

2. The experimental work of Euler and Hedelius has been confirmed, but the writers present evidence to show that these results are due to the presence of zinc in the silver used.

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HEXAFLUORODISILANE¹

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The only binary fluoride of silicon that has been definitely established up to the time of the present writing is the tetrafluoride, SiF_4 . To be sure, H. St. C. Deville,² and Troost and Hautefeuille³ reported the formation of substances which they believed to be subfluorides when (a) aluminum and silicon tetrafluoride were heated; (b) the gaseous tetrafluoride was passed over hot silicon; or (c) when a spark was passed through the tetrafluoride between silicon electrodes. The supposed subfluorides were described as gaseous, liquid, and solid.

In more recent times Jacquerod and Tourpaian,⁴ working upon the density of silicon tetrafluoride, attempted to account for observed high values by the assumption that the passage of the gas over glass wool at red heat might have the effect reported by Troost and Hautefeuille, although the latter investigators passed the gas over elementary silicon at a much higher temperature. Furthermore, since no analyses either for silicon or fluorine were mentioned, and since the high densities referred to may be accounted for in several other ways, the evidence in favor of a subfluoride must be considered as based largely upon the work of the earlier experimenters.

Repetition of this work has failed to confirm the results claimed. Thus Ruff⁵ states that he failed to obtain the subfluoride, of unknown composition, either by passage of the tetrafluoride over molten silicon and rapid cooling of the vapors, or by reduction of the tetrafluoride by graphite at 2000° , or by reduction with hydrogen; and Mellor⁶ states that "the evidence for the existence of the subfluoride is not unimpeachable; and its composition is unknown."

¹ The present paper constitutes the detailed account of the work upon Si_2F_6 referred to in our communication to the Editor published in *THIS JOURNAL*, **53**, 3191 (1931).

² H. St. C. Deville, *Ann. chim. phys.*, [3] **49**, 76 (1857).

³ Troost and Hautefeuille, *ibid.*, [5] **7**, 464 (1876).

⁴ Jacquerod and Tourpaian, *J. chim. phys.*, **11**, 19 (1913).

⁵ Ruff, "Die Chemie des Fluors," 1920, p. 119.

⁶ Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," 1925, Vol. VI, p. 934.

In spite of the negative character of the earlier work just referred to, the strong presumption remains that binary silicon fluorides other than the tetrafluoride should be capable of independent existence. This belief is strengthened by the fact that analogous compounds of carbon with fluorine have been prepared by Chabrié⁷ and more recently have been referred to by Ruff.⁸ Thus Chabrié prepared tetrafluoroethylene, C_2F_4 , by heating silver fluoride and tetrachloroethylene in a sealed tube. Reactions were also observed by him to take place when hexachloroethane, C_2Cl_6 , and hexachlorobenzene, C_6Cl_6 , were separately heated in a sealed tube with silver fluoride, but the products formed were not identified. Ruff, in studying the reaction of various varieties of carbon with fluorine, has recently reported that, in addition to a very large proportion of carbon tetrafluoride, small quantities of less volatile products were condensed, which he believes contain such substances as hexafluoroethane, C_2F_6 , and dodecafluorocyclohexane, C_6F_{12} . Further details concerning these products were promised by the authors.

In view of these facts, it is proposed to describe in this paper the preparation and some of the properties of hexafluorodisilane, Si_2F_6 , together with other observations which have been made in this Laboratory during a study of the reaction of silicon with fluorine. The extension of this work to include the preparation of higher members of the series, Si_nF_{2n+2} , is now in progress.

It was decided to observe first whether when silicon burns in fluorine any product other than the tetrafluoride could be detected. The procedure followed was much the same as that previously described⁹ in our study of sulfur hexafluoride, the fluorine generator being connected by copper tubing to a copper trap, cooled by a carbon dioxide-alcohol bath to about -78° , wherein any hydrogen fluoride was very largely condensed; then to a copper tube containing granular sodium fluoride to catch any remaining hydrogen fluoride. With reasonably dry electrolyte ($KF \cdot HF$) the amount of hydrogen fluoride present in the gas after the generator has been operating a short time is very small, so that the provisions for removal of this gas proved to be more than adequate. The silicon employed was the crystalline variety, broken into small lumps, and was contained in a 2.54-cm. copper tube coupled to the rest of the apparatus. Inasmuch as the combination of silicon with fluorine is an intensely vigorous reaction, the copper tube was cooled externally with water from time to time. After leaving the reaction tube the gases passed through two glass condensing tubes, cemented to the copper with deKhotinsky cement, the first condenser being cooled with a carbon dioxide-alcohol mixture, the second with liquid air.

After a continuous run of fourteen hours, practically nothing had collected in the condenser at -78° , while about 200 g. of solid silicon tetrafluoride had been condensed by the liquid air. From the results of this preliminary experiment, it appeared probable that any fluorides less volatile than SiF_4 , if formed, must be present in exceedingly small proportions. It is probable that the temperature in the zone of reaction is so high that any such compound would not be stable and with the rupturing of the Si-Si linkage

⁷ Chabrié, *Compt. rend.*, **110**, 279 (1890); *Bull. soc. chim.*, [3] **7**, 18 (1892).

⁸ Ruff and Keim, *Z. anorg. allgem. Chem.*, **192**, 249 (1930).

⁹ Schumb and Gamble, *THIS JOURNAL*, **52**, 4302 (1930).

only SiF_4 would result. Rapid chilling of the gaseous products would favor the formation of such compounds and further experimentation along this line is anticipated.

Fluorine was next passed through the same apparatus over ferrosilicon containing 84.5% Si, with the aim of moderating the intensity of the reaction and of favoring the formation of silicon fluorides of higher molecular weight, but again the condenser, cooled to -78° , in which such fluorides would naturally be expected to be retained, yielded practically nothing.

It appeared to us probable, however, that the most promising method for the preparation of the fluorides derived from disilane, trisilane, etc., would be to start with the corresponding chlorides, Si_2Cl_6 , Si_3Cl_8 , etc., and to bring about replacement of chlorine by fluorine. This was in fact accomplished by warming together hexachlorodisilane, Si_2Cl_6 , with anhydrous zinc fluoride, condensing and fractionating the products. The hexachlorodisilane was prepared by the chlorination of silicon alloys, such as "calcium silicon" and "calcium manganese silicon."¹⁰ The temperature of the reaction tube containing the alloy was kept only high enough to maintain a continuous reaction—not far from 180° . From the crude product, yields of Si_2Cl_6 as high as 20 to 25% were obtained, considerably exceeding the yields reported by Martin,¹¹ who employed 50% ferrosilicon for this purpose.

For the preparation of hexafluorodisilane, "anhydrous" zinc fluoride was dried overnight at 110° , and to 100 g. of it contained in a dry Erlenmeyer flask was added 40 g. of freshly distilled Si_2Cl_6 (b. p. $145 \pm 0.5^\circ$). The flask was sealed to two receivers, cooled by carbon dioxide-alcohol and by liquid air, respectively, and to a drying tube communicating with the outer air. Upon warming to $50-60^\circ$, a vigorous reaction was noted which, once started, continued without further application of heat for about one and one-half hours. Both receivers contained considerable quantities of white solids; that in the liquid air proved to be silicon tetrafluoride, which sublimed without residue. The other receiver contained a mixture of a small amount of unchanged Si_2Cl_6 together with about 9-10 g. of Si_2F_6 , which was obtained from the mixture in a condition of purity by repeated sublimation. As the equilibrium pressure of this substance at room temperature is too great to permit preserving it safely in glass, the bulb containing it was kept cool throughout the subsequent work.

Hexafluorodisilane thus prepared is a colorless gas at ordinary temperatures, which instantly hydrolyzes in moist air with the formation of white solid hydrolysis products (see below); when cooled it condenses to snowy white crystals, which on warming, under slightly more than normal atmospheric pressure, melt to a colorless liquid.

Vapor Pressure Measurements.—The measurements of vapor pressure were carried out in the same apparatus and in the same manner as that described⁹ in a former paper concerning sulfur hexafluoride, and the attainment of equilibrium pressures was insured by the agreement in the values observed with falling and with rising temperatures. About 8 g. of the resublimed material was taken at the start and the purity of the substance was tested by the constancy of the equilibrium pressures obtained after successive portions of the substance had been vaporized, as well as by the fact that the gas density determined upon the same material, as described below, remained constant for the first as well as for the very last portions to vaporize.

¹⁰ Supplied us by the Electro Metallurgical Sales Corp., Niagara Falls. "Calcium-silicon" contained 30-35% Ca, 60-65% Si; "calcium-manganese-silicon" contained 17-18% Ca, 8-10% Mn, 55-60% Si.

¹¹ Martin, *J. Chem. Soc.*, **105**, 2836 (1914).

The vapor pressures of hexafluorodisilane, both as solid and as liquid, were determined over the range -79 to -4° . The temperatures were observed upon a toluene thermometer entirely immersed in the alcohol in the large Dewar tube thermostat; the thermometer had been checked by the Bureau of Standards at a number of points. Manometer readings, corrected to 0° , are recorded in Table I and the accompanying graph. It will be noted in the graph that the curve for the liquid was extended well into the supercooled region.

The melting point of the substance as determined by the intersection of the two branches of the vapor pressure curve agrees well with the direct observation of the temperatures of melting and solidification which were repeatedly carried out on the same material. The melting point of hexafluorodisilane, under the pressure of its own vapor, was thus found to be $-18.7 \pm 0.1^{\circ}$.

TABLE I
VAPOR PRESSURE OF HEXAFLUORODISILANE

Experimental data			Interpolated from graph		
Corr. emp., $^{\circ}\text{C}$.	Corr. press., mm.	Corr. temp., $^{\circ}\text{C}$.	Corr. press., mm.	Temp., $^{\circ}\text{C}$.	Corr. press., mm.
-78.9	3.0	-19.4	738.4	-75	3
-60.7	13.5	-18.9	773.2	-70	5
-59.2	15.5	-19.4	755.7	-65	7
-51.3	37.9	-20.1	731.5	-60	14
-50.2	42.8	-20.6	720.8	-55	25
-45.1	73.7	-21.1	693.4	-50	45
-44.6	77.2	-21.9	662.6	-45	77
-37.5	152.4	-22.5	644.2	-40	125
-36.6	175.8	-24.1	592.7	-35	197
-32.8	237.5	-24.6	576.5	-30	304
-32.4	247.5	-25.1	561.6	-25	467
-29.5	319.6	-25.6	544.4	-20	703
-27.8	367.0	-26.5	515.8	-15	937
-25.6	448.5	-27.5	487.7	-10	1195
-25.1	464.8	-28.0	456.5	-5	1505
-24.9	492.0	-18.6	779.6		
-23.7	528.8	-18.5	784.6		
-23.4	537.3	-18.3	794.5		
-22.4	589.5	-18.1	804.0		
-22.3	595.0	-17.1	839.3		
-21.4	631.8	-15.1	929.9		
-20.4	680.1	-12.6	1048.9		
-20.3	685.1	-9.6	1217.8		
-20.2	692.6	-6.5	1402.1		
		-3.7	1579.3		

^a Region of supercooled liquid. Pressures throughout are for mercury at 0° .

From the graph, the temperature at which the vapor pressure of this substance becomes 760 mm. is found to be -19.1° , that is, very slightly below

its melting point, a circumstance that is not uncommon among fluorides of this type.

Gas Density.—The formula, Si_2F_6 , was checked by four determinations of the density of the substance in the gaseous condition, whence the molecular weight could be calculated approximately. The densities were

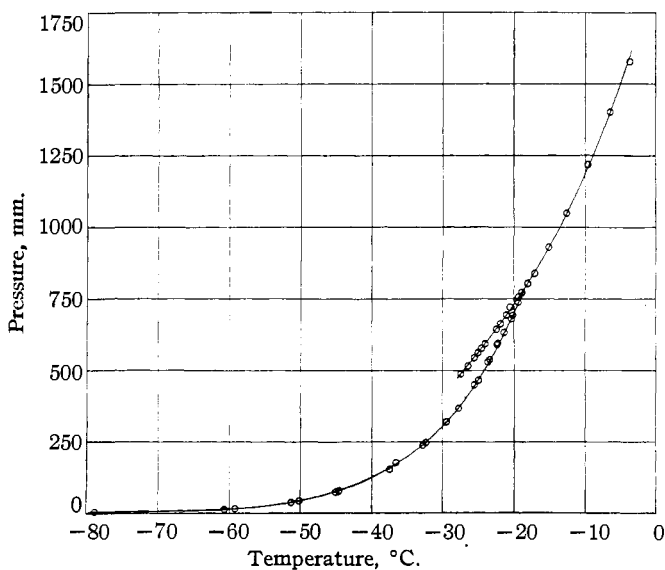


Fig. 1.

determined by observing the gain in weight of an evacuated glass globe (volume, before evacuation, 495.58 cc.) when filled with the gas at a known pressure and temperature. The weighings were done by the counterpoise method, and the precautions and corrections customary in such work were observed.

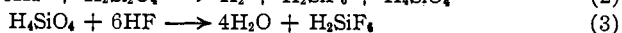
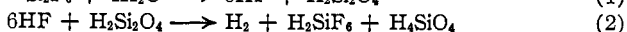
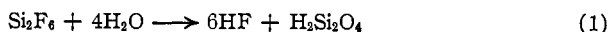
GAS DENSITY RESULTS

Corr. pressure, mm. at 0°	Temp., °C.	Wt. of gas, g.	Mol. wt.
702.6	21.4	3.2842	173.2
754.6	20.0	3.5658	174.2
753.9	20.0	3.5654	174.5
306.7	24.8	1.4175	173.2

The calculated molecular weight is in sufficiently close agreement with the theoretical value for Si_2F_6 , 170.1, to serve as a check upon the composition of the substance. The mean value of the density of the gas at 0°, 760 mm., calculated from the data given, is 7.759 g. per liter; the relative density referred to air being 5.997, assuming the average molal weight of air to be 28.98.

Hydrolysis.—The hydrolysis of hexafluorodisilane differs sharply

from that of silicon tetrafluoride in that hydrogen gas is formed as one product. Other products are 1,2-bis-(oxy-oxo)-disilane, or "silico-oxalic acid," $\text{H}_2\text{Si}_2\text{O}_4$, fluosilicic acid, H_2SiF_6 , and silicic acid. Quantitative evidence was sought in order to establish a reasonable hypothesis for the mechanism of the hydrolysis. The experiments, which will be briefly described, lead us to believe that the hydrolytic action consists of three consecutive reactions, as follows



Corroborative evidence of reaction (2) is found in the fact that "silico-oxalic acid," when separately treated with hydrofluoric acid, yields hydrogen. The extent to which the separate reactions proceed will depend upon such conditions as the temperature, time of contact, quantity of water employed, etc.

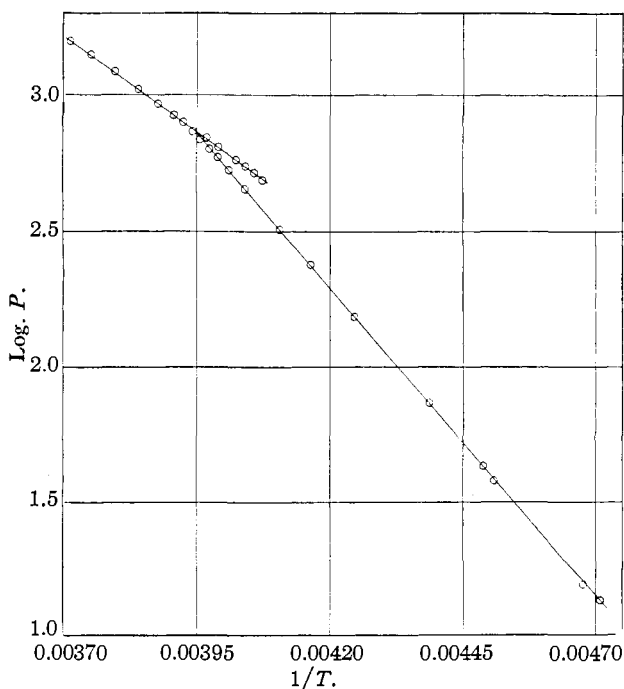


Fig. 2.

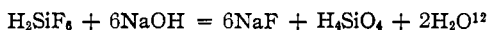
Cylindrical glass bulbs (volume approximately 120 cc.), supplied with stopcocks at each end, were evacuated and gaseous hexafluorodisilane was admitted, the weight of gas being determined by the gain in weight of the bulb, using a similar glass counterpoise. One end of the bulb was now dipped into distilled water; in one case previously chilled water was used, in two other trials the water was at room temperature. On opening the

lower stopcock and slightly cooling the upper part of the bulb water was drawn into the bulb and the gas instantly hydrolyzed with the separation of a white solid. When about 30 cc. of water had entered, the lower cock was closed and the bulb shaken for some time so as to obtain thorough mixing of the contents.

The hydrolysis products contained in the bulb were examined as follows. The gaseous portion was drawn over into a gas buret and proved to be hydrogen. The bulb was next broken open and the liquid contents filtered; the solid residue consisting mainly of silicic acid was dried and ignited to SiO_2 . The filtrate was treated with a known weight of potassium chloride and alcohol was added in volume equal to that of the solution, thereby precipitating the fluosilicate as K_2SiF_6 , which was filtered off, dried at 110° and weighed; the chloride thus introduced was later recovered quantitatively as silver chloride, thus indicating the absence of any appreciable quantity of chloride in the original hexafluorodisilane. In a typical experiment, 0.8420 g. of the gas on hydrolysis and subsequent treatment as already described, yielded 86.8 cc. of hydrogen (reduced to dry basis, 0° , 760 mm.); a total of 0.3592 g. SiO_2 ; 0.9280 g. K_2SiF_6 ; and no chloride. These data are in reasonable agreement with the series of reactions given, and the assumption that, while reaction (1) proceeds very rapidly to completion, only about 80% of the "silico-oxalic acid" formed reacts with HF according to (2)—the rest of the HF reacting in (3) with some of the silicic acid liberated in (2).

Analysis.—The elementary analysis of hexafluorodisilane proved to be somewhat troublesome, but the method finally employed yielded very satisfactory results. A known weight of the substance, which had been repeatedly sublimed, was introduced into a well-evacuated glass bulb which was provided with a stopcock at each end; the gain in weight of the bulb, which had a volume of about 65 cc., gave the weight of the sample. The bulb was now connected at one end with a source of dry nitrogen and at the other end with a tube ending in a funnel-shaped opening which dipped below the surface of distilled water in a beaker. The gas within the bulb was now swept out at a very slow rate by the stream of nitrogen into the water and was hydrolyzed thereby instantly and completely. The water was kept stirred so that the surface did not become caked over with solid hydrolysis products. The sweeping process was continued for about half an hour, which proved to be adequate for the complete displacement of the gaseous fluoride.

The contents of the beaker were filtered and the filter was thoroughly washed; the filtrate, containing hydrofluoric and fluosilicic acids, was titrated with standard, carbonate-free alkali (0.4972 *N* NaOH), using phenolphthalein as an indicator. Hereby not only the hydrofluoric acid but also the fluosilicic acid is quantitatively converted into sodium fluoride



From the results of this titration the percentage of fluorine in the sample was calculated.

The silicon in the sample was determined as SiO_2 ; the bulk of this was obtained by collecting, drying and igniting the solid hydrolysis products—silicic acid and 1,2-bis-(oxy-oxo)-disilane—or "silico-oxalic acid"; the rest was obtained by evaporating the filtrate, after neutralization with alkali as above described, baking the residue at 115° , leaching out the soluble matter, filtering, drying and igniting the silica. From the combined weights of silica the percentage of silicon in the sample was calculated.

¹² The validity of this method, which was employed by Sahlbom and Hinrichsen [*Ber.*, 39, 2609 (1906)], was demonstrated by separate experiments made with pure sodium fluosilicate, which it was found may be quantitatively converted into the fluoride by titration with 0.5 *N* alkali, using phenolphthalein as an indicator.

THE ESSENTIAL DATA AND RESULTS

Sample, g.	0.4972 N NaOH used, cc.	Total SiO ₂ , g.	F, %	Si, %
0.4635	32.76		66.77	
.4616	32.65		66.82	
.4652		0.3223		32.37
.4625		.3243		32.76
		Theory for Si ₂ F ₆	67.01	32.99

In conclusion, it seemed to us important to determine whether the reaction employed to produce hexafluorodisilane could be applied in an analogous manner to the preparation of the corresponding fluoride of carbon, C₂F₆, which, as stated above, Chabrié⁷ very probably had first prepared by heating silver fluoride with hexachloroethane in a sealed tube. In this case, however, unsatisfactory results were obtained at ordinary pressure with anhydrous zinc fluoride and hexachloroethane, because when heated together in a flask, the chloride sublimes unchanged; when the vapors of the chloride were passed over zinc fluoride contained in a large graphite boat inside a Pyrex tube at 250–300° the same results were obtained; and when higher temperatures (400–450°) were used partial decomposition of the chloride occurred, yielding chlorine and tetrachloroethylene, as well as a large amount of unchanged original chloride, but no detectable amount of volatile fluoride. A solution of hexachloroethane in diphenyl, refluxed with zinc fluoride at the boiling point of the solution, likewise failed to give the desired results. Further experimentation is planned along these lines, especially under increased pressure.

Summary

1. Hexafluorodisilane, Si₂F₆, has been prepared by gently warming hexachlorodisilane with anhydrous zinc fluoride, followed by condensation and fractionation of the products.

2. This substance is gaseous under ordinary conditions of temperature and pressure, but may be condensed to a white solid melting at –18.7° under 780 mm. pressure. The vapor pressures of the substance as solid and liquid have been determined from –79 to –4°; the vapor pressure becomes 760 mm. at –19.1°.

3. The molecular weight, 173.8, calculated from gas density determinations, agrees reasonably well with the theoretical for Si₂F₆ (170.1).

4. The hydrolysis of this substance yields hydrogen, silicic acid, fluosilicic acid, 1,2-bis-(oxy-oxo)-disilane or "silico-oxalic acid" and some hydrofluoric acid. The mechanism of this process, which was studied quantitatively, is discussed.

5. The preparation of hexafluoroethane by the interaction of hexachloroethane and zinc fluoride has failed to give satisfactory results under ordinary pressure.

6. In the preliminary preparation of hexachlorodisilane greatly improved yields were obtained by the chlorination of calcium–silicon alloys or calcium–manganese–silicon alloys in place of ferrosilicon.