are 15.5 and 38.6 cm.^{3}, respectively. On this basis we would expect the refractivity of UCl_2F_2 to be somewhere near the mean of these values, or 27 cm.^{3}. Therefore the formula $UClF_3$ fits the observed refractivity much better than does UCl_2F_2.

A portion of the material weighing 448.7 mg. and containing (by microscopic estimation) at least 95% of this mixed halide, the balance being entirely UCl_4, was analyzed for total U, F and Cl. The material was not found to be readily water soluble, but was dissolved in a strong, aqueous solution of NaOH to which H_2O_2 was added. Aliquot portions of this solution were checked for uranium content by a standard ceric titration, for fluorine by a triphenyl tin precipitation, and for chloride by a silver chloride gravimetric method. The results gave 371 mg. of U, 91 mg. of F, and 47.9 mg. of Cl, or 70.6% U, 20.3% F, and 10.7% Cl (a total of 101.6%). Table I compares these results with the theoretical values for the formulas indicated.

TABLE I

	Wt. %		
	U	Cl	F
As found	70.6	10.7	20.3
UCl_2F_2	68.61	20.44	10.95
$UClF_3$	72.03	10.73	17.25

The fluorine analysis, being the most uncertain, was rechecked by a different method on a new sample taken from the same mixture. The basic solution was acidified, care being taken not to heat the acid solution and drive off any HF; and from 1 liter of solution 10-ml. aliquots were steam distilled by the method of Huckaboy, Welch and Metler[3] to separate the fluorine from the uranium. The distillate was then titrated against a standard thorium nitrate solution according to the method of Willard and Winter[4] using a zirconium nitrate–alizarin indicator, with sodium fluoride as the primary standard. The results of these titrations indicated 17–19% F and thus tended to confirm the formula as $UClF_3$.

From these results, it seems most likely that previous analyses of the suspected UCl_2F_2 were made on mixtures of $UClF_3$ and UCl_4 in such proportions that the overall composition had a U:F:Cl mole ratio of closer to 1:2:2.

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The Formation and Decomposition of Trichloromonogermane and Germanium Dichloride[1]

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Various methods of preparing $GeHCl_3$ have been tested. The most efficient method appears to be the reaction of gaseous HCl with GeS and an improvement of this procedure has been obtained. Both $GeHCl_3$ and $GeCl_2$ have been found more unstable than indicated in the literature. $GeHCl_3$ is apparently highly ionized in acidic aqueous solutions even at high hydrogen ion concentrations. $GeCl_2$ has been prepared as residue of the low temperature distillation of $GeHCl_3$. The dichloride has been shown to decompose into polymeric subchlorides even at low temperatures. The results have been correlated with the observations of other workers.

In efforts to prepare trichloromonogermane, $GeHCl_3$, in a high state of purity, we have been surprised to find that this substance is even less stable than the literature would indicate.[2–4] Furthermore, it appears that the product of the dissociation of $GeHCl_3$, germanium chloride, when free of $GeHCl_3$ and HCl, decomposes readily at much lower temperatures than one would expect from earlier descriptions of this compound.[2,5,6]

Even at temperatures in the neighborhood of −30°, $GeHCl_3$ loses HCl readily and when the $GeHCl_3$ has been converted in this way to $GeCl_2$, the dichloride even at these low temperatures decomposes into subchlorides of the type formed by Schwarz and Baronetzky[7,8] at high temperatures by the cracking of $GeCl_4$.

The results of this study are of interest in relation to the recent findings of Schumb and Smyth[9] who showed how readily and similarly Ag_2O and O_2 react with $GeHCl_3$ to form $GeCl_2$, and who suggested that the silver oxide might act as a chemical acceptor for HCl in this reaction. Earlier, Brewer and Dennis[6] tried, with only partial success, to prepare $GeCl_2$ by chemical removal of HCl from $GeHCl_3$. They were able, however, to prepare $GeBr_2$ from $GeHBr_3$ on removal of HBr by physical means.

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[1] Taken from a dissertation submitted by Charles W. Moulton in partial fulfillment of the requirements for the Ph.D. degree, University of Pennsylvania, 1955.

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Experimental

Materials.—Germanium metal and germanium dioxide were obtained from the Eagle–Picher Company. Qualitative tests showed no arsenic was present in the dioxide. The *n*-heptane was a product of the Westvaco Chlorine Products Corporation and was redistilled, only the portion boiling at 99.0–99.2° being retained. It was dried over silica gel. The hydrogen chloride was Matheson Company anhydrous gas.

Preparation of $GeHCl_3$.—The Dennis–Orndorff–Tabern method[2] was tried first and found unsatisfactory even after much effort was expended in constructing the apparatus in a way to minimize the thermal decomposition of the $GeCl_2$ formed in the first stage of the method. The modification of this method proposed by Schwarz and Baronetzky[7] was also unsatisfactory; the same fundamental objection applied, namely, that at the temperature required for reaction between $GeCl_4$ and Ge metal, the $GeCl_2$ decomposed too extensively. From the results described below, this decomposition is now seen to consist of not only the direct reformation of Ge and $GeCl_4$ but also formation of subchlorides which do not react with HCl.

Among additional methods tried, two were based on the equilibrium between $GeHCl_3$ and its ionization products, a proton and the $GeCl_3^-$ ion in acidic aqueous solution,[3,10–12] and on the lack of ionization of $GeHCl_3$ in non-polar solvents.[13,14] Although Tchakirian[10] has stated that $GeHCl_3$ does not distil from weakly acid aqueous solution, it was hoped that the ionization which prevents distillation or extraction of $GeHCl_3$ might be repressed by a higher concentration of acid, especially in view of the fact that the solubility of the closely related $GeCl_4$ is reduced practically to zero in concentrated aqueous hydrochloric acid.[15] Accordingly, efforts were made to prepare $GeHCl_3$ by forming the compound in aqueous solution saturated with HCl at room temperature and either fractionally distilling the solution or extracting with *n*-heptane, in which it was established that $GeHCl_3$ is soluble to the extent of at least 1 g. per 10 ml. The efforts failed; no germanium appeared in the distillates or in the *n*-heptane layer. It is obvious that $GeHCl_3$ remains soluble and highly ionized in aqueous solution even up to high hydrogen ion concentrations.

Good success was obtained by reaction of hydrogen chloride with germanium monosulfide.[16] The GeS was prepared by the method of Foster[17] and dried in an evacuated desiccator. The HCl was dried over phosphorus pentoxide before passage into the Pyrex glass apparatus, in which formation and purification of the $GeHCl_3$ took place.

It was found that it is not necessary to heat the GeS as originally prescribed,[16] for reaction with HCl takes place at room temperature. Although slow initially, the reaction is exothermic and soon reaches a convenient velocity if the pressure of the hydrogen chloride is maintained in the range of 65 to 75 cm. of mercury.

At the end of a run all of the volatile substances were collected in one bulb of the apparatus by means of a liquid-air bath which was then replaced by one of Dry Ice–isopropyl alcohol (−78°), a large part of the hydrogen chloride thereby being expelled from the system through a mercury blow-off tube. Following this, a bath of melting chlorobenzene (−45°) was placed about the bulb, both HCl and H_2S then being expelled. The system was finally pumped at this temperature for 1.5 to 2 hours to remove from the product the remainder of these gases. In this same apparatus, the purified $GeHCl_3$ was distilled into another storage bulb and then into small ampoules by use of liquid air-baths.

Retreatment of the remaining GeS with fresh HCl produced a small additional amount of $GeHCl_3$, so that the overall yield was nearly 40%. After the second treatment there still remained a considerable bulk of solid in the reaction chamber. It may be that the GeS becomes coated with decomposition products. The residue was noticeably lighter in color than the starting material. When a furnace was used to heat the reaction tube, reaction was more rapid, but there remained greater fractions of unreacted GeS. When these residues were removed by washing the reaction tube with sodium hydroxide solution, a gas with a pungent, phosphine-like odor formed. If this gas was germane, it would indicate the presence of material other than GeS in the residue.

A large part of the residue may have been due to impurities contained in the original GeS. We did not analyze this GeS, but Schumb and Smyth[9] found as much as 20% chloride in GeS prepared by the "Inorganic Syntheses" method. They also found that these impurities did not react with HCl even at 50°, so that no contamination of $GeHCl_3$ should result from this source. A sample of the $GeHCl_3$ prepared by this procedure was analyzed for Ge (as GeO_2) and Cl (as AgCl), the average of duplicate determinations yielding the Ge:Cl ratio 1:3.04.

Preparation and Properties of $GeCl_2$.—In the storage of the $GeHCl_3$, it was noticed that small amounts of a white material, initially amorphous in appearance, were formed where the surface of the liquid $GeHCl_3$ contacted the walls of the storage ampoules. It was further observed in some cases that on standing for several days this white deposit had acquired a crystalline appearance. When the liquid was subsequently distilled from the ampoule at low temperature, the color of this initially white deposit changed in the usual pattern observed for $GeCl_2$, becoming first yellow and then orange. Similar behavior was observed when one of the $GeHCl_3$ samples under its own vapor pressure was chilled with liquid air; as evidenced by a slight foaming action, there occurred some distillation from the surface of the white wall deposit and portions of the deposit then became light yellow-orange in color. On condensing dried gaseous HCl into the bulb with a bath of liquid air, and subsequently pumping away the excess HCl while cooling the bulb with baths of Dry Ice–isopropyl alcohol and then of melting chlorobenzene, the remainder of the white deposit disappeared. The white, apparently crystalline material had evidently reacted with hydrogen chloride, indicating that it was a form of $GeCl_2$. The portion which had become discolored did not seem to be in the least affected by the HCl.

To obtain a repesentative sample of $GeCl_2$ by physical removal of HCl from $GeHCl_3$, the $GeHCl_3$ was distilled at several temperatures in a Pyrex glass apparatus containing a removable collecting bulb which could be weighed in advance. The $GeHCl_3$ was placed in this bulb by condensation with a liquid air-bath and was then brought to a higher temperature in the range −24 to −33°. In this range, provided by baths of melting carbon tetrachloride or liquid ammonia, it was pumped until all the liquid distilled from the bulb. During this slow distillation, HCl was removed sufficiently more rapidly than the $GeHCl_3$ by the pumping so that the $GeCl_2$ accumulated in the $GeHCl_3$ in which it is somewhat soluble and remained behind when the $GeHCl_3$ had left the system.

At higher temperatures the breakdown of $GeHCl_3$ was more rapid, but the removal of the HCl was not as complete so that less $GeCl_2$ accumulated during the distillation. Furthermore, even at −20°, the decomposition of the $GeCl_2$ to subhalide was rapid.

The $GeCl_2$ deposits formed in the distillation at −24 to −33° were generally white in color with only occasional traces of yellow. Two such deposits were analyzed for Ge and Cl and gave the same value, 2.11, for the atomic ratio of Cl to Ge.

The residues of the distillation of $GeHCl_3$ at room temperature were chlorine-deficient $GeCl_2$ of widely varied composition. On standing at room temperature, these residues underwent rapid change in color from white through yellow to orange and red-orange, with accompanying lowering of the chlorine content. A volatile substance, apparently $GeCl_4$ from its physical properties, was given off during the decomposition.

The further decomposition of one of these subhalides was studied at higher temperatures. This sample had been formed by distillation of $GeHCl_3$ at room temperature and had been allowed to stand for approximately eight days at this temperature before analysis. During that time its color had changed from white to red-orange. Small drops

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of a clear colorless liquid, presumably $GeCl_4$, had formed and had condensed on the walls of the storage ampoule. This was pumped off and the ampoule was then opened under an atmosphere of dry nitrogen and some of the solid material removed for the thermal decomposition studies. The remainder was analyzed, showing the composition $GeCl_{0.64}$.

In the thermal studies of this subhalide the substance was heated under reduced pressure, volatile products being collected in a trap cooled by a Dry Ice–isopropyl alcohol mixture. The heating was carried out with continuous pumping for periods of about 2 hours each at a series of increasing temperatures between 35 and 400°; after each period, dry nitrogen was admitted into the apparatus and the sample was reweighed. Apparently the decomposition takes place at a rather constant rate above 35°, for the small losses in weight were nearly the same at each of the eighteen temperatures used above 35°. The trap collected very small quantities of a solid which melted to a clear, colorless liquid on warming to room temperature; on addition of small amounts of distilled water, this liquid hydrolyzed to a white precipitate. The color of the subhalide steadily darkened from the original red-orange to red-brown at about 75°, dark brown between 200 and 300°, and finally brown-black at 400°.

At about 150° a white deposit appeared on the unheated upper wall of the sample tube, and at 165° there also appeared a slight iridescence resembling a metallic mirror of extreme thinness. The extent of the first deposit increased with rising temperature, and it became yellow in part.

Discussion of Results

The demonstrated instability of germanium dichloride accounts for a fundamental defect in the Dennis–Orndorff–Tabern synthesis of trichlorogermane. On the other hand, the discovery that germanium monosulfide and hydrogen chloride react to form $GeHCl_3$ satisfactorily without heating is of great advantage in this alternate procedure. Better yields of $GeHCl_3$ can be obtained in this way, both because of the lowered decomposition of any $GeCl_2$ which may form as an intermediate and because of lack of undesirable side reactions. The original temperature proposed[16] for this method was 150°, but Schumb and Smyth[9] recently used it successfully at a much lower temperature, 50°.

It has been shown that trichlorogermane exhibits greater instability than hitherto noted. An equilibrium dissociation into germanium dichloride and hydrogen chloride now appears to be well established. At normal temperatures and under conditions which would not otherwise disturb the equilibrium, dissociation is slight in extent. But during distillation, dissociation is promoted by more rapid diffusion of hydrogen chloride than of $GeHCl_3$. It is rather surprising that such behavior has not been reported earlier for $GeHCl_3$, especially since it was noted long ago[6] for $GeHBr_3$. Perhaps the solubility of $GeCl_2$ in $GeHCl_3$ has hidden this dissociation from earlier observation.

Dissociation must have significant consequences on attempts to purify $GeHCl_3$ by distillation, leading to samples which may be either enriched or deficient in hydrogen chloride. The instability of $GeHCl_3$ must also raise some doubts concerning the vapor pressure values reported[2] for the substance.

The report by Delwaulle[13] of decomposition of $GeHCl_3$ in alcoholic solution, resulting in evolution of hydrogen, suggests that such a reaction might likewise occur for the pure state. Although little information is available concerning the nature of this reaction, the fact[18] that dichlorogermane decomposes with evolution of hydrogen indicates that similar behavior for trichlorogermane should not be ruled out. However, it is noteworthy that samples which have been sealed in ampoules for periods up to several years have not shown the buildup of gas pressure expected from evolution of hydrogen.

Concerning $GeCl_2$, it now appears that the amorphous form has only a transient existence when it is isolated at room temperature. In contact with trichlorogermane, amorphous $GeCl_2$ seems to persist, but when the $GeHCl_3$ is removed, there ensues decomposition, the progress of which is visible in the succession of colors which appear. There is some indication that amorphous $GeCl_2$ alters into a crystalline modification. The deposits in which this was observed remained white in color as long as liquid $GeHCl_3$ was present at room temperature, but chilling the sample with liquid air effected decomposition, due to distillation of some volatile substance, probably $GeCl_4$, from the deposit.

Schwarz and Baronetzky[8] obtained a yellow, crystalline form of $GeCl_2$ from thermal treatment of crystalline germanium monochloride. They stated that decomposition of crystalline $GeCl_2$ begins at 75°, but that it can be produced from the monochloride within a temperature range of 210 to 1200° if it is removed sufficiently rapidly from the heater zone by appropriate apparatus design. Formation of a yellow, apparently crystalline sublimate, possibly identical with the crystalline germanium dichloride of these workers, was observed in this study when the red-brown subchloride of composition $GeCl_{0.64}$ was heated to about 200°.

The non-stoichiometric compounds formed by decomposition of $GeCl_2$ resemble the subchlorides described by Schwarz and Baronetzky,[7,8] although in no case were those encountered in this research formed above room temperature. While the subchlorides met here showed signs of non-homogeneity, they are certainly not to be regarded as heterogeneous mixtures of metallic germanium and $GeCl_2$. This was demonstrated by dissolving the subchlorides in solvents such as benzene, dioxane or diethyl ether. In no case was the undissolved material elemental germanium. The observation that hydrogen chloride has no effect on these subchlorides further supports this finding. These materials are rather to be regarded as mixtures of polymeric substances similar in formation and nature to the chlorine-deficient silicon chlorides.[8,19,20] Thermal decomposition causes continuous approach to the pure metal, presumably due to splitting, from an extended chain or network of small fragments which can then reunite to form germanium tetrachloride. It is probable that the decomposition reaction usually written for $GeCl_2$, $2\ GeCl_2 = Ge + GeCl_4$, does not lead immediately to metallic germanium, but always involves intermediate subhalides.

PHILADELPHIA 4, PA.

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