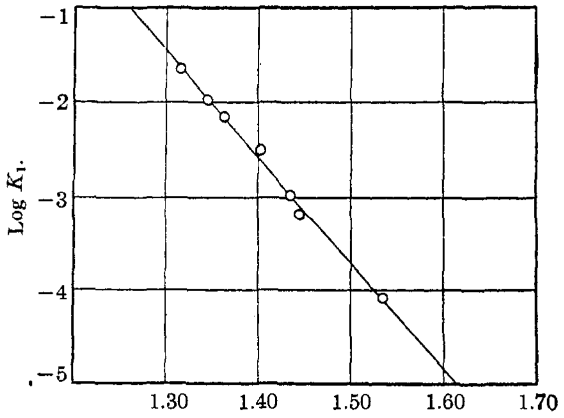

Fig. 5.

The Effect of Surface upon the Reaction.—In clean glass reaction vessels the decomposition of silane is apparently heterogeneous. At the lower temperatures the silicon formed as a result of the decomposition is deposited upon the walls of the reaction vessel in a dense metallic mirror having a high luster. During the early stages of the reaction, and before the glass has been completely covered by silicon, the rate of decomposition is many times that measured in a coated vessel. At the higher temperatures the silicon deposits as an extremely fine gray powder. All the rate measurements recorded above were made in reaction vessels which had been completely covered with silicon. To test the homogeneity of the reaction, experiments were carried out at 440, 425 and 380° in reaction vessels which had been packed with sufficient thin-walled glass tubing to increase the surface–volume ratio at least sixfold. Before these experiments were carried out, the surfaces of both the reaction vessel and enclosed tubes were coated with a thin layer of silicon by allowing silane to decompose slowly in the vessel at temperatures below 380°. In each case the experiments with packed tubes gave first order rate constants which agreed, within the experimental error, with the values calculated for those temperatures. The relatively high heat of activation provides further evidence of the essential homogeneity of the reaction.

The Induction Period.—In the experiments carried out at temperatures below 450° an induction period was observed which varied from one to two minutes at 425° to five to ten minutes at 380°. The induction period did not seem to be influenced appreciably by a change in the surface–volume ratio. It also appeared to be independent of the pressure of silane. Several attempts were made to detect disilane, Si_2H_6, in the reaction products, but these attempts were unsuccessful. It does not seem likely that the induction period could be due to the formation of polymerized silicon hydrides, although such a possibility cannot be entirely overlooked. In view of the fact that Kassel[3] found a similar phenomenon in the thermal decomposition of methane, it seems likely that this induction period is not due entirely, as he has suggested, to some peculiarity of the experimental arrangements.

Equilibrium.—Von Wartenburg,[2] who studied the decomposition of silane in the presence of finely divided nickel, assumed an equilibrium to exist between silane, silicon and hydrogen. However, he did not make an attempt to obtain information relative to the reverse reaction, namely, the formation of silane from silicon and hydrogen. In the adsorption experiments described above, in which the hydrogen was allowed to come in contact with very finely divided silicon over a considerable range of temperature for several days, no evidence whatsoever was obtained for the presence of silane in the gas mixture; it could not be detected when the hydrogen was removed from the apparatus nor was there any change in the hydrogen pressure to indicate the formation of silane. In view of these facts and of the rather inconsistent results of Von Wartenburg it is not permissible to make any definite statements one way or the other regarding the equilibrium.

Discussion

The unimolecular decomposition of silane might be considered as taking place initially in two ways

$$\text{(I) } SiH_4 = SiH_2 + H_2 \text{ and}$$
$$\text{(I-a) } SiH_4 = SiH_3 + H$$

Although there is no definite evidence as to which is the primary reaction, (I) appears to be the more plausible for several reasons. In the first place Ogier[1] has shown that silane, under the influence of the silent electric discharge, decomposes to give a solid which is a mixture of unsaturated hydrogen compounds and has a composition of about $(SiH_{1.5})_x$. Schwarz and Heinrich[7] have recently obtained similar results and, in addition, have prepared polysilene, $(SiH_2)_x$, by the action of acetic acid on calcium silicide, CaSi, in alcohol solution. It thus appears that the SiH_2 group is a relatively stable combination. Kassel,[3] on the basis of very good thermal and kinetic evidence, has selected as the initial stage in the decomposition of methane the reaction: $CH_4 = CH_2 + H_2$.[8] By comparison with methane the energy of dissociation of reaction (I-a) should be considerably greater than the activation energy we have found. On the other hand, the energy of dissociation for (I) very probably is not greater than the activa-

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(7) Schwarz and Heinrich, *Z. anorg. Chem.*, **221**, 277 (1935).

(8) Rice and Dooley [THIS JOURNAL, **56**, 2747 (1934)] oppose Kassel's interpretation of the methane decomposition and propose the reaction: $CH_4 = CH_3 + H$, as the initial stage in the decomposition. They give 100 ± 6 kcal. as the activation energy for the primary process. Kassel later defended his interpretation [THIS JOURNAL, **57**, 833 (1935)] by showing that the experimental data could not be explained satisfactorily by a mechanism which involves methyl radicals, whereas they could be explained by one which considers the methylene radical to be produced in the primary process. The thermal evidence introduced by Kassel seems valid and, since the heat of activation for the silane decomposition is much less than that for methane, we have additional evidence for choosing (I) as the primary process.

tion energy. These facts make it more reasonable that reaction (I) represents the primary process in the dissociation of silane.

Choosing (I) as the primary stage in the decomposition, we may represent the mechanism by the following subsequent reactions

$$\text{(II)} \quad SiH_2 = Si + H_2$$
$$\text{(III)} \quad SiH_2 + H_2 = SiH_4$$

The rate of decomposition of silane will then be

$$-d(SiH_4)/dt = k_1(SiH_4) - k_3(SiH_2)(H_2) \qquad (4)$$

(k_1, k_2 and k_3 represent the appropriate rate constants for the three steps, respectively). After a small interval of time, the concentration of the SiH_2 molecules reaches steady state conditions, *i. e.*, $d(SiH_2)/dt = 0$, and then the concentration of SiH_2 is given by

$$k_2(SiH_2) = k_1(SiH_4) - k_3(SiH_2)(H_2) \qquad (5)$$

This reduces to

$$(SiH_2) = \frac{k_1/k_2(SiH_4)}{1 + k_3/k_2(H_2)} \qquad (6)$$

Substituting the value for (SiH_2) found in (6) into equation (4) we obtain for the rate of decomposition of silane

$$-d(SiH_4)/dt = \frac{k_1(SiH_4)}{1 + k_3/k_2(H_2)} \qquad (7)$$

Although there is no definite information concerning steps (II) and (III) in the above mechanism, it is possible to make some general predictions regarding these reactions. It seems probable that k_2 should have a relatively large temperature coefficient as compared with k_3. In addition, k_2 is probably many times larger than k_3 at the temperature of decomposition. Thus the ratio k_3/k_2 is small and will decrease with increasing temperature. At high temperatures and low pressures of hydrogen, k_3/k_2 will be small as compared with unity and the reaction will be of the first order. If either the temperature is lowered or the hydrogen pressure increased, $k_3/k_2(H_2)$ will become larger as compared with unity and the rate of decomposition will fall off. This will explain qualitatively the behavior of the reaction as observed. Several attempts have been made to assign definite values at given temperatures to the ratio k_3/k_2 in order to give a quantitative description of the inhibiting effect of the hydrogen. This ratio is obtained from slopes of the rate curves. The magnitude of the experimental errors involved would not permit of a precise value being given to the ratio k_3/k_2. In the absence of any information regarding either the existence or the properties of any possible products of the pyrolysis of silane, it does not seem desirable to postulate any more complex mechanism than that already given.

Summary

The thermal decomposition of silane has been studied at several temperatures ranging from 380 to 490° and over a considerable pressure range. The results show the reaction to be homogeneous and of the first order.

The hydrogen produced by the decomposition of silane is found to act as an inhibitor for the reaction. This effect does not appear to be due to the adsorption of hydrogen by the silicon.

The results give no indication of a reaction between hydrogen and silicon to form silane.

A simple mechanism is suggested for the decomposition of silane.

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