

tively short-lived, lasting about twenty minutes in the case of the HCl-produced material and only two minutes in the case of the H₂S-produced material. Nevertheless, the plastic state was observed to exist, and in contrast to the immediate solidification of the material formed in the presence of the inert gases nitrogen and ammonia, its life in this state was quite appreciable. The corresponding increases in the proportion of insoluble sulfur present in the hardened samples is also indicative of the ability of hydrogen chloride and hydrogen sulfide to act similarly to sulfur dioxide in the formation of the plastic and insoluble modifications.

Thus, theories postulating the indispensability of sulfur dioxide in the formation of plastic sulfur or for the maintenance of insolubility in the hardened mass appear, on the basis of these facts, to be untenable. The suggestions by Deines and by Meyer that foreign substances other than sulfur dioxide might be effective in causing similar results are upheld by the experimental evidence.

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Preparation of Germanium Tetrachloride, GeCl₄

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When germanium dioxide, GeO₂, is boiled with hydrochloric acid, germanium tetrachloride, GeCl₄, volatilizes if the concentration of hydrogen chloride approaches 6 *N*.¹ It has been observed in this Laboratory and elsewhere, however, that if the concentration of hydrogen chloride is too high, germanium tetrachloride vapor is carried uncondensed through a water cooled condenser.² The loss of germanium is readily explained. When the acid concentration is high, germanium tetrachloride is not hydrolyzed and, in addition, is not very soluble in such acid solutions. Its vapor pressure, furthermore, is quite high at the temperature of the cooling water in the condenser. When 6 *N* hydrochloric acid, approximately the constant boiling mixture, is used, both the acid and the germanium tetrachloride are completely condensed; when mixtures with higher concentrations of hydrogen chloride are boiled, however,

gaseous hydrogen chloride passes through the condenser and carries considerable germanium tetrachloride along with it.

Aitkenhead and Middleton^{2b} took advantage of this phenomenon in the analysis of minerals for small amounts of germanium; germanium tetrachloride was distilled in a stream of hydrogen chloride gas, thus removing the germanium completely from the rest of the dissolved sample. The gases which escaped from the top of a reflux condenser were absorbed in a small volume of water and the germanium content readily determined.

At very low temperatures (−72°) no complexes form between germanium tetrachloride and hydrogen chloride³ so that it is possible to separate the two by judicious cooling. It has been found that if the vapors which emerge from the top of a reflux condenser, after being dried, are cooled in a "dry-ice"-isopropyl alcohol mixture, the hydrogen chloride (b. p. −85°) escapes uncondensed and the germanium tetrachloride freezes out as a pure white solid (m. p. −49.5°). The method has the added advantage that the germanium dioxide is more readily dissolved in the boiling flask when the concentration of hydrogen chloride is kept high.

Procedure.—Germanium oxide is suspended in 6 *N* hydrochloric acid and the suspension is boiled gently under a reflux condenser. Hydrogen chloride is passed into the flask at a rapid rate at first so that some of it escapes slowly through a sulfuric acid trap at the end of the train. Later, when the absorption in the boiling flask nears completion, the rate of flow is reduced. As the gases pass through the reflux condenser, condensed germanium tetrachloride and constant boiling hydrochloric acid return to the flask, but the gases escaping through the condenser carry a high percentage of germanium tetrachloride and gradually all of it is volatilized. The gas mixture, having been cooled to the dew point of the germanium tetrachloride at the temperature of the cooling water, will be unsaturated at room temperature and will not deposit liquid germanium tetrachloride in the calcium chloride tower used to remove residual moisture. When passed through the tube cooled by means of dry-ice, however, the germanium tetrachloride is completely removed and entrains very little hydrogen chloride. An all glass apparatus is preferable, but no difficulties are encountered if rubber connections are used. By this procedure 5 to 10 g. of GeO₂ may be converted to the tetrachloride within an hour. Residual hydrogen chloride may be removed by allowing the product to stand over sodium carbonate, filtering and distilling in dry apparatus.^{1b}

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RECEIVED OCTOBER 2, 1942

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