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FLUROCHLORIDES OF SILICON

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Although an extensive series of silicon mixed halides has long been known,¹ those containing fluorine as one constituent appear not to have been isolated. Interest in the preparation of such compounds is to be found in the fact that the analogous carbon compounds, such as difluorodichloromethane, have recently come into prominence as excellent refrigerants.

With the isolation of hexafluorodisilane, Si_2F_6 , a convenient way² was open for the preparation of such mixed halides as SiF_3Cl , SiF_2Cl_2 and SiFCl_3 , and in the present paper the isolation and the properties of the first two of these compounds, trifluorochlorosilane and difluorodichlorosilane, will be described.

When hexafluorodisilane and chlorine are mixed at room temperature there is no apparent reaction, but when the mixture is strongly heated at one point for a few seconds a mild explosion occurs, resulting in the formation of silicon tetrafluoride, trifluorochlorosilane and difluorodichlorosilane. When an excess of hexafluorodisilane is used in the reaction, amorphous silicon is formed at the same time as the gaseous products of the reaction.

The hexafluorodisilane used in this work was prepared by the action of zinc fluoride on hexachlorodisilane as previously described.² The apparatus as shown in Fig. 1 was adopted to carry out the reaction between hexafluorodisilane and chlorine. Condenser A was evacuated and hexafluorodisilane distilled into it, solid carbon dioxide and alcohol being used to cool this condenser. Dry chlorine was passed into condenser C, which was cooled by carbon dioxide and alcohol, and was thereby condensed to a liquid. With condensers A and C in liquid air, the entire system was completely evacuated. To measure out a known volume of hexafluorodisilane, the Dewar was removed from around condenser A, and the tube B allowed to fill with gas to a pressure of one atmosphere. The alcohol in the Dewar containing C was kept about -35° or the approximate boiling point of chlorine; thus D could be filled with chlorine at a pressure of approximately one atmosphere. The hexafluorodisilane from B and the chlorine from D were next condensed in E by means of liquid air and the stopcocks to B and D closed. The Dewar surrounding E was then removed and the mixture of hexafluorodisilane and chlorine distilled into the explosion chamber F. When there was no more solid or liquid in E the stopcock between E and F was closed and the flame of a small blast burner applied to F at one point, whereupon in fifteen to thirty seconds a mild explosion would take place in F. This explosion was accompanied by a flash of light and a whistling noise. The products of the reaction were then completely removed from F by condensing them out in G, which was cooled by liquid air. The process of filling the chamber F and exploding the mixture therein was then repeated until all the hexafluorodisilane had been brought into reaction.

¹ See, for example, Friend, "A Textbook of Inorganic Chemistry," Vol. V, p. 198.

² Schumb and Gamble, THIS JOURNAL, 54, 583 (1932).

Although the explosions in F were never sufficient to do any damage to the apparatus it was thought advisable to wrap this combustion tube with wire gauze. The chamber B for measuring out the hexafluorodisilane had a volume of about 150 cc., D for measuring the chlorine a volume of about 300 cc., and the combustion chamber about 600 cc. Thus about two volumes of chlorine were mixed with one volume of hexafluorodisilane and exploded under a total pressure less than atmospheric.

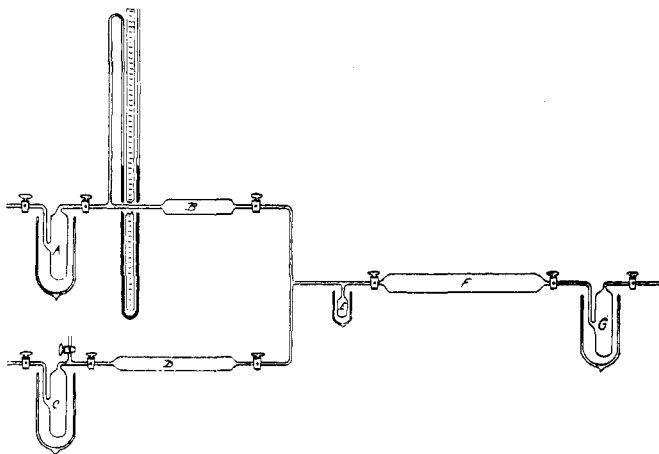


Fig. 1.

To remove the excess of free chlorine from the mixture of the gases, the products of combustion were transferred to an evacuated flask containing mercury and shaken occasionally until no further decrease in pressure was observed on the manometer attached to the flask. The removal of chlorine in this way appeared to be complete in about twenty-four hours.

To separate the mixture of silicon tetrafluoride, trifluorochlorosilane and difluorodichlorosilane, the fractionation apparatus as shown in Fig. 2 was used. In the construction of this apparatus certain features of the precision type columns developed by Podbielniak³ in the separation of highly complex mixtures of hydrocarbons were adopted.

The column was a 7-mm. Pyrex tube 65 cm. high, the lower 20 cm. being vacuum jacketed. A spiral made of small copper wire, about five turns to the inch, and fitting snugly to the inside of the column served to conduct the capillary films of condensed liquid back to the bulb. The upper 45 cm. of the column was surrounded with a jacket containing carbon dioxide and alcohol. This cooling of the column was so effective that the temperature of the escaping gases varied only slightly from the sublimation temperature of carbon dioxide. The manometer M_1 registered the pressure in the column; the rate at which the gases were distilled was controlled by the adjustment of stopcock S. From the change of pressure observed on manometer M_2 while the gases were being collected in a 100-cc. bulb (D) the rate of flow could be established quite accurately. The evacuated one-liter globes B, C and F and the two-liter globe E served to hold the gas fractions as they were collected; the tube G, cooled by liquid air, served to condense all the gases which were to be collected during the intervals when the pressure was not constant. As the temperature of the gases leaving the column was almost constant, the

³ Podbielniak, *Ind. Eng. Chem., Anal. Ed.*, **3**, 177 (1931).

change in pressure on M_1 served as a guide in determining where the fractions should be cut.

After the elimination of the free chlorine as above described, the mixture of silicon tetrafluoride, trifluorochlorosilane and difluorodichlorosilane was transferred quantitatively from the flask to the small bulb A at the bottom of the column by means of liquid air. A was then placed in a carbon dioxide-alcohol bath until most of the silicon tetrafluoride had distilled; the carbon dioxide bath was then gradually lowered, the gases being collected at the rate of about 600 cc. per hour.

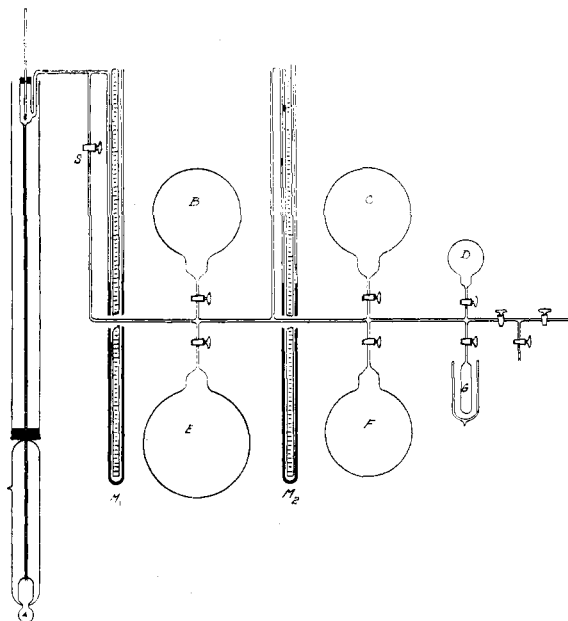


Fig. 2.

This procedure yielded three fractions of approximately the same volume, together with a very small amount of higher boiling material.⁴ As a check upon the composition of each of these fractions, their molecular weights were determined by the gas density method. A globe of known weight and volume (495.58 cc.) was attached to the end of the fractionation apparatus and thoroughly evacuated. The fraction the molecular weight of which was to be determined, was drawn into G by means of liquid air and then admitted to the globe to be weighed. The temperature of the room was taken as the temperature of the gas (after standing for twenty minutes) and the pressure was taken from manometer M_2 . The first fraction gave the molecular weight of 103.6; the theoretical value for SiF_4 is 104.06. The results of three determinations on the second fraction were 121.5, 121.7 and 121.3, which are in reasonable agreement with the theoretical value for SiF_2Cl , 120.52. The results of three determinations on the third fraction were 138.9, 138.4 and 138.7; calcd. for SiF_2Cl_2 , 136.97.

Under ordinary conditions trifluorochlorosilane and difluorodichlorosilane are

⁴ Because of the difficulty of purifying the small quantity of this higher boiling residue, its composition was not definitely established, but it is probable that a little of a third fluorochloride, SiFCl_3 , was contained therein.

gases with very pungent odors, resembling that of silicon tetrafluoride. They are readily hydrolyzed on coming into contact with the moisture of the air. Trifluorochlorosilane boils at -70.0° and melts at -138° ; difluorodichlorosilane boils at -31.7° and melts at -144° .

Vapor Pressures.—The apparatus and method used for measuring the vapor pressures of trifluorochlorosilane and difluorodichlorosilane were essentially the same as previously used in work⁵ with sulfur hexafluoride. In taking the measurements for trifluorochlorosilane over the temperature interval below that which could be obtained with carbon dioxide and alcohol, the bath was chilled by the addition of small lumps of solid alcohol, which had been frozen by means of liquid air. The purity of the samples was assured by obtaining check readings of the vapor pressure with variable amounts of liquid, *i. e.*, with part of the sample being withdrawn from the apparatus between readings. Figure 3 shows the results obtained for the vapor pressures of trifluorochlorosilane and difluorodichlorosilane when the reciprocal of the absolute temperature is plotted against the logarithm of the pressure.

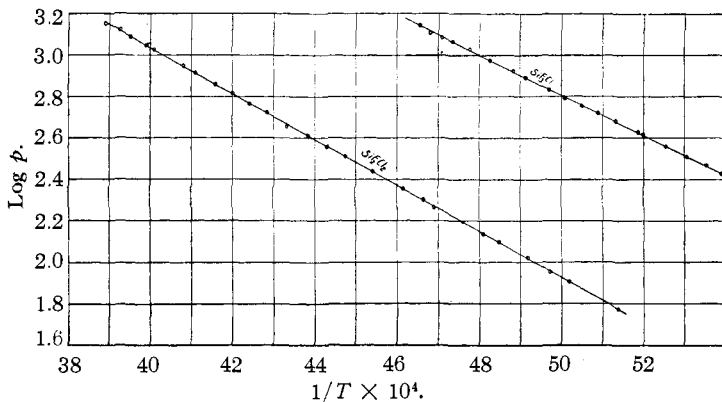


Fig. 3.

The vapor pressure of these two liquids is represented by the following empirical equations; for trifluorochlorosilane

$$\log p = 7.6440 - \frac{967.16}{T}$$

and for difluorodichlorosilane

$$\log p = 7.4832 - \frac{1111.1}{T}$$

In the following tables are shown the values of the observed pressure (expressed in mm. of mercury at 0°) and the values as calculated from the above equations at the same temperature.

⁵ Schumb and Gamble, *THIS JOURNAL*, **52**, 4302 (1930).

TRIFLUOROCHLOROSILANE					
Temp., °C.	<i>P</i> obs., mm.	<i>P</i> calcd., mm.	Temp., °C.	<i>P</i> obs., mm.	<i>P</i> calcd., mm.
-86.3	293.0	292.8	-72.0	683.0	683.3
-83.6	342.8	346.9	-69.3	796.1	791.2
-81.8	386.4	387.4	-65.8	955.2	951.5
-80.7	416.0	414.2	-65.6	959.6	961.6
-78.2	481.5	477.6	-63.6	1066.	1065.
-75.1	581.5	574.6	-61.2	1198.	1202.
-73.3	637.1	635.9	-57.9	1409.	1412.

DIFLUORODICHLOROSILANE					
Temp., °C.	<i>P</i> obs., mm.	<i>P</i> calcd., mm.	Temp., °C.	<i>P</i> obs., mm.	<i>P</i> calcd., mm.
-78.5	59.7	59.4	-45.2	408.7	405.2
-72.0	90.1	90.8	-39.7	527.7	528.1
-68.4	113.0	113.6	-35.0	655.6	655.7
-66.8	125.5	125.2	-31.6	759.6	762.8
-63.0	154.3	156.6	-28.0	886.0	881.2
-58.0	206.0	207.8	-23.7	1064.	1067.
-52.8	276.0	275.2	-20.3	1214.	1226.
-50.2	315.1	315.1	-16.3	1405.	1431.

By means of the Clausius-Clapeyron equation and the equations for the vapor pressures of trifluorochlorosilane and difluorodichlorosilane the heats of vaporization have been calculated as 4420 cal. and 5080 cal., respectively. From these values Trouton's constant for trifluorochlorosilane, 21.8, and for difluorodichlorosilane, 21.1, were calculated.

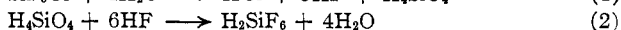
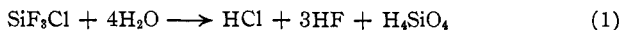
By placing p equal to 760 in the equations for the vapor pressures of the two substances, the boiling point of trifluorochlorosilane is found to be -70.0° and that of difluorodichlorosilane -31.7° . These values are believed to be accurate to within $\pm 0.2^\circ$.

Melting Point.—The melting point of trifluorochlorosilane was determined as -138° and that of difluorodichlorosilane as -144° . These melting points, which are probably accurate to $\pm 2^\circ$, were determined as follows. A small sample of the substance, sealed in a thin-walled melting point tube and attached to the bulb of a pentane thermometer, was immersed in a cryoscopic liquid (50–60 cc.) contained in a double-walled tube (not evacuated), which was in turn immersed in an unsilvered Dewar tube containing liquid air. To prevent frosting of the inner tube and to facilitate observation, a slow stream of well-dried air was circulated through the upper part of the inner tube. The non-inflammable cryoscopic liquid, which was kept stirred during these measurements, was one recommended by Kanolt.⁶ The pentane thermometer was checked at the freezing point of pure carbon bisulfide and the boiling point of oxygen.

Hydrolysis.—When trifluorochlorosilane and difluorodichlorosilane are passed into water, hydrochloric, hydrofluoric, silicic and fluosilicic acids

⁶ Kanolt, U. S. Bur. Standards, Sci. Paper, No. S520, 20, 619 (1924–1926).

are formed. As in the case of the other silicon halides, these compounds are also readily hydrolyzed by the moisture of the air. When trifluorochlorosilane is hydrolyzed with an excess of water at ordinary temperatures, the following reactions take place



The first reaction is very rapid and the speed of the second will depend upon the conditions under which the hydrolysis takes place, such as concentration and temperature. The hydrolysis of difluorodichlorosilane is analogous to that of trifluorochlorosilane. It will be noted that the hydrolysis of these two compounds cannot be satisfactorily accounted for by the mechanism usually given for silicon tetrafluoride.

Analysis.—The method used for the analysis of trifluorochlorosilane and difluorodichlorosilane was quite similar to that used in the analysis of hexafluorodisilane and previously described in detail.² The combined chlorine and fluorine in the hydrolyzed sample was determined by titration with standard sodium hydroxide, the silicon was calculated from the weight of silica collected, and the chlorine was determined as silver chloride; the fluorine in the sample was determined as the difference between the combined chlorine and fluorine and the chlorine alone. The results obtained are shown in the tables.

TRIFLUOROCHLOROSILANE				
	Si, %	(F + Cl), %	Cl, %	F, %
	22.87	76.68	29.29	47.39
	23.04	76.58	29.31	47.27
Calcd.	23.28	76.72	29.42	47.29
DIFLUORODICHLOROSILANE				
	Si, %	(F + Cl), %	Cl, %	F, %
	20.13	79.37	51.50	27.77
	20.35	79.04	51.13	27.91
Calcd.	20.49	79.51	51.77	27.74

Summary

1. The reaction of chlorine with hexafluorodisilane, Si_2F_6 , has yielded two new fluorochlorides of silicon, SiF_3Cl and SiF_2Cl_2 . The formulas have been verified by molecular weight determinations and analysis of the compounds.

2. Trifluorochlorosilane boils at -70.0° and melts at -138° ; difluorodichlorosilane boils at -31.7° and melts at -144° . The existence of a third substitution product, SiFCl_3 , is indicated, but an insufficient quantity to establish its identity has been obtained.

3. The vapor pressure of liquid SiF_3Cl has been measured from -86 to -58° ; that of SiF_2Cl_2 from -78 to -16° . Empirical equations representing these data are given, together with calculated values for the heats of vaporization and Trouton's constant.

4. The hydrolysis of these substances, which served as the basis for the elementary analysis, is discussed. The resemblance of these compounds to the analogous compounds of carbon, as is to be expected, is for the most part merely a matter of similarity in formula.

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[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION OF THE U. S. BUREAU OF MINES]

THE THERMAL DECOMPOSITION OF METHANE¹

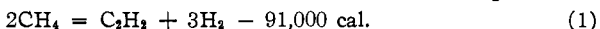
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Introduction

The thermal decomposition of methane has been repeatedly studied, but none of the results obtained has been of much value from the standpoint of reaction kinetics. The only previous work which need be considered here is that of Holliday and his co-workers.³ It was found that the earlier stages of the reaction, at 900–1200°, were homogeneous in silica vessels; the reaction is retarded very greatly by the hydrogen produced, and the final slow stages of the decomposition are at least partly heterogeneous. It is a practical impossibility to attain equilibrium without a catalyst; the "false equilibrium" which is reached from the methane side is characterized by a "constant," $(\text{CH}_4)^2/(\text{H}_2)^3$; the temperature coefficient of this constant corresponds to a heat term of 72,000 cal. Holliday worked only at temperatures where the first few per cent. of decomposition occurred too rapidly for measurement in static systems; nevertheless, Holliday and Gooderham decided that the initial reaction was the bimolecular process



They gave two reasons for this proposal; the first of these was the rather surprising statement that "homogeneous, unimolecular reactions are rare, and a bimolecular process is much more probable than one of higher order";⁴

¹ Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.) A portion of this work was presented at the New Orleans meeting of the American Chemical Society, March, 1932.

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³ Holliday and Exell, *J. Chem. Soc.*, 1066 (1929); Holliday and Gooderham, *ibid.*, 1594 (1931).

⁴ Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Company, 1932, lists 20 reactions which are probably unimolecular, seven which may be bimolecular, excluding the large group of bimolecular reactions which involve free atoms; of these seven, four involve the participation of two different substances, and hence could not be expected to be unimolecular. From the available statistical data, therefore, the odds are 20 to 3 that the initial step in the decomposition of a gaseous substance will be unimolecular.