[Contribution from the Morley Chemical Laboratory, Western Reserve University]

Chlorofluorides of Germanium[1]

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Introduction

The purpose of this investigation was to study the fluorination of germanium tetrachloride by the action of antimony trifluoride in the presence of antimony pentachloride as a catalyst. Swarts[2] was the first to use antimony fluoride as a fluorinating agent with a catalyst such as chlorine or antimony pentachloride. Booth and Swinehart[3] of this Laboratory applied the Swarts reaction to the fluorination of non-polar inorganic halides and observed that germanium tetrachloride yielded a gaseous product when treated with antimony trifluoride in the presence of antimony pentachloride.

There should be four possible fluorination products of germanium tetrachloride, three chlorofluorides, having the formulas $GeFCl_3$, GeF_2Cl_2 and GeF_3Cl, and the tetrafluoride, GeF_4. Dennis and Laubengayer[4] prepared the latter by the thermal decomposition of barium fluogermanate. Predicting from the boiling points of germanium tetrachloride (83.1°) and germanium tetrafluoride (sublimes at $-37°$) one of the chlorofluorides, the monofluoride, should be a liquid, the trifluoride a gas, and the difluoride a low boiling liquid.

Fluorination of Germanium Tetrachloride

Preliminary Fluorination.—In a preliminary fluorination of germanium tetrachloride with antimony trifluoride using 25 cc. of germanium tetrachloride and three of antimony pentachloride, in a small three-necked flask equipped with a stirrer inserted through a gas-tight packing gland in the larger neck, a reflux condenser in the second neck, and a solid feed for adding antimony fluoride in the third neck, at the boiling point of the germanium tetrachloride three definite products were obtained, corresponding to GeF_3Cl, GeF_2Cl_2 and $GeFCl_3$ and boiling at approximately -20, -3 and $+20°$, respectively.

Description of Generator.—After the preliminary fluorination, the generator was redesigned as shown in Fig. 1. The reaction vessel (A) was a Claissen flask with a side-arm, fitted with a solid feed (B) for adding antimony trifluoride. Since there was usually an excess of antimony fluoride in the reaction vessel so that the mass became very viscous, the usual high speed blade type stirrer was replaced by a slow speed stirrer consisting of a bicycle sprocket chain on the lower end of a brass rod extending through a gas-tight packing gland. This stirrer was found to be more effective in breaking up the lumps which formed. The generator fractionating column, (C), which was filled with small glass beads and was insulated by a vacuum jacket, returned the unfluorinated or only partially fluorinated reactants to the generator. Above the column was the constant temperature generator head which consisted of a glass coil (D) in a constant temperature bath, the temperature at which this bath was maintained thermostatically, depended on the fluorinated product desired.

The two electrical connections in the generator manometer were so placed that, as the fluorination progressed and the atmospheric pressure was reached, the mercury in the manometer completed the electrical circuit to the relay, actuating the automatic stopcock. When this automatic stopcock (E_1) opened, the gas was bled off from the generator until the pressure dropped below one atmosphere. This automatic stopcock opener consisted of a small bicycle pump which was pivoted and attached by a lever to the handle of the stopcock in question. When the sounder (S_3) was depressed it closed an escape in the air line leading to the pump, this forced the piston up and opened the stopcock. When the sounder circuit was broken the sounder released the air escape and the spring in the pump returned it to its normal position with the stopcock closed. The rate control stopcock just below the automatic stopcock governed the "bleed-off" of the fluorinated gases. The standard taper, conical joint cap (G) was removed for the addition of antimony trifluoride to the solid feed. The traps F_1, F_2, F_3, surrounded by ice, "dry-ice"-acetone mixture and liquid nitrogen, respectively, were for the condensation, collection, and storage of the fluorinated gases bled off.

Fluorination.—After adding the antimony trifluoride to the solid feed (B) the generator was evacuated and the germanium tetrachloride and catalyst were added to the generator and the stirrer started. The antimony trifluoride was added to the reaction vessel slowly. Heat was supplied to the generator by an electrically heated water-bath maintained thermostatically at 75°, the temperature at which it was found the fluorination could be controlled most advantageously. As the fluorination progressed the pressure in the generator gradually built up to one atmosphere and was held there by the automatic stopcock.

Control of Fluorination.—It was found that fluorination could be controlled very closely by controlling the generator head temperature (in D), thus refluxing the unfluorinated or only partially fluorinated chloride back to the generator. By maintaining the head temperature at $-20°$, GeF_2Cl_2, $GeFCl_3$ and $GeCl_4$ were returned to the generator and the chief product was GeF_3Cl; at $+6°$, (tap water) GeF_2Cl_2 was the chief product; and at $+35$, $GeFCl_3$ was mainly produced.

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[1] From a part of a thesis submitted to the Graduate School of Western Reserve University by William C. Morris, May, 1935, in partial fulfilment of the requirements for the degree of Doctor of Philosophy. Reported in the Symposium on Rare Elements, New York Convention of the American Chemical Society, April, 1935.

[2] Swarts, *Bull. Acad. Roy. Belg.*, **24**, 309 (1892).

[3] Booth and Swinehart, This Journal, **54**, 4750 (1932).

[4] Dennis and Laubengayer, *Z. physik. Chem.*, **130**, 520 (1927).

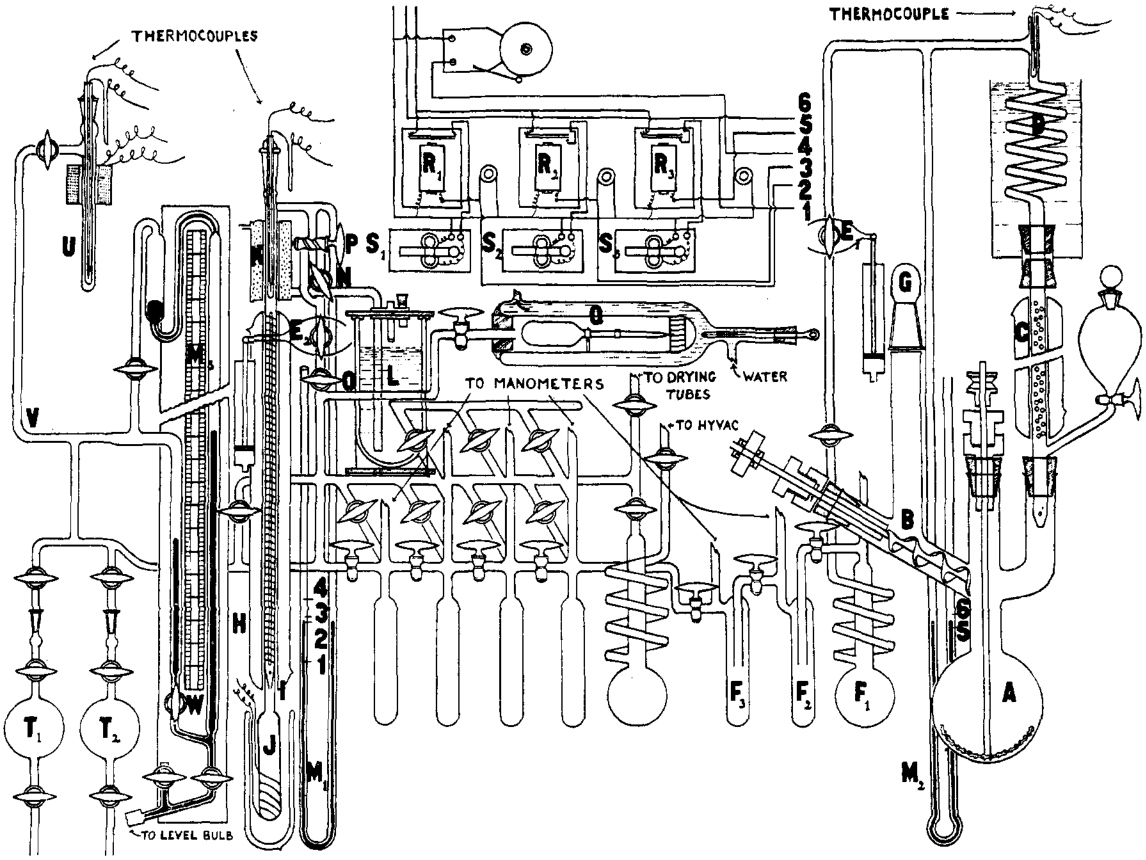

Fig. 1.

Purification.—The fluorinated products collected in the generator traps were, after several ampoule to ampoule distillations, separated into their pure components by fractional distillation in an apparatus similar to that described by Booth and Bozarth.[5] The apparatus differed from that described by the above writers only in the spiral used in the fractionating column.

A great deal of difficulty was met with in distilling the chlorofluorides of germanium in the first fractionating column which contained a copper spiral. Several small explosions were experienced at different times after the distillation had started and was apparently running smoothly. Each time a white residue remained in the column; this residue gave a positive test for fluoride and chloride ion and reduced potassium permanganate solution, indicating a germanous compound, probably a mixture of germanous chloride and fluoride.

Dennis and Laubengayer[4] found that at an elevated temperature metallic copper reduced germanium tetrafluoride. It was thought that the copper spiral caused the reduction of the gases and resulted in the explosion. The copper spiral was replaced by a glass spiral and no further difficulty was experienced in the fractional distillation of the germanium chlorofluorides.

Identification of the Chlorofluorides of Germanium.—The purified gases from the still were identified by their density, which was determined by means of the gas density balance, and by their analyses.

Determination of the Molecular Weights.—The molecular weights of the chlorofluorides of germanium (in Table III) were determined by means of a modified form of the Edwards[6] gas density balance.

Analyses.—The analyses of the chlorofluorides of germanium were carried out in the following manner: the samples were weighed in the analysis bulbs (T_1 and T_2), absorbed in dilute sodium hydroxide solution and diluted to two hundred milliliters. One half of each solution was taken for chloride determination and the other half for germanium determination. The chloride was determined gravimetrically as the silver salt in the usual manner.

Germanium was determined gravimetrically as the oxide by the method of Johnson and Dennis.[7] The results of the analyses are given in Table I.

A positive qualitative test for fluorine was obtained with each sample.

Melting Points (Triple Points).—The melting points of the chlorofluorides of germanium were determined from the cooling curves, which were recorded by means of a specially sensitive, high speed Leeds and Northrup Micromax recording potentiometer connected to the thermocouple extending to the bottom of the melting point cell

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(5) To be published shortly in the *Analytical Edition of Industrial and Engineering Chemistry*.

(6) J. D. Edwards, "A Specific Gravity Balance for Gases," Technologic Paper of the U. S. Bureau of Standards, No. 89, 1917.

(7) Johnson and Dennis, THIS JOURNAL, **47**, 791 (1925).

TABLE I

ANALYSES OF THE CHLOROFLUORIDES OF GERMANIUM

Wt. sample	% Chlorine	% Germanium
	Analysis of GeF_2Cl_2	
0.2517		39.83
.2363		39.97
.1796	38.93	40.38
.2520	38.92	
Mean	38.93	40.06
Theory	39.07	39.91
	Analysis of GeF_3Cl	
0.1906	21.43	44.08
.2065	21.42	44.06
.2579	21.39	
.1684	21.43	
Mean	21.42	44.07
Theory	21.48	43.99
	Analysis of $GeFCl_3$	
0.2022	53.08	36.74
.1906	53.06	36.72
Mean	53.07	36.73
Theory	52.96	36.68

(U). The sample in the cell was stirred by means of a magnetic stirrer. The point at which crystals began to form in the melting point cell, which coincided with the break in the cooling curve, was taken as the melting point (see Table III).

Vapor Pressure and Boiling Point Determinations.—The vapor pressures of the chlorofluorides of germanium were determined by the static method. The thermostat temperature was controlled by a platinum resistance connected in an unbalanced Wheatstone bridge circuit, of a controlling potentiometer. The temperature was measured by means of a carefully calibrated platinum resistance thermometer. The pressure was measured on a Germann manometer,[8] as modified by Booth and Swinehart.[9] Each reading of both temperature and pressure was checked carefully to ascertain that equilibrium had been established, and during the course of the determination part of the sample was boiled away to check the purity. Table II contains the vapor pressure–temperature data of the chlorofluorides of germanium. Table III contains the boiling points of the germanium chlorofluorides, the values being taken from the vapor pressure curves as the temperatures at which the vapor pressure of the gas was equal to 760 mm. of mercury. The latent heat was calculated by the Clausius–Clapeyron equation and the critical constants by the "three-halves" rule.

TABLE II

Temp., °C.	Press. obsd., mm. Hg	Press. calcd.	Deviation
Vapor Pressure of $GeFCl_3$. $\log p = 8.76 - 1825/T$			
−30.7	2.9		
−15.94	40.7	42.0	+1.3
−14.30	43.6	45.0	+1.4
− 7.38	76.1	77.7	+1.6
− 7.39[a]	76.1	77.7	+1.6
+ 2.97	159.8	153.0	−6.8
6.88	208.2	204.0	−4.2
23.11	453.6	443.0	−10.6
28.47	559.8	553.0	−6.0
31.86	625.8	619.0	−6.8
36.81	743.8	741.4	−2.2
39.56	819.2	818.4	−0.8
43.36	931.7	934.0	+2.3
Vapor Pressure of GeF_2Cl_2. $\log p = 8.22 - 1441/T$			
−47.28	1.8		
−45.13	4.6		
−40.50	12.8		
−30.40	98.3	108.0	+10.0
−26.80	182.2	187.0	+4.8
−24.53	282.4	279.0	−3.2
−24.54[a]	282.4	279.0	−3.2
−17.60	376.5	374.0	−2.1
−14.10	509.7	505.0	−4.7
− 9.89	593.0	596.0	+3.0
− 6.84	657.2	658.0	+0.8
− 3.80	733.5	737.0	+3.5
− 2.20	888.0	882.0	−6.0
Vapor Pressure of GeF_3Cl. $\log p = 11.05 - 2062/T$			
−64.08	6.2		
−60.04	12.8		
−53.81	36.1		
−49.45	66.7	63.1	−3.6
−46.82	92.2	91.3	−1.9
−44.61	116.0	110.0	−6.0
−41.82	150.7	148.0	−2.7
−41.84[a]	150.7	148.0	−2.7
−37.62	224.1	218.0	−6.1
−31.12	266.7	275.0	+8.3
−29.78	345.3	347.0	+1.7
−28.73	522.7	523.0	+0.3
−25.50	614.8	618.0	+3.2
−20.92	725.7	724.0	−1.7
−20.52	763.8	759.0	−3.2

[a] Part of sample distilled away.

TABLE III

PHYSICAL PROPERTIES OF THE CHLOROFLUORIDES OF GERMANIUM

Subs.	Molecular weight From gas density balance	Molecular weight Calcd. from formula	M. p., °C.	B. p., °C.	Latent heat of vapor., cal./mol.	Calcd. crit. temp., °C.
GeF_4	149.1	147.90	Sublimes			
GeF_3Cl	167.0	164.36	−66.2	−20.3	5290	107.6
GeF_2Cl_2	183.0	180.82	−51.8	− 2.8	5650	132.4
$GeFCl_3$	198.2	197.28	−49.8	+37.5	6580	192.8
$GeCl_4$	214.0	213.7	−49.5	+83.1		

Chemical Properties of the Germanium Chlorofluorides.—Although no definite investigation of the chemical properties of the three chlorofluorides of germanium was made, the following properties were observed.

1. All of the chlorofluorides of germanium are colorless in both the liquid and gaseous state, and freeze to white solids.

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(8) Germann, THIS JOURNAL, **36**, 2456 (1914).

(9) Booth and Swinehart, *ibid.*, **57**, 1333 (1935).

2. The chlorofluorides of germanium fume in air much more readily than does the tetrachloride.
3. The three gases have a slight garlic-like odor.
4. Glass and mercury are both attacked slowly by the chlorofluorides of germanium.
5. Copper causes them (probably in the liquid state) to decompose, sometimes explosively, into germanous chloride and germanous fluoride.
6. The gases react rapidly with water, forming a white precipitate of germanic oxide.
7. The gases react vigorously with dilute sodium hydroxide solution, but do not form a precipitate.
8. The gases are all soluble in absolute alcohol.
9. The three chlorofluorides of germanium dissolve in stopcock grease rather rapidly but react with it rather slowly.
10. The three chlorofluorides of germanium are all unstable and rearrange on standing at carbon dioxide snow temperature to form the tetrachloride and the tetrafluoride.

The following equations probably represent the rearrangement mentioned above.

$$2GeF_2Cl_2 = GeF_3Cl + GeFCl_3 \quad (1)$$
$$4GeF_3Cl = 3GeF_4 + GeCl_4 \quad (2)$$
$$4GeFCl_3 = GeF_4 + 3GeCl_4 \quad (3)$$

This rearrangement was first noticed in the fractional redistillation of a sample of GeF_2Cl_2 which had been carefully purified on the previous day. Relatively large amounts of GeF_4, GeF_3Cl, GeF_2Cl_2 and $GeCl_4$ were obtained from the purified sample of GeF_2Cl_2. To study this rearrangement further a second sample of GeF_2Cl_2 was distilled, the molecular weight of the entire sample being determined by means of the density balance, and held for two weeks in an ampoule surrounded by dry ice (−78°). The results of the distillation analysis of this sample after standing for two weeks at carbon dioxide snow temperature are given in Table IV. In a like manner the rearrangement of GeF_3Cl (Table V) and of $GeFCl_3$ (Table VI) was studied with similar results except that practically all of the sample that rearranged went completely to the tetrafluoride and the tetrachloride with only slight traces of the intermediate compounds.

TABLE IV

REARRANGEMENT OF GeF_2Cl_2

Distillation analysis after 14 days at −78°

Substance	Pressure, cm.	Composition, %
GeF_4	6.8	21.8
GeF_3Cl	4.3	13.8
GeF_2Cl_2	8.4	26.9
$GeFCl_3$	5.1	16.3
$GeCl_4$	6.6	21.2
Total	31.2	100.0

$$4GeF_2Cl_2 \longrightarrow GeF_3Cl + GeFCl_3 + GeCl_4 + GeF_4$$

TABLE V

REARRANGEMENT OF GeF_3Cl

Distillation analysis after 20 days at −78°

Substances	Pressure, cm.	Composition, %
GeF_4	20.3	53.2
$GeFCl_3$	11.2	29.3
$GeCl_4$	6.7	17.5
Total	38.2	100.0

$$4GeF_3Cl \longrightarrow 3GeF_4 + GeCl_4$$

TABLE VI

REARRANGEMENT OF $GeFCl_3$

Distillation analysis after 14 days at −78°

Substance	Pressure, cm.	Composition, %
GeF_4	7.24	18.2
$GeFCl_3$	11.18	28.1
$GeCl_4$	21.37	53.7
Total	39.79	100.00

$$4GeFCl_3 \longrightarrow GeF_4 + 3GeCl_4$$

This tendency of the chlorofluorides to rearrange prevented the determination of the critical constants.

Acknowledgment.—We wish to acknowledge our indebtedness to Dr. Warren C. Johnson of the University of Chicago for advice on the chemistry of germanium and for supplying the germanium tetrachloride used in this research. The preparation of the germanium tetrachloride was made possible by a grant from the Julius Rosenwald Fund to Prof. Johnson.

Summary

The fluorination of germanium tetrachloride by means of antimony trifluoride in the presence of antimony pentachloride yields monofluorotrichlorogermane, a liquid melting at −49.8° and boiling at 37.5°; difluorodichlorogermane, a gas melting at −51.8° and boiling at −2.8°; trifluoromonochlorogermane, a gas melting at −66.2° and boiling at −20.3°; and germanium tetrafluoride.

These chlorofluorides hydrolyze in air much more readily than does the tetrachloride. They are unstable and tend to rearrange and form the tetrachloride and the tetrafluoride, even at −78°. They are explosively reduced by metallic copper under certain conditions to the germanous salts.

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