2. The use of the new acid and its salts for the colorimetric determination of germanium is suggested.

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NITROGEN COMPOUNDS OF GERMANIUM. I. THE PREPARATION AND PROPERTIES OF GERMANIC NITRIDE

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According to the literature silicon[1] combines directly with nitrogen, when heated at 1300 to 1450°, to form the normal nitride, Si_3N_4. A similar reaction takes place when this element is heated in an atmosphere of ammonia at high temperatures. Analogous reactions in the case of germanium, tin and lead are lacking.

Carbonic anammonide, $(C_3N_4)_x$, has been obtained[2] as a highly polymerized, orange powder by heating mercuric thiocyanate. Pauly[3] has reported $(C_3N_2)_x$, carbonous nitride or anammonide, as being obtained by the thermal decomposition of tetra-iodo-imidazole. This has since been shown[4] in all probability to be a mixture of carbon and paracyanogen, $(C_2N_2)_x$. Bergstrom[5] prepared stannous imide, SnNH, by reacting potassium ammono stannite, SnNK, with a solution of ammonium bromide in liquid ammonia. The imide was deammonated by heating in a vacuum at 340°. The reaction resulted in the formation of stannous anammonide or nitride, Sn_3N_2. This nitride is the only definite one known of the fourth outer group elements exhibiting a valence of two. Carbonic nitride and silicic nitride are the only representatives of these elements functioning with a valence of four.

Recently Schwarz and Schenk[6] studied the ammonolysis of germanium tetrachloride in liquid ammonia solution. Their results indicate that the hexammonate described by Thomas and Pugh[7] may not exist in liquid ammonia. Schwarz and Schenk allowed germanium tetrachloride to ammonolyze, separated the ammonium chloride and found a definite combination in the imide, $Ge(NH)_2$. At 150° the imide was found to lose ammonia with the formation of the germanam, Ge_2N_3H. This latter

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[1] Weiss and Engelhardt, *Z. anorg. Chem.*, **65**, 78 (1910); Funk, *ibid.*, **133**, 67 (1924).

[2] King and Chamberlain, "Theses," Stanford University, **1924**, and **1930**, respectively.

[3] Pauly, *Ber.*, **43**, 2243 (1910).

[4] Wenzel, "Dissertation," Stanford University, **1927.**

[5] Bergstrom, *J. Phys. Chem.*, **32**, 433 (1928).

[6] Schwarz and Schenk, *Ber.*, **63**, 296 (1930).

[7] Thomas and Pugh, *J. Chem. Soc.*, 1051 (1926).

combination was found to be stable at 300° but at higher temperatures to decompose, with loss of ammonia, to the nitride, Ge_3N_4. Their evidence for the formation of the nitride is based entirely upon the changes in weight resulting from the decomposition of the germanam and of the imide; no analyses are reported to substantiate the existence of germanic nitride. In the case of the decomposition of the imide the ammonia liberated was determined. Since these changes in weight are very small, especially when minute quantities of the substances are used, it is difficult to state the purity of the nitride without analytical data on the germanium and nitrogen content. However, it is the belief of the writer that Schwarz and Schenk have prepared germanic nitride.

Before the work of these investigators appeared, Kraus and E. G. Johnson[8] studied the ammonolysis of germanium tetrachloride. Their results are in agreement with those of Schwarz and Schenk in the formation of the imide and the germanam, and definitely substantiate the existence of the nitride.

The following described investigation confirms the results of the above-mentioned workers in that germanic nitride is prepared by the action of ammonia gas on metallic germanium at elevated temperatures. Some of the physical and chemical properties of the nitride are also determined.

Experimental

Source of Material.—The germanium was obtained as germanous sulfide from germanite ore according to the procedure described by Kraus and Johnson.[9] The sulfide was oxidized with nitric acid to germanic oxide, which was then reduced with hydrogen at 600° to the gray germanium powder. For purification, the metal was heated in a stream of chlorine gas at 250° to form germanium tetrachloride, the chloride was hydrolyzed to the oxide, and finally the oxide was again reduced with hydrogen to germanium. This procedure gave germanium in a finely divided state and of fairly high purity.[10]

Anhydrous ammonia of commerce was siphoned from its container into a small steel cylinder containing several small pieces of sodium, which served to remove the water completely. During the course of a reaction the ammonia was allowed to escape from this cylinder as a gas.

Preparation of Germanic Nitride

(a) **The Action of Ammonia on Germanium.**—A weighed amount of the powdered germanium, obtained from the reduction of germanic oxide, was placed in a weighed alundum boat in a vitreosil tube. The tube extended horizontally through an electric

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[8] Kraus and E. G. Johnson, Brown University, private communication.

[9] Kraus and Johnson, Paper given at the Swampscott Meeting of the American Chemical Society, September, 1928.

[10] It has been shown by Dennis, Tressler and Hance, THIS JOURNAL, **45**, 2034–5 (1923), that small amounts of germanium dioxide may be reduced quantitatively with hydrogen, but when several grams of the oxide are used, the reduction does not appear to be complete. This fact accounts for the low yields of germanic nitride obtained in the following described experiments.

furnace the temperature of which was measured with a thermocouple. A fairly rapid stream of ammonia gas was allowed to pass over the germanium at different temperatures. A slow reaction was observed at 650°; at 700° the formation of nitride appeared to be quite rapid, only three hours being required to convert 1 g. of germanium to the nitride. The samples of germanium were heated in an atmosphere of ammonia until no increase in weight of the boat was observed to indicate the continued formation of nitride. The nitride appeared as a light brown powder.

The following data show the formation of germanic nitride.

Ge, g.	Ge_3N_4 (obtained), g.	Ge_3N_4 (calcd.), g.
0.4603	0.5756	0.5787
4.2852	5.3718	5.3878

When ammonia was passed over germanium at temperatures in the neighborhood of 850° and above, no nitride was formed. Since, as was found in later experiments, the nitride is readily reduced with hydrogen at elevated temperatures, the absence of its formation at 850° is readily accounted for by the high concentration of hydrogen present in the gas mixture due to the dissociation of ammonia.

(b) **The Action of Ammonia on Germanic Oxide.**—Ammonia was found to react slowly with germanic oxide at 700° and much more rapidly at 750°. The ammonia served to reduce the oxide to germanium, which in turn reacted with additional ammonia as described above. The probable course of the reaction is

$$3GeO_2 + 4NH_3 = Ge_3N_4 + 6H_2O$$

The formation of the nitride in this reaction was indicated by the light brown color and the following changes in weight.

GeO_2, g.	Ge_3N_4 (obtained), g.	Ge_3N_4 (calcd.), g.
0.4808	0.4188	0.4195
4.1299	3.6074	3.6039

The Reduction of Germanic Nitride. The Determination of Germanium and Nitrogen.—Preliminary experiments showed that the usual methods for the determination of nitrogen were not highly satisfactory. Concentrated sulfuric acid and also a mixture of this acid with concentrated nitric acid reacted slowly with the nitride even on boiling. Several days were required to dissolve a small amount of the nitride when this procedure was followed. A concentrated solution of sodium hydroxide, even when boiled, did not liberate ammonia and appeared to have no effect on the nitride. It was found, however, that, when the nitride was heated at a temperature as low as 600° in a stream of hydrogen gas, reduction took place readily to metallic germanium and ammonia. At 700° the reduction process was found to be extremely rapid. The reaction evidently proceeds as follows

$$6H_2 + Ge_3N_4 = 3Ge + 4NH_3$$

Likewise, the reaction to the left expresses the process for the formation of the nitride from germanium and ammonia.

In collecting the ammonia resulting from the reduction of the nitride, the gas stream was allowed to pass through two wash bottles containing a known amount of standard hydrochloric acid solution. The strength of the acid was 0.1032 *N*. When the reduction was completed, the solutions were titrated back with standard sodium hydroxide solution and the amount of acid used to combine with the ammonia was calculated accordingly. The residue remaining in the boat after complete reduction of the nitride was germanium in the elementary state.

Quantitative results were obtained in this procedure when a rapid stream of hydrogen was used so that the ammonia would be rapidly swept out of the hot regions of the furnace. A slow gas stream permitted the ammonia to dissociate into nitrogen and hydrogen and low results were obtained.

The results of the reduction are given in Table I. In the first column is given the weight of germanic nitride reduced, in the second and third columns, the weight of germanium found in the boat after complete reduction and the theoretical amount, respectively; in the fourth, the volume of standard acid solution used to neutralize the ammonia collected; and in the fifth and sixth columns, the amount of nitrogen as calculated from the titration and the theoretical amount, respectively.

TABLE I

ANALYSIS OF GERMANIC NITRIDE FOR GERMANIUM AND NITROGEN

Ge_3N_4, g.	Ge (found), g.	Ge (calcd.), g.	HCl, cc.	N_2 (found), g.	N_2 (calcd.), g.
0.5000	0.3989	0.3977	70.17	0.1020	0.1023
.6586	.5270	.5238	91.14	.1318	.1348
.5732	.4553	.4559	82.65	.1195	.1173

The Oxidation of Germanic Nitride.—Germanic nitride was found to be exceedingly stable toward the usual oxidizing agents. Even a mixture of fuming nitric and fuming sulfuric acids caused only a slow oxidation on boiling. When the compound was heated in air at the temperature of the Mêker burner, oxidation took place with difficulty. Pure oxygen gas was found to oxidize the nitride at 850–900°; on the other hand, the reaction proceeded slowly at 800°. White germanic oxide was formed in this reaction; the condition of the nitrogen was not determined but, without doubt, it was eliminated as elementary nitrogen.

Anal. Subs., 0.5766, 0.9777. Calcd. GeO_2: 0.6607, 1.1203. Found: 0.6593, 1.1180.

The Chlorination of Germanic Nitride.—Germanic nitride, 0.4321 g., was weighed in an alundum boat which was introduced into a vitreosil tube. A slow stream of chlorine gas, emitted from a tank and dried with concentrated sulfuric acid, was allowed to pass over the nitride at different temperatures. The temperature was controlled as previously described. The first heating was carried out at 400–450° for a period of two hours; only 2.3 mg. loss in weight resulted. When the temperature was increased to 600° for four hours, more than one-third of the material was found to have left the boat. The color of the remaining material was brown, but of a little lighter shade than that of the original sample. The heating was continued for several hours at temperatures ranging from 500–575° but no indication of reaction was found; however, at 600–700°, the reaction proceeded rapidly, as all but 50 mg. of the original sample of the nitride disappeared from the boat during a four-hour heating. The color of the remaining nitride was still a light brown. It was found possible, on further heating at the last-named temperature, completely to remove the nitride from the boat by the reaction with chlorine gas. Germanium tetrachloride was observed as one of the products of the reaction. The following equation expresses the probable course of the reaction

$$Ge_3N_4 + 6Cl_2 = 3GeCl_4 + 2N_2$$

Color.—Schwarz and Schenk state that germanic nitride is white when pure. In the decomposition of their germanam they obtained a brown colored nitride, but they attribute the color to the presence of finely divided germanium. In view of the above-described experiment on the chlorination of the nitride, it is impossible to ascribe the color to any appreciable amount of metallic germanium. Germanium is well known to react with chlorine readily at temperatures as low as 100°.

In the above, the brown color persisted after the nitride had been heated for many hours in chlorine at temperatures ranging from 400–700°. If any germanium were present with the nitride, one would expect it to be quickly removed as germanium tetrachloride, which is thermally stable at the temperatures of the experiments. Since the brown color did appear to vary in intensity in the different preparations and since the chlorine rendered them lighter in color, undoubtedly a small amount of germanium was present. This amount is accounted for in the first loss in weight recorded in the chlorination experiment, namely, 2.3 mg., but no loss resulted when the same material was later heated at 500–575°. On the other hand, the persistence of the color throughout the entire reaction either means that the nitride is normally a light brown or that another constituent is present, possibly germanium or a lower nitride, which is so finely dispersed throughout the mass of the material as to render its separation difficult.

The presence of an appreciable amount of germanous nitride[11] with the germanic nitride is not substantiated by experiments. This nitride is quite volatile and would be removed from the germanic nitride at the temperatures required for the preparation of the latter.

It may also be suggested that the color is due to the polymerization of the germanic nitride molecule.

The Dissociation of Germanic Nitride.—The decomposition of the nitride at 900–1000° resulted in the production of germanium and nitrogen. (A small amount of material, black to brown in color, appeared on the walls of the tube. This is thought to be germanous nitride.)[12] The results obtained by Schwarz and Schenk at the high temperatures are confirmed in this experiment. It should be stated, however, that in our experiments the nitrogen was removed rapidly by means of a Hyvac pump while the dissociation proceeded.

When the nitride was decomposed in a closed system at lower temperatures, 600–700°, a considerable amount of material collected on the walls of the tube in the cooler regions. The pressure developed by the nitrogen was measured at different intervals over a period of several weeks and was found to increase gradually. There was no indication of any equilibrium values. If dissociation at this temperature produces nitrogen and germanium, there must necessarily result some germanous nitride, which would volatilize and collect on the walls of the tube. It will be necessary to study the dissociation of germanic nitride under dif-

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[11] Germanous nitride, Ge_3N_2, has been prepared in this Laboratory by Mr. J. R. Hart. It is formed readily when metallic germanium is heated in nitrogen at 800–950°. Thin layers of this nitride appear brown in color while the substance in a compact form appears black. It is readily volatile at a temperature as low as 650°. The results concerning its preparation and properties will appear in a forthcoming publication.

[12] Observations by Mr. J. R. Hart.

ferent conditions, and, if possible, to obtain equilibrium values before any definite statement may be made concerning the mechanism of the process.

Other Properties.—Germanic nitride resembles the corresponding compound of silicon in its remarkable stability. It is not affected by air at ordinary temperatures. It is insoluble in water and all the common inorganic solvents. It is not attacked by water at 100°. A boiling solution of sodium hydroxide does not liberate nitrogen as ammonia from the nitride. Strong acids appear to affect it slightly.

Summary

Germanic nitride has been prepared by reacting metallic germanium with ammonia gas at 700°. Germanic oxide may be used in place of germanium in this reaction.

The nitride is readily reduced by hydrogen at 700° to germanium and ammonia. This process serves as a method of analysis for the germanium and nitrogen.

The oxidation of the nitride to germanic oxide by means of oxygen at 850° proceeds rapidly. Chlorine gas reacts with germanic nitride at high temperatures.

The color, dissociation and other properties are discussed.

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A SPECTROSCOPIC STUDY OF THE DECOMPOSITION AND SYNTHESIS OF ORGANIC COMPOUNDS BY ELECTRICAL DISCHARGES. I. THE ELECTRODELESS DISCHARGE

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1. Introduction

While the effects of electrical discharges upon organic gases and vapors have been investigated extensively, little has been known concerning the mechanism of their action. Thus the final condensation products have been studied, but there has been practically no knowledge of the decomposition products formed initially in the discharge.

In certain respects the conditions in low voltage discharges resemble those in flames, although the velocities of the free electrons are commonly greater in the former. In flames produced by the combustion of organic hydrogen compounds in oxygen, molecules of water, of hydroxyl (OH), of carbon (C_2) and of carbon monoxide, are present. These molecules also exist in electrical discharges which pass through organic vapors,