

might have been expected on the basis of the above argument, is not surprising because the reduction undoubtedly starts on the surface with the result that the surface may have an average oxidation state of 3.5 while the manganese oxide in the body of the material is still largely unreduced.

Since no hydrogen ion is used in the reactions of the mechanism, the activity changes caused by hydrogen ion must be due to some other effect. The hydrogen ion concentration decreases during the reaction, and manganous ion can be detected in the clear solution after the catalyst has been allowed to settle. The manganous ion concentration at the end of a run can be calculated roughly from the change in hydrogen ion concentration determined by pH measurement. This calculation shows that even with the lowest initial pH, 3.5, the amount of manganese that dissolved would be only 6% of that present (considering a sample containing 4.60 mg. of manganese). The dissolving of this manganese and the oxygen evolved during its reduction does not change the kinetics of the reaction from first order, and, therefore, would not affect the validity of the results as a measure of catalytic activity.

Broughton and Wentworth found no catalysis with manganous solutions until manganese dioxide

formed. The oxidation of a manganous ion in solution by hydrogen peroxide is not a very probable reaction since it involves either the formation of the unstable manganic ion or a nucleus of solid manganese dioxide. Manganous ion adsorbed on the surface of manganese dioxide, however, may be more active in catalysis since on oxidation it can join the already formed manganese dioxide lattice. The adsorbed manganous ion could either take part in the reactions itself or form a site for the formation of a crystal of manganese sesquioxide. This latter reaction seems the more likely since the samples of catalyst which contained all the manganese in the plus three state showed no increased activity with decreasing pH. These samples showed, however, an increase in activity with an increase in pH. This can be explained in a manner similar to the above in which an ion such as manganate or permanganate acts to form MnO₂ sites on an Mn₂O₃ surface.

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Some Metathetical Reactions of the Gaseous Fluorides of Group IV¹

BY WALTER C. SCHUMB AND DONALD W. BRECK²

The extent of conversion of the tetrafluorides of carbon, silicon and germanium to the corresponding chlorides, or to mixed chlorofluorides, by reaction with anhydrous metal chlorides under known conditions of temperature and pressure, was measured. The metal chlorides selected were either (a) non-volatile, convertible to a non-volatile fluoride (chlorides of magnesium, calcium or barium) or (b) easily volatile, convertible to a non-volatile fluoride (aluminum or ferric chlorides). Reactions were carried out both at atmospheric and under increased pressures (in a steel autoclave). The order of increasing reactivity of the respective fluorides toward metal chlorides was found to be: CF₄ < SiF₄ < GeF₄; and the order of increasing thermal stability of the chlorofluorides of these elements, MCl_nF_{4-n}, was found to progress in the reverse direction: Ge < Si < C.

Introduction

In view of the existence of a complete series of chlorofluorides of carbon,³ silicon⁴ and germanium,⁵ it seemed of interest to establish the conditions under which conversion of carbon, silicon and germanium tetrafluorides into the corresponding tetrachlorides, or into intermediate chlorofluorides, might be attained. The simplest and most direct method appeared to be the use of suitable anhydrous metal chlorides in a metathetical process.

Boron trifluoride may be converted to the trichloride or tribromide by the action of anhydrous aluminum chloride or bromide.⁶

Boron fluorochlorides or fluorobromides were not

(1) Presented in part at the Cleveland Meeting of the American Chemical Society, April 11, 1951. Based upon a thesis presented by D. W. Breck to the Department of Chemistry in partial fulfillment of the requirements for the Ph.D. degree.

(2) U. S. Rubber Fellow, 1950-1951.

(3) O. Ruff and R. Keim, *Z. anorg. Chem.*, **192**, 249 (1930).

(4) W. C. Schumb and E. L. Gamble, *THIS JOURNAL*, **54**, 3943 (1932); H. S. Booth and C. F. Swinehart, *ibid.*, **57**, 1333 (1935); H. H. Anderson, *ibid.*, **72**, 2091 (1950); R. V. Lindsey, Jr., *ibid.*, **73**, 371 (1951).

(5) H. S. Booth and W. C. Morris, *ibid.*, **58**, 90 (1936).

(6) E. L. Gamble, P. Gilmont and J. F. Stiff, *ibid.*, **62**, 1257 (1940).

isolated and heating sodium fluorosilicate with aluminum chloride gave only silicon tetrachloride. By reaction with aluminum chloride, tris-(*n*-propyl)-fluorosilane is converted into the corresponding chloro-compound.⁷ Henne and Newman⁸ found that aluminum chloride converts benzotrifluoride into benzotrichloride in the presence of acetyl chloride, and 1,1,2-trichlorotrifluoroethane undergoes halogen exchange with aluminum chloride to form 1,1-difluorotetrachloroethane and hexachloroethane.⁹

Two types of chlorinating agents were considered. The first type was a non-volatile chloride possessing a non-volatile fluoride, and the second type a metal chloride which is easily volatilized and which possesses a relatively non-volatile fluoride. Anhydrous magnesium, calcium and barium chlorides were used as examples of the first type, and for the second type anhydrous aluminum and ferric chlorides were utilized. In addition, an-

(7) C. Eaborn, *J. Chem. Soc.*, 2755 (1949).

(8) A. L. Henne and M. S. Newman, *THIS JOURNAL*, **60**, 1697 (1938).

(9) W. T. Miller, *ibid.*, **62**, 993 (1940).

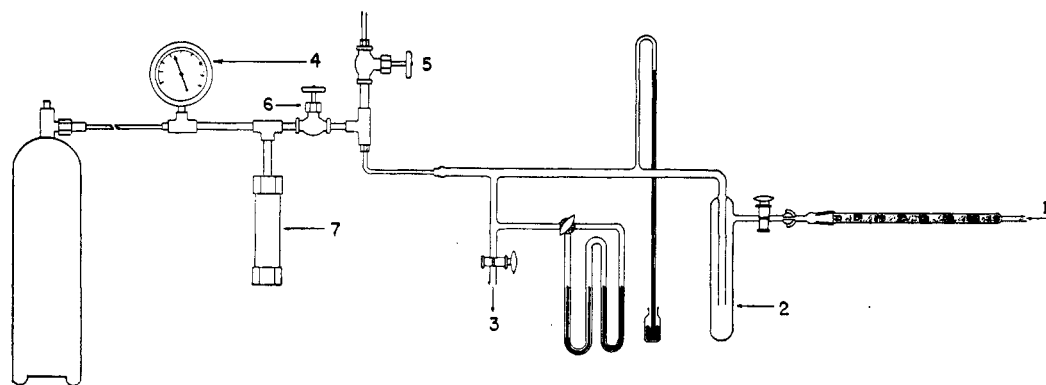


Fig. 1.—Apparatus for filling cylinder or autoclave with silicon tetrafluoride: 1, silicon tetrafluoride inlet; 2, Pyrex condensation trap; 3, to vacuum pump; 4, pressure gage; 5 and 6, bronze valves; 7, brass condensation trap.

hydrous aluminum iodide was used in several attempts to prepare the iodofluorides of carbon and silicon.¹⁰ Reaction with carbon tetrafluoride and silicon tetrafluoride under pressure was also used.

Experimental

Materials.—Carbon tetrafluoride was obtained in a high degree of purity as the compressed gas.¹¹ The infrared spectrum of this material from two to fifteen microns agreed closely with the published data.¹² Two methods were employed for the preparation of silicon tetrafluoride. One utilized the action of concentrated sulfuric acid on a mixture of finely divided silicon dioxide and sodium fluorosilicate of C.P. grade.¹³ The second method employed the thermal decomposition of barium fluorosilicate. Purification was accomplished by passage of the evolved gas through a tube packed alternately with glass-wool and phosphorus pentoxide. By means of the apparatus shown in Fig. 1, the silicon tetrafluoride was condensed in a Pyrex trap, sublimed under vacuum into a brass trap connected to a cylinder and pressure gage and then transferred to the previously evacuated cylinder. By a repetition of this process, the cylinder was filled with silicon tetrafluoride at a convenient pressure. A steel autoclave was attached to the system for filling with silicon tetrafluoride under pressure. The infrared spectrum of this material agreed closely with published data.¹⁴

Germanium tetrafluoride was prepared by the thermal decomposition of barium fluorogermanate.¹⁵ Germanium dioxide used for the preparation of the barium fluorogermanate was of 99.9+ % purity.¹⁶

Anhydrous C.P. aluminum chloride was resublimed before use. Anhydrous magnesium chloride was prepared by the thermal decomposition of $MgCl_2 \cdot NH_4Cl \cdot 6H_2O$ in a current of dry hydrogen chloride. Anhydrous C.P. barium and cadmium chlorides were dried by heating in a current of dry nitrogen. C.P. anhydrous ferric chloride was employed without further purification. Aluminum iodide was prepared by the reaction between iodine of reagent grade and an excess of metallic aluminum in an atmosphere of dry helium, following by distillation in a helium atmosphere, and collection in a suitable receiver.

Analytical.—Silicon was determined gravimetrically as silicon dioxide. A weighed sample of the silicon chlorofluoride was hydrolyzed in aqueous sodium hydroxide, the

solution neutralized and evaporated to dryness in a platinum dish, and the residue baked at 120°. After leaching out the soluble constituents with hot water, the silicon dioxide was filtered off, ignited and weighed in a platinum crucible.

Fluoride was determined by a suitable fusion, or hydrolysis of the sample, followed by steam distillation of the fluoride as fluorosilicic acid in an apparatus identical with that of Huckaby, Welch and Metler,¹⁷ and titration of the fluoride ion with standard thorium nitrate.¹⁸

Iodide was determined as silver iodide and chloride as silver chloride. Aluminum and magnesium were determined by precipitation with 8-hydroxyquinoline. Germanium was determined as the dioxide by the method of Johnson and Dennis.¹⁹

Procedure.—The apparatus used for studying the reactions of carbon and silicon tetrafluoride at atmospheric pressure is illustrated in Fig. 2. The reactor was a Vycor tube, 30 mm. in diameter and 1 meter in length, fitted with ground Vycor joints at each end. This was placed horizontally in a cylindrical furnace 30 cm. in length and an adjacent smaller movable furnace. Chromel-alumel thermocouples were placed externally in contact with the tube and protected by asbestos sheet. Temperatures were indicated by a Brown pyrometer and a portable potentiometer.

The exit end of the reactor was attached to a train of condensation traps to enable the collection and separation of products. A removable vapor storage globe and transfer tube allowed the transfer of volatile products to a low-temperature distillation column. The gaseous tetrafluoride was admitted to the reactor at a measured rate of flow. For the carbon tetrafluoride experiments, the first condensation trap was maintained at -78° and the second at -115° ,²⁰ and only unreacted carbon tetrafluoride was permitted to leave.

For reaction with non-volatile chlorides, the solid chloride was distributed over a 45-cm. length of the reaction tube and the entire mass heated by using both furnaces at the same temperature. Reaction with the volatile chlorides was studied by distributing the chloride over a 20-cm. length of the reactor ahead of the stationary furnace and slowly vaporizing it in a stream of the gaseous fluoride by advancing the movable furnace which was maintained at a temperature slightly higher than the normal sublimation point. In general, the temperature of the stationary furnace was considerably higher.

The Vycor reactor was charged with the anhydrous metal chloride concerned by weighing it inside a "dry-box" into a section of 20-mm. tubing, closed at both ends with rubber stoppers. After drying the reaction apparatus thoroughly by passing through dry nitrogen while heating, the gas inlet connection was removed. One stopper was removed from the tube containing the metal halide and the latter quickly inserted into the reactor. After removing the other stopper,

(10) CF_2I has been prepared by Banks, *et al.* (A. A. Banks, H. J. Emelús, R. N. Haszeldine and V. Kerrigan, *J. Chem. Soc.*, 2188 (1948)), and more recently by Henne and Finnegan (A. L. Henne and W. C. Finnegan, *THIS JOURNAL*, 72, 3806 (1950)). The iodofluorosilanes were prepared by Anderson (H. H. Anderson, *ibid.*, 72, 2091 (1950)).

(11) Kinetic Chemicals Company, Carney's Point, N. J.

(12) C. R. Bailey, J. B. Hale and J. W. Thompson, *Proc. Roy. Soc. (London)*, A167, 555 (1938).

(13) J. A. Gierut, F. J. Sowa and J. A. Nieuwland, *THIS JOURNAL*, 58, 786 (1936).

(14) E. A. Jones, J. S. Kirby-Smith, P. J. H. Woltz and A. H. Nielsen, *J. Chem. Phys.*, 19, 242 (1951).

(15) L. M. Dennis and A. W. Laubengayer, *Z. physik. Chem.*, 130, 520 (1927).

(16) Eagle-Picher Company, Cincinnati, Ohio.

(17) W. B. Huckaby, E. T. Welch and A. V. Metler, *Anal. Chem.*, 19, 154 (1947).

(18) R. H. Kinballa and L. E. Tufts, *ibid.*, 19, 150 (1947).

(19) E. B. Johnson and L. M. Dennis, *THIS JOURNAL*, 47, 791 (1925).

(20) The -115° trap was cooled by means of a hollow aluminum block, tapered at the lower end. The block was cooled to the desired temperature by immersion of the tip in a Dewar flask containing liquid nitrogen. A thermocouple well drilled in the block contained a copper-constantan thermocouple for indicating the temperature.

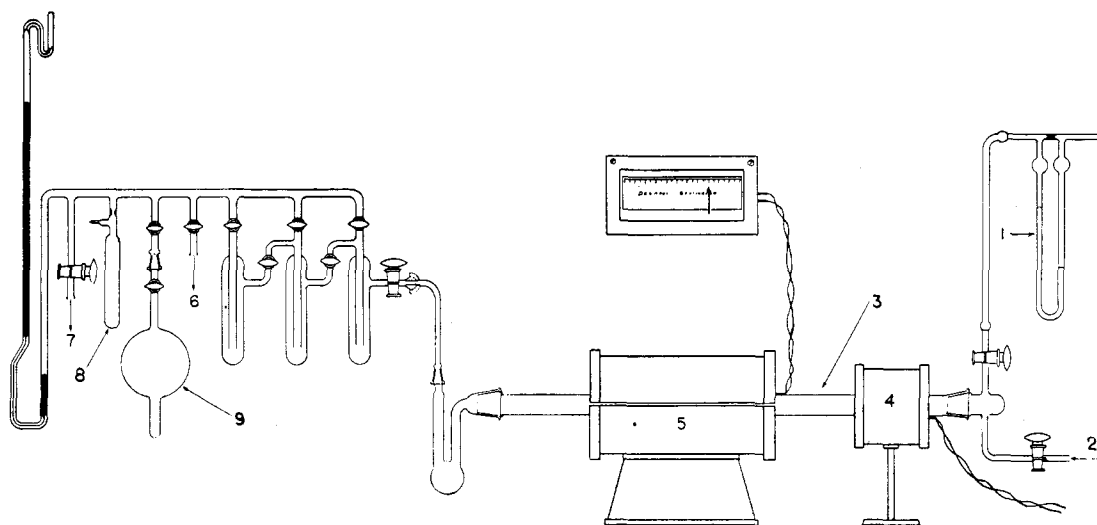


Fig. 2.—Reaction apparatus: 1, flowmeter; 2, nitrogen inlet; 3, Vycor reactor; 4, movable furnace; 5, stationary furnace; 6, outlet to hood; 7, to vacuum pump; 8, transfer tube; 9, storage vessel.

the metal halide was pushed into the reactor with a glass rod, the tube withdrawn, and the gas inlet connection restored. All ground joints and stopcocks were lubricated with a fluorocarbon grease.²¹

A separate apparatus was employed for the separation and identification of volatile products. This was very similar to the distillation apparatus described by Booth and Bozarth²² and consisted of a fractionating column and the necessary vacuum apparatus for the storage and sampling of purified gas fractions. In some instances, a Baird recording infrared spectrophotometer was employed for product identification.²³

The apparatus employed for carrying out reactions with aluminum iodide is shown in Fig. 3. Short lengths of aluminum wire spiral were placed in the reaction flask and an

roughly dried by flushing with dry helium, and with helium entering at 2 and leaving at 1, the iodine was added slowly and the reaction flask heated gently. When the iodine was added more heat was applied and the liquid aluminum iodide refluxed until it became colorless. The helium flow was then reversed, *i.e.*, entering at 1 and leaving at 2, and the aluminum iodide was distilled over into the receiver 8. After the distillation, the receiver was sealed off at 4. The aluminum iodide was heated at a temperature above the melting point by the small vertical furnace and the gaseous tetrafluoride admitted at a measured rate of flow to bubble through the liquid. The vapors of both swept into the reaction tube heated by the stationary furnace. A receiver at room temperature and condensation trap at -78° served to collect reaction products.

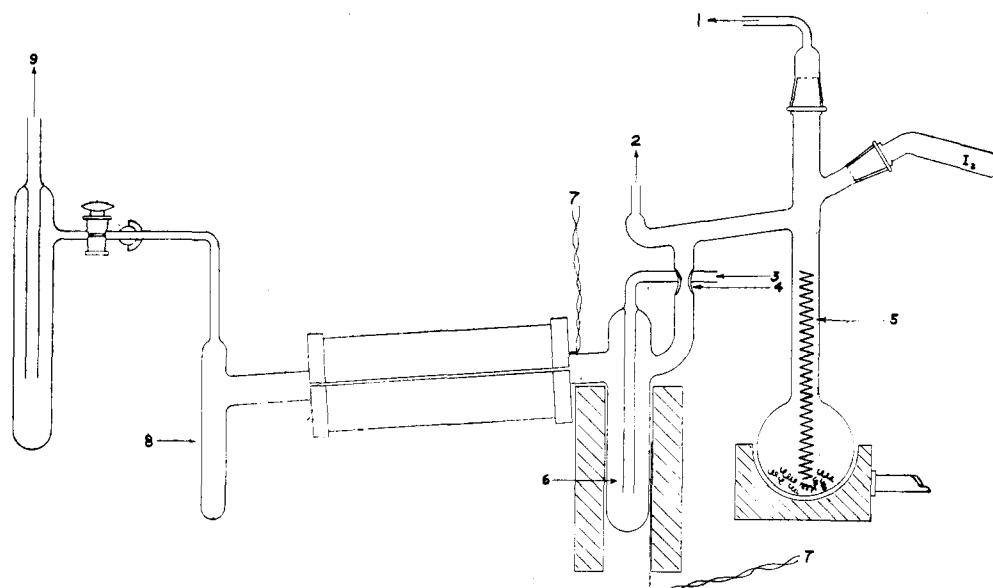


Fig. 3.—Apparatus for preparation and reactions of aluminum iodide: 1, helium outlet during preparation; 2, helium outlet during distillation; 3, silicon or carbon tetrafluoride inlet; 4, constriction for sealing; 5, aluminum wire spiral; 6, vaporization chamber; 7, thermocouple; 8, receiver for carbon or silicon tetraiodide; 9, outlet to hood and vacuum line.

aluminum spiral in the column. The apparatus was tho-

(21) "Fluorolube," a fluorochlorocarbon grease, from Hooker Electrochemical Company, Niagara Falls, N. Y.

(22) H. S. Booth and A. R. Bozarth, *Ind. Eng. Chem.*, **29**, 470 (1937).

(23) Baird Associates, Cambridge, Mass.

The reactions of germanium tetrafluoride were studied by means of apparatus shown in Fig. 4. Barium fluorogermanate, previously dried at 120° , was placed in the Vycor tube (2.0×20 cm.), and the tube then connected to the condensation trap, 5, by means of a rubber stopper. The entire system was evacuated while heating the barium fluorogermanate to 300° . Stopcock 3 was closed, the fur-

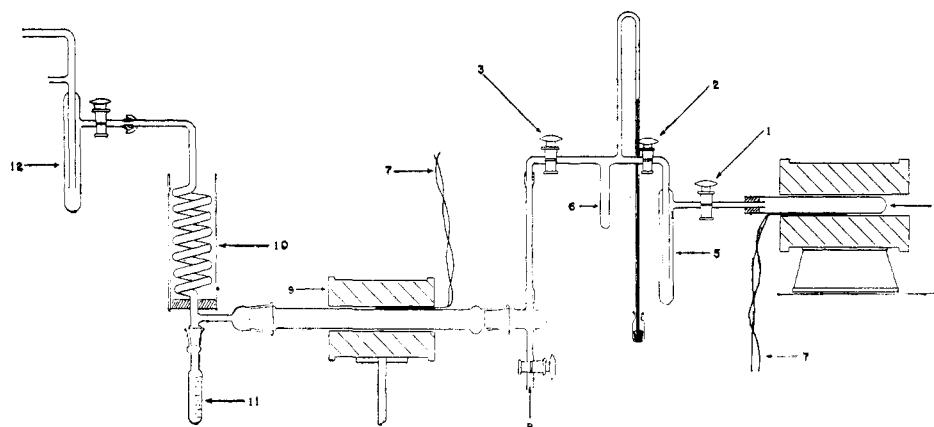


Fig. 4.—Apparatus for preparation and reactions of germanium tetrafluoride: 1, 2 and 3, stopcocks; 4, Vycor tube; 5, Pyrex condensation trap; 6, sublimation tube; 7, thermocouple; 8, nitrogen inlet; 9, furnace; 10, condenser at 0°; 11, receiver for germanium tetrachloride; 12, condensation trap.

nance temperature raised to 700° and the condensation trap cooled with liquid nitrogen. When the condensation of germanium tetrafluoride ceased, stopcock 1 was closed and the tetrafluoride transferred to the sublimation tube, 6. After heating the reactor containing the metal halide to the desired temperature, stopcock 2 was closed and the sublimation tube permitted to warm up. When atmospheric pressure was reached, stopcock 3 was opened and germanium tetrafluoride admitted to the reactor. The condenser was cooled to 0° and the condensation trap to -78°. By means of the graduated receiver, the volume and weight of liquid condensate (germanium tetrachloride), was determined.

A standard 500-ml. steel hydrogenation autoclave equipped with high pressure fittings and gage was used for the high pressure experiments. The autoclave was charged with the metal halide contained in a Pyrex lining tube in a "dry-box," sealed, evacuated and the tetrafluoride admitted to the desired pressure. After heating and cooling, the gaseous products and unreacted tetrafluoride were exhausted through the series of condensation traps. Upon attaining atmospheric pressure, the autoclave was evacuated through a liquid nitrogen-cooled trap, dry air admitted, and the autoclave was then opened. The solid contents were removed for further examination.

Results

(1) **Carbon Tetrafluoride.**—Carbon tetrafluoride was passed over magnesium chloride at 605° for six hours. No condensate was found in the traps at -78° and -115°.

Five experiments were carried out using aluminum chloride and carbon tetrafluoride. The stationary furnace temperature was varied from 200 to 650°, the flow-rate from 25 to 46 cc./min., and a total of 13 hours of running time were consumed. No reaction was observed in any case. With a stationary furnace temperature of 710–730°, and a flow-rate of 40 cc. of carbon tetrafluoride per minute, no reaction between carbon tetrafluoride and ferric chloride was observed. Carbon tetrafluoride was bubbled through aluminum iodide heated to about 380° for three hours. The stationary furnace was maintained at 410° and no condensate was found in the trap at -78°. No substance identifiable as carbon tetraiodide was separated from the aluminum iodide.

A series of three experiments using about 0.33 mole of aluminum chloride and carbon tetrafluoride at initial pressures of 31 to 73 atmospheres resulted in the formation of carbon tetrachloride in each case. Data for these experiments are summarized in Table I. After treatment with dilute nitric acid, the solid residue was filtered off, dried and analyzed for fluoride. Found: F, 65.0; calcd. for AlF_3 , F, 67.88. In the first run, the molecular weight of the gas from the autoclave agreed with the calculated molecular weight of carbon tetrafluoride. The infrared spectrum of the gas showed only the presence of carbon tetrafluoride and carbon tetrachloride in the third run. The liquid product was identified as carbon tetrachloride by its boiling point, refractive index and infrared spectrum. Despite a variation in the $CF_4/AlCl_3$ molar ratio, initial pressure and heat-

ing period, about the same yield of carbon tetrachloride was obtained, and no evidence of the formation of intermediate chlorofluoromethanes was found.

TABLE I

REACTION OF CARBON TETRAFLUORIDE WITH ANHYDROUS ALUMINUM CHLORIDE UNDER PRESSURE

Run No.	1	2	3
Moles $AlCl_3$ used	0.33	0.40	0.32
Moles CF_4 used ^a	1.5	.62	.73
$CF_4/AlCl_3$ molar ratio	4.6	1.5	2.3
Pressure, initial, atm.	75	31	37
Pressure, final, atm.	54	10
Temperature, °C.	190–260	190–267	190–220
Time, minutes	180	60	18
Mol. wt. gaseous product	87.3 ^b
B.p. distillate, °C.	76.6	76.7	76.6
Refractive index liquid, 25°	1.4555 ^c	1.4530
Yield of CCl_4 , %	30	28	25

^a Calculated from pressure, temperature and volume.

^b Measured molecular weight of CF_4 from cylinder was 87.9.

^c Refractive index of CCl_4 (25°), 1.4555.

The autoclave was charged with 0.36 mole of ferric chloride and 30.2 atmospheres, 0.62 mole, of carbon tetrafluoride. After heating at 290–320° for 50 minutes and cooling, no pressure decrease was observed. The infrared spectrum of a gas sample from the autoclave agreed exactly with that of the carbon tetrafluoride. No liquid distillate was obtained from the solid residue.

With aluminum iodide, 0.205 mole and 36.4 atmospheres of carbon tetrafluoride, and heating at 300–320° for 40 minutes, the final pressure was the same as the initial pressure after cooling. No condensate was collected in the condensation traps and the infrared spectrum of a gas sample from the autoclave showed only the presence of carbon tetrafluoride.

(2) **Silicon Tetrafluoride.**—The data obtained in a series of experiments utilizing silicon tetrafluoride and anhydrous magnesium, calcium and barium chlorides are summarized in Table II.

Silicon tetrachloride was identified by its boiling point and chemical analysis. Found: Si, 16.48; Cl, 83.3; b.p. 57.6°; calcd. for $SiCl_4$: Si, 16.53; Cl, 83.47; b.p. 57.6°. Chlorotrifluorosilane was identified by molecular weight.²⁴ Found: mol. wt., 119.7, 120.9; calcd. for $SiClF_3$: mol. wt., 120.52. For dichlorodifluorosilane, the molecular weight was found to be 136.1, 136.5 and the boiling point -31.5° which agrees well with the calculated value of 136.97 for the

(24) Molecular weights were calculated by the Berthelot equation, using the critical constants of Booth and Swinehart (H. S. Booth and C. F. Swinehart, *THIS JOURNAL*, **57**, 1337 (1935)).

TABLE II
REACTION OF SILICON TETRAFLUORIDE WITH ANHYDROUS
NON-VOLATILE CHLORIDES AT ATMOSPHERIC PRESSURE

Reactant	MgCl ₂	CaCl ₂	BaCl ₂
Temperature, °C.	630	650	850
SiF ₄ , moles	0.19	0.75	0.5
Metal halide, mole	0.24	1.0	0.67
Time, minutes	210	265	140
Mole SiCl ₄ found	0.021	0.009	None
Mole SiCl ₃ F found ^a	0.016	0.016	None
Mole SiCl ₂ F ₂ found ^a	0.033		
Mole SiClF ₃ found ^a	0.018		
Yield of SiCl ₄ , % ^b	11		
Conversion, %	47		

^a Calculated from the measured temperature and pressure of a known volume of the vapor. ^b Based on SiF₄.

molecular weight and the known boiling point of -31.7°. The third fraction was found to have a molecular weight of 153.9 and boiling point of 12.2° which is in good agreement with the calculated molecular weight of 153.43 and known boiling point of 12.2° for trichlorofluorosilane. In the experiment with magnesium chloride, solid magnesium fluoride was removed from the reactor and analyzed for magnesium. Found: Mg, 36.6; calcd. for MgF₂: Mg, 39.05. The low result is probably due to the presence of unreacted magnesium chloride.

The data from five experiments using aluminum chloride at atmospheric pressure are summarized in Table III. Aluminum fluoride was identified as the solid reaction product by analysis of a sample removed from the reaction zone. Found: F, 65.9; calcd. for AlF₃: F, 67.88. A chlorofluoride of aluminum was apparently not produced.

TABLE III
REACTION OF SILICON TETRAFLUORIDE WITH ANHYDROUS
ALUMINUM CHLORIDE AT ATMOSPHERIC PRESSURE

Run	1	2	3	4	5
Temp., °C.	610	610	500	215-230	250
SiF ₄ , mole	0.5	0.5	0.63	0.26
SiF ₄ , cc./min.	50-65	50-75	32
AlCl ₃ , mole	0.20	0.38	0.55	0.33	0.21
Time, min.	150	120	250	240	180
Mole SiCl ₄	0.097	0.089	0.19	0.012	0.018
Mole SiCl ₃ F	0.065	0.044	0.065	0.073	0.020
Mole SiCl ₂ F ₂					0.028
Mole SiClF ₃	0.047				0.011
SiCl ₄ , % of product	47	67	75	14	23
Yield of SiCl ₄ , % ^a	65	31	47	5	11
Conversion, %	42	27	41	30

^a Based on AlCl₃.

In all five runs, no aluminum fluoride was found to be deposited in the high temperature zone, that is, the section of the reactor heated by the stationary furnace, but the solid aluminum fluoride was deposited as a finely divided powder only in the aluminum chloride vaporization chamber. From this it was concluded that halogen exchange between the fluoride and chloride occurred rapidly in the vaporization chamber with the formation of all of the chlorofluorosilanes as well as silicon tetrachloride. It is also evident that the per cent. of silicon tetrachloride in the product was considerably greater when the reaction zone was at a higher temperature. A decrease in the temperature of the stationary furnace from 500 to 230° caused a decrease in the per cent. of silicon tetrachloride from 75 to 14%, with essentially the same rate of flow. It was therefore concluded that the mixed chlorofluorosilanes formed by metathesis with the aluminum chloride in the vaporization chamber rearranged upon passing through the high temperature zone to form ultimately more silicon tetrachloride and tetrafluoride.

Using anhydrous ferric chloride and a stationary furnace temperature of 500 to 600°, no condensate was found in the condensation traps after passing silicon tetrafluoride through the reactor at 28 cc./min. for 3.3 hours.

Silicon tetrafluoride was passed into molten aluminum

iodide at a temperature slightly below the boiling point at 30 cc./min. for one hour. Immediate reaction was evident since no gas flow from the system was observed and the liquid level in the aluminum iodide chamber was seen to increase until the chamber was filled. Examination of the aluminum iodide chamber revealed the presence of a white solid in the bottom. By distillation under reduced pressure, a pale yellow crystalline solid was distilled out of the aluminum iodide into the receiver. After redistillation over copper at reduced pressure a pale yellow solid was obtained. This was analyzed for silicon and iodine and the melting point taken. Found: Si, 5.28; I, 94.66; m.p. 120-121°. For SiI₄ the calculated composition is Si, 5.24; I, 94.76; and the melting point is listed as 120.5°. Analysis of a portion of the white solid in the bottom of the chamber revealed a fluorine/aluminum atomic ratio of 3.1. These results were confirmed by a second experiment.

A series of three experiments was conducted using aluminum chloride and silicon tetrafluoride under pressure. The initial pressure, heating period and temperature were maintained fairly constant but the SiF₄/AlCl₃ molar ratio was varied from 0.66 to 1.5. Reaction data are given in Table IV. A well-defined decrease in the per cent. of silicon tetrachloride in the product is evident. With a slight excess of aluminum chloride (SiF₄/AlCl₃ molar ratio of 0.66) only silicon tetrachloride was found in the high yield of 83%. An increase in the SiF₄/AlCl₃ ratio caused an increase in the per cent. of chlorofluorosilanes in the product.

When the autoclave was charged with 0.26 mole of ferric chloride and 9.2 atmospheres (0.19 mole) of silicon tetrafluoride and heated at 270-380° for 25 minutes no gaseous or liquid product was obtained.

TABLE IV
REACTION OF SILICON TETRAFLUORIDE WITH ANHYDROUS
ALUMINUM CHLORIDE UNDER PRESSURE

Run No.	1	2	3
Mole AlCl ₃ used	0.29	0.14	0.13
Mole SiF ₄ used	.19	.17	.19
SiF ₄ /AlCl ₃ ratio	.66	1.2	1.5
Initial pressure, atm.	8.8	8.0	9.2
Final pressure, atm.	0.7	1
Temperature, °C.	195-244	195-260	195-250
Time, minutes	75	85	70
Mole SiCl ₄ produced	0.16	0.056	0.044
Mole chlorofluorosilanes	None	0.020	0.086
SiCl ₄ , % of product	100	76	34
SiCl ₄ , % yield ^a	83	34	23
Conversion, %	83	46	71

^a Based on SiF₄.

(3) Germanium Tetrafluoride.—The reaction of germanium tetrafluoride with anhydrous aluminum, magnesium and ferric chlorides was studied. The only germanium product found was the tetrachloride which was identified by analysis of a sample after redistillation. Found: Ge, 34.05; Cl, 66.0; calcd. for GeCl₄: Ge, 33.86; Cl, 66.14. Data for these experiments are given in Table V. No volatile prod-

TABLE V
REACTION OF GERMANIUM TETRAFLUORIDE AT ATMOSPHERIC
PRESSURE

Anhydrous metal halide Run →	AlCl ₃		MgCl ₂	FeCl ₃
	1	2	3	4
Temp., °C.	200	210	610	350
GeF ₄ , mole	0.044	0.045	0.036	0.043
Metal halide, mole	0.058	0.29	0.071	0.14
Moles GeCl ₄ found	0.019	0.035	0.016	0.017
Yield of GeCl ₄ , % ^a	43	78	45	40
Moles metal fluoride found		0.047	0.037	0.02
Moles metal fluoride calcd. ^b		0.047	0.032	0.023

^a Based on GeF₄. ^b Based on GeCl₄ found.

TABLE VI
 REACTIVITY OF GROUP IV GASEOUS FLUORIDES

Fluoride		Metal halide					AlI ₃
		MgCl ₂	AlCl ₃	FeCl ₃	FeCl ₃	AlI ₃	
CF ₄	T, °C.	605	220-260	720	290-320	380	300-320
	P, atm.	1	30-75	1	30	1	36
	Product	N.r. ^a	CCl ₄	N.r.	N.r.	N.r.	N.r.
SiF ₄	T, °C.	620-630	215-610	500	270-380		400
	P, atm.	1	1, 8-9	1	9		1
	Product	SiCl ₄	SiCl ₄				SiI ₄
		SiCl ₂ F	SiCl ₂ F	N.r.	N.r.		
		SiCl ₂ F ₂	SiCl ₂ F ₂				
GeF ₄	T, °C.	610	200-210	350			
	P, atm.	1	1	1			
	Product	GeCl ₄	GeCl ₄	GeCl ₄			

^a No reaction.

TABLE VII

HEATS AND FREE ENERGIES OF REACTION

Equation	T, °K.	ΔH	ΔF
CF ₄ (g) + 2MgCl ₂ (s) = CCl ₄ (g) + 2MgF ₂ (s)	900	-14.6	-12.9
3CF ₄ (g) + 2Al ₂ Cl ₆ (g) = 3CCl ₄ (g) + 4AlF ₃ (s)	500	-59.1	+11.6
3CF ₄ (g) + 2Fe ₂ Cl ₆ (g) = 3CCl ₄ (g) + 4FeF ₃ (s)	1000	16.3	-17.9
3CF ₄ (g) + 2Al ₂ I ₆ (l) = 3CCl ₄ (l) + 4AlF ₃ (s)	500	-174	-117.5
SiF ₄ (g) + 2MgCl ₂ (s) = 2MgF ₂ (s) + SiCl ₄ (g)	900	-2.1	-0.7
SiF ₄ (g) + 2CaCl ₂ (s) = 2CaF ₂ (s) + SiCl ₄ (g)	900	20.5	24.9
SiF ₄ (g) + 2BaCl ₂ (s) = 2BaF ₂ (s) + SiCl ₄ (g)	1100	57.6	51.3
3SiF ₄ (g) + 2Al ₂ Cl ₆ (g) = 3SiCl ₄ (g) + 4AlF ₃ (s)	500	-21.4	46.2
3SiF ₄ (g) + 2Fe ₂ Cl ₆ (g) = 3SiCl ₄ (g) + 4FeF ₃ (s)	600	29.2	95.8
3SiF ₄ (g) + 2Al ₂ I ₆ (l) = 3SiI ₄ (l) + 4AlF ₃ (s)	500	5.4	61.5
GeF ₄ (g) + 2MgCl ₂ (s) = GeCl ₄ (l) + 2MgF ₂ (s)	298	-100	-100
3GeF ₄ (g) + 2Al ₂ Cl ₆ (s) = 3GeCl ₄ (l) + 4AlF ₃ (s)	298	-265	-259
3GeF ₄ (g) + 2Fe ₂ Cl ₆ (s) = 3GeCl ₄ (l) + 4FeF ₃ (s)	298	-196	-194
3GeF ₄ (g) + 2Al ₂ I ₆ (s) = 3GeI ₄ (l) + 4AlF ₃ (s)	500		-305

ucts, germanium tetrafluoride or mixed chlorofluorogermanes were collected in the trap at -78°. Therefore, germanium tetrafluoride undergoes metathesis readily to form only the completely chlorinated product, germanium tetrachloride.

A comparison of the results of the reactions of carbon, silicon and germanium tetrafluorides with magnesium, aluminum and ferric chlorides and aluminum iodide is given in Table VI.

Discussion

Utilizing tabulated thermodynamic data,²⁵ the free energy and heat of reaction were calculated for pertinent reactions. The heat of formation of carbon tetrafluoride at 298°K. was taken to be -231 ± 3 kcal./mole.²⁶

The equations and calculated heats and free energies of reaction are given in Table VII.

Germanium tetrafluoride was expected to be the most reactive of the three fluorides and this conclusion is verified by the experimental results. From the thermodynamic data, silicon tetrafluoride was not expected to react with calcium or barium chlorides to any appreciable extent and this is verified by the results obtained. However, the

(25) L. L. Quill, "Chemistry and Metallurgy of Miscellaneous Materials, Thermodynamics," McGraw-Hill Co., Inc., New York, N. Y., 1950; K. K. Kelley, U. S. Bur. Mines, Bull. 476, 477.

(26) ΔH²⁹⁸ for CF₄ was determined by von Wartenberg and Schütte to be -162 kcal./mole (H. von Wartenberg and R. Schütte, *Z. anorg. Chem.*, **211**, 222 (1933)) but more recently a new value of -231 ± 3 kcal./mole has been reported (H. von Wartenberg, *Nachr. Ges. Wiss. Göttingen*, 57 (1946).

heats and free energies for the other reactions are not generally in agreement with the experimental results.

The absence of chlorofluoromethanes in the product of the reaction of carbon tetrafluoride with aluminum chloride under pressure may be explained by the disproportionation of these compounds in the presence of aluminum chloride as a catalyst.²⁷ Although rearrangement reactions of the chlorofluorosilanes have not been reported, the rearrangement of all of the fluorosilanes, namely, trifluorosilane, difluorosilane and fluorosilane, has been described.²⁸

The increase in the per cent. of silicon tetrachloride in the product obtained by the reaction of silicon tetrafluoride with aluminum chloride at atmospheric pressure with an increase in temperature may be due to the thermal disproportionation of the chlorofluorosilanes, since the autoclave experiments, using aluminum chloride and silicon tetrafluoride, produced a regular increase in the proportion of chlorofluorosilanes with an increase in the SiF₄/AlCl₃ molar ratio. An aluminum chloride-catalyzed disproportionation of the chlorofluoro-

(27) C. W. Croco, U. S. Patent 1,994,035 (1935); C. B. Miller and F. H. Bratton, U. S. Patent 2,478,201 (1949); C. W. Murray, U. S. Patents 2,426,637; 2,426,638 (1947); and E. I. du Pont de Nemours and Company, British Patent 628,165 (1949).

(28) J. H. Simons, "Fluorine Chemistry," Academic Press, Inc., New York, N. Y., 1950, p. 109; H. J. Emeléus and A. G. Haddock, *J. Chem. Soc.* 293, (1944).

silanes in the pressure experiments should have resulted in much lower percentages or even none of the chlorofluorosilanes, as was the case with carbon tetrafluoride. Therefore, it may be concluded that the chlorofluorosilanes apparently undergo extensive thermal disproportionation at 500°, whereas at lower temperatures, in the presence of aluminum chloride, no disproportionation was evident.²⁹ The disproportionation of the chlorofluorogermanes has been reported to take place even at -78° and under the conditions of the reactions employed in this work, the existence of these compounds, if formed, would be transitory. Hence,

(29) The possibility of some catalytic activity on the part of aluminum chloride in furthering the disproportionation of the chlorofluorosilanes cannot be entirely excluded, however. For example, the fact that silicon tetrachloride represented a much higher per cent. (76%) of the total products formed in Run 2, Table IV, than in Run 5 Table III (23%), may conceivably be attributed to the fact that in the former case the products were held under pressure in contact with aluminum chloride.

no chlorofluorogermanes were formed in these reactions.

The order of increasing ability to undergo halogen exchange with metal halides may be stated as follows: reactivity increases $\rightarrow \text{CF}_4 < \text{SiF}_4 < \text{GeF}_4$.

The lack of reactivity of carbon tetrafluoride is undoubtedly due to its closely-packed structure even though the heat and free energy for such reactions are favorable. High activation energies would be expected for these reactions, whereas, in the loosely-packed silicon and germanium tetrafluorides, the central atom is easily approached and normal activation energies are apparent.

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X-Ray Studies of Fused Salt Systems.¹ II. Indium(III) Iodide

By R. E. WOOD AND H. L. RITTER

An analysis of the X-ray diffraction pattern of fused InI_3 by the method of Warren, Krutter and Morningstar is reported. The results indicate tetrahedral coordination of I atoms around In atoms rather than trigonal or octahedral coordination. The length of the In-I bond is 2.70 Å. It is not possible to establish definitely from the radial distribution curve whether liquid indium iodide is predominantly monomeric or dimeric. It seems probable that both species are present. A geometrical configuration for the dimer which is consistent with the radial distribution curve is proposed.

Introduction

An earlier communication from this Laboratory¹ reported on the structure of aluminum chloride in the molten state. The stoichiometric similarity of AlCl_3 to InI_3 and the similarity of the ratio of covalent radii, Al/Cl and In/I, raise the question of whether there may not also be a structural similarity. The structure of InI_3 in the gaseous state has been studied by Brode² by means of electron diffraction. Studies of the structures of the liquid and solid states of this substance have not been reported. Brode proposed for the gas a structure consisting of a shared-edge double tetrahedron similar to that found by Palmer and Elliott³ for gaseous aluminum chloride and to that reported from this Laboratory for liquid aluminum chloride. Stevenson and Schomaker⁴ have re-examined Brode's data. They confirmed the existence of dimeric In_2I_6 under Brode's experimental conditions but were unable either to confirm or modify the conformation of the dimer proposed by Brode. We have now examined the X-ray diffraction pattern of liquid InI_3 in order to determine its structure and to compare it with the structure of liquid aluminum chloride.

Experimental

The indium iodide was prepared by gentle heating of a mixture of indium metal shavings and iodine crystals. After

the exothermic reaction had subsided, the product was extracted with anhydrous ether and recrystallized twice from the same solvent. The resulting yellow crystalline powder was analyzed for indium using 8-hydroxyquinoline. Found: In, 23.10; calcd: In, 23.16. The anhydrous salt is extremely hygroscopic and the sample tube had to be filled in a dry atmosphere. The crystals in the sample tube were melted alternately under vacuum and atmospheric pressure in order to force all the liquid into one continuous body in the bottom of the capillary tube.

The camera and experimental arrangement have been described before.¹ Crystal-monochromated $\text{Mo-K}\alpha$ radiation at 40 kv. and 20 ma. was allowed to irradiate the sample for 128 hours. The sample, held at 210° during the exposure, was contained in a Pyrex tube 0.31 mm. i.d. and 0.031 mm. wall thickness. The diffraction photograph was microphotometered on a Leeds and Northrup recording microphotometer and film densities used as a measure of relative intensity. The raw intensity curve was corrected for absorption, diffraction effects due to the container, polarization and incoherent scattering in the usual way. The fully corrected diffraction pattern, intensity vs. the diffraction angle, θ , is shown in Fig. 1. The intensity scale is absolute, the curve having been fitted at large diffraction angles to the calculated curve for the independent scattering of one In and three I atoms.

The procedure for reducing the data of Fig. 1 to a radial distribution curve has been described by its originators, Warren, Krutter and Morningstar¹ and by the present authors.¹ The density of liquid indium iodide was measured by pycnometer and taken as 4.35 g./cc. The "effective" atomic numbers, K_{In} and K_{I} , were taken as equal to the true atomic numbers. This is an excellent approximation for elements of high atomic number. The necessary numerical integrations were carried out using the trapezoidal rule and the International Business Machines CPC electronic computer.

(1) Paper I of this series deals with aluminum chloride: R. L. Harris, R. E. Wood and H. L. Ritter, *This Journal*, **73**, 3151 (1951).

(2) H. Brode, *Ann. Physik*, **37**, 344 (1940).

(3) K. J. Palmer and N. Elliott, *This Journal*, **60**, 1852 (1938).

(4) D. P. Stevenson and V. Schomaker, *ibid.*, **64**, 2514 (1942).

(5) B. E. Warren, H. Krutter and O. Morningstar, *J. Am. Ceram. Soc.*, **19**, 202 (1936).