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GERMANIUM. XXVII. GERMANIUM DICHLORIDE[1]

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Introduction

Winkler stated[2] in 1886 that germanium dichloride is formed when hydrogen chloride is passed over heated germanium. In the following year he announced[3] that the product of this reaction is germanium chloroform and not germanium dichloride. It has since been ascertained by Laubengayer[4] that in the reaction employed by Winkler both germanium chloroform, $GeHCl_3$, and germanium tetrachloride are formed, and that these two substances are not separable by long-continued fractionation in the vacuum apparatus.[5] Germanium chloroform was finally prepared by Tabern[4] by passing the vapor of germanium tetrachloride over heated germanium, which formed what was presumably germanium dichloride, and then causing this product to unite with hydrogen chloride. Tabern made a preliminary study of the germanium dichloride and the extension of our knowledge of this interesting substance was the objective of the present investigation.

Experimental

Germanium chloroform is readily hydrolyzed by water with the formation of hydrated germanous oxide (GeO) and hydrochloric acid, whereas silicon chloroform yields upon hydrolysis silicon dioxide and hydrogen. It was therefore thought possible to prepare germanium dichloride from the chloroform by removing from the latter an atom of chlorine and the atom of hydrogen. This was tried with a number of different substances but germanium dichloride was not obtained.

Attempts were next made to reduce germanium tetrachloride by various powerful reducing agents, but in no case was there definite evidence of the formation of the dichloride. Because of the negative character of these results, the method that was employed in the preparation of $GeHCl_3$ (see above) was then again taken up: $Ge + GeCl_4 = 2GeCl_2$.

Metallic germanium[6] was powdered and fused under salt to remove so far as possible traces of germanium dioxide that it might contain. The resulting button of metal was finely powdered.

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[1] This article is based upon the thesis presented to the Faculty of the Graduate School of Cornell University by H. L. Hunter in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Winkler, *J. prakt. Chem.*, **142** (N. S. **34**) 222 (1886).

[3] Winkler, *ibid.*, **144** (N. S. **36**) 188 (1887).

[4] Dennis, Orndorff and Tabern, *J. Phys. Chem.*, **30**, 1049 (1926).

[5] Laubengayer and Corey, *ibid.*, **30**, 1043 (1926).

[6] Prepared by the method of Tressler and Dennis, *ibid.*, **31**, 1429 (1927).

Germanium tetrachloride[7] was freed from hydrochloric acid by first passing air through it at 40° and then distilling it over into a bulb containing solid sodium carbonate and calcium chloride. Some hours of contact with these substances removes water and the last traces of hydrogen chloride. The purified germanium tetrachloride was then distilled into the bulb M, while that bulb was still attached to the vacuum apparatus[5] by a "normal" interchangeable slip-joint.

The apparatus that was used for carrying out the reaction is shown in Fig. 1. The tube AB is of pyrex glass. All other parts are of soft glass. The ground slip-joints are "normal," interchangeable connections. The pyrex tube is joined to the soft-glass tubes by pieces of "varnished" rubber tubing which can withstand high pressures and is quite impervious to gases.

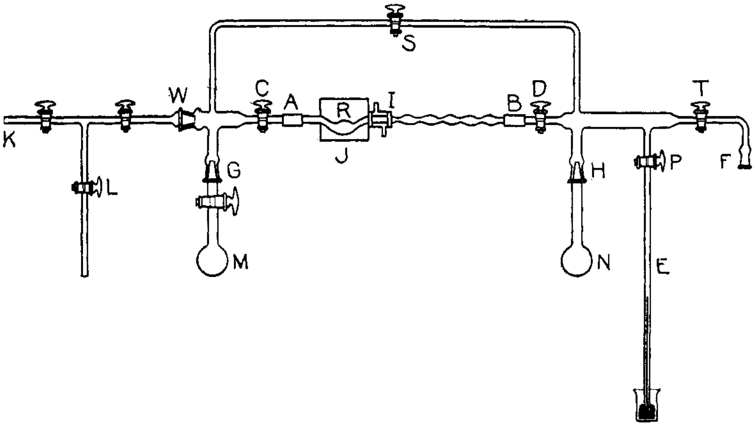

Fig. 1.

The metallic germanium was placed in a widened part of the tube, R, which is surrounded by an electric furnace, J. A short water-jacket, through which water can be run, surrounds the tube just beyond the furnace.

The germanium tetrachloride was solidified by cooling the bulb M with liquid air while it was still attached to the fractionating apparatus, the stopcock was closed and the bulb was then slipped off from that apparatus and attached to the chain (Fig. 1) by the "normal" joint at G. While the tetrachloride was kept frozen, the whole apparatus was exhausted by a pump through K. The stopcock S was then closed.

The current was now turned on the furnace, the temperature being measured by a thermometer or thermocouple throughout the experiment. When the furnace temperature had reached 300°, the stopcocks C and D were opened and the germanium tetrachloride was slowly distilled through the tube into the bulb N by surrounding the latter with a refrigerant and removing the liquid air from around M.

Reaction began at 350°, a white deposit appearing at I just beyond the water-jacket. The temperature of the furnace was held at about 430°. After all of the liquid had distilled over into N, the stopcocks C and D were closed, S was opened and the tetrachloride was returned to M by cooling this bulb and warming N. This

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[7] Prepared by the method of Tabern, Orndorff and Dennis, THIS JOURNAL, 47, 2040 (1925).

procedure was repeated until a sufficient amount of the white deposit had collected in the tube between I and B. The excess of germanium tetrachloride was then removed from the tube by cooling the bulb M with liquid air and closing the stopcock of the bulb after condensation was complete.

Analysis.—Since germanium dichloride is instantly decomposed by moisture and is slowly acted upon by oxygen, the samples for analysis were obtained by passing dry nitrogen through the tube, AB, and breaking off sections of the tube at the constrictions, dropping each segment immediately into a dry weighing bottle that stood in a desiccator filled with nitrogen. The bottle was stoppered and weighed, and the segment of tube was then dropped into a solution of sodium hydroxide to which had been added an amount of hydrogen peroxide sufficient to oxidize the sample. After solution was complete, chlorine was precipitated by silver nitrate, the excess of silver was removed from the filtrate by hydrochloric acid, sulfuric acid was added to the resulting solution until the acid concentration was 6 *N* and germanium was precipitated as the white disulfide.

Anal. Subs., 0.0695, 0.3101. Calcd. for $GeCl_2$: Cl, 0.03434, 0.1532; Ge, 0.0351, 0.1569. Found: Cl, 0.0343, 0.1530; Ge, 0.0350, 0.1558.

Properties.—At room temperature germanium dichloride in a thin layer is almost white; the color deepens through a cream to a light yellow tint as the layer becomes thicker. When some of the compound was caused to deposit on the sides of a thin-walled test-tube, and the tube was evacuated and then heated in an oil-bath, dissociation of the dichloride began at 74.6°, and as the temperature rose the substance became first cream-colored, then lemon-yellow, orange, reddish-brown, dark brown, and finally black at about 450°, at which temperature dissociation into $GeCl_4$ and Ge was complete. Because of this ease of dissociation, the compound cannot be sublimed either in a vacuum or in a current of an inert gas.

Germanium dichloride is insoluble in, or reacts with, many of the usual solvents that were added to it. It is not affected by 95% ethyl alcohol or by chloroform. It is fairly soluble in germanium tetrachloride. Water hydrolyzes it, and ammonium hydroxide converts it to an orange-colored substance. Concentrated hydrochloric acid changes it to a white solid which soon dissolves in the acid, with the probable formation of trichloromonogermane.

Dry oxygen slowly acts upon germanium dichloride. After about fifteen minutes' contact, the dichloride begins to turn white, due to the formation of germanium dioxide. A volatile substance that is simultaneously formed was identified as germanium tetrachloride (mol. wt., 213. Theoretical, 214.4). This reaction is, therefore, $2GeCl_2 + O_2 = GeO_2 + GeCl_4$.

When moist oxygen is passed over the compound, the reaction shown in the preceding equation probably takes place to a slight extent, but the moisture acts much more vigorously on the substance than does the oxygen. The first stage is doubtless $GeCl_2 + 2H_2O = Ge(OH)_2 + 2HCl$. The hydrogen chloride then instantly combines with unchanged germanium dichloride to form germanium chloroform, which is carried out of the tube by the current of oxygen.

Chlorine rapidly attacks germanium dichloride with the formation of pure germanium tetrachloride. Bromine forms a colorless liquid, which on fractionation was found to consist almost entirely of germanium tetrachloride and tetrabromide. Not more than a trace of a double halide was produced. Hydrogen sulfide acts at once upon germanium dichloride at room temperature. Quantitative examination of the products showed that the reaction is essentially $GeCl_2 + H_2S = GeS + 2HCl$.

Summary

This article describes the preparation and properties of germanium dichloride.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE LABORATORY OF GENERAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

A CONDUCTANCE-DIFFUSION METHOD FOR STUDYING THE COAGULATION OF COLLOIDAL FERRIC OXIDE[1,2]

BY C. HARVEY SORUM

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Introduction

The knowledge that electrolytes will coagulate colloids dates back to the work of Thomas Graham.[3] The study of this particular phenomenon from all of its various angles has proceeded almost without a halt from Graham's time up to the present, with the result that an enormous amount has been written on the subject of coagulation. To review this mass of literature would only be repeating items already summarized in a number of modern books on Colloid Chemistry. Sufficient if, passing in review the most important experimental facts gleaned from the work of a great

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[1] The substance of this article was included in a paper presented at the Midwest Regional Meeting of the American Chemical Society, University of Chicago, May 27–28, 1927. A preliminary version was submitted for publication in THIS JOURNAL, October 10, 1927.

[2] An extract from a thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy, University of Wisconsin, June, 1927. All work was carried out under the direction of Professors F. C. Krauskopf and J. H. Walton, to whom the author is deeply and gratefully indebted.

[3] Graham, *J. Chem. Soc.*, **15**, 216 (1862); **17**, 318 (1864).