

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

GERMANIUM HYDRIDE

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In 1902, Voegelen¹ drew attention to the existence of a volatile hydride of germanium and pointed out certain similarities which this compound bears to the familiar hydrides of arsenic and antimony. At that time Voegelen worked with small quantities and did not succeed in preparing the hydride in the pure state. The investigation carried out by him was concerned chiefly with a determination of the composition of the hydride existing in dilute mixture with hydrogen from which gas he was unable to separate the hydride. The striking similarity in the behaviors of the hydride of germanium and arsine did not attract the attention which would ordinarily be expected, on account of the extreme rarity of germanium at that time, and since the publication of Voegelen's paper nothing further concerning the hydride has been reported.

Briefly, the following facts have been established by this previous work. First, that the formula probably corresponds to GeH_4 , as determined by the composition of the silver germanide precipitated by action of germanium hydride upon a silver salt and several analyses of the diluted gas by passage over finely divided sulfur, whereby the germanium hydride content of the gas was converted to sulfide. The results of these experiments were not entirely satisfactory, as frankly admitted by Voegelen, but pointed to the probable existence of the hydride, GeH_4 . Second, the spots formed by allowing the burning hydride to impinge upon porcelain surfaces were described as somewhat similar to arsenic spots and the solubility of the metallic germanium in those solvents commonly used for the confirmation of arsenic was recognized.

The present investigation was undertaken with the object of making a further study of the hydride of germanium and its methods of preparation, and especially to ascertain to what extent the hydride reaction is applicable to the detection of minute quantities of germanium. The similarity of the mirrors which germanium and arsenic give in the Marsh test operation has also suggested to the authors the necessity for a more careful study of these deposits and a comparison of them by spectroscopic examination of the light which thin films of these metals transmit.

Experimental

Preliminary experiments were carried out to ascertain the most satisfactory means of producing the nascent hydrogen for the formation of germanium hydride. For this purpose standard solutions of pure ger-

¹ Voegelen, *Z. anorg. Chem.*, **30**, 325 (1902).

manic acid were prepared, known volumes of which were added to various types of hydrogen generators. Measurements were made of the minimum quantities of germanium dioxide required to produce distinct mirror deposits of the metal in definite time intervals. The hydride-bearing hydrogen was in each case led through a heated tube, constricted at the heated portion as in the ordinary Marsh apparatus.

Sulfuric acid and zinc, both of which were shown to be free from arsenic, antimony and germanium by blank tests, gave results indicating a very low velocity of hydride formation, the introduction of as much as 0.0234 g. of germanium dioxide in aqueous solution being required to give a distinct deposit of metal in the heated tube. At the same time a brown finely divided deposit was produced in the hydrogen generator, indicating the formation of either metal or some lower hydride. Only very small quantities of germanium were carried over in the hydrogen stream as hydride.

Hydrochloric acid, specially prepared and free from arsenic and antimony, gave slightly better results. The brown deposit did not appear, but experiments with quantities of germanium dioxide weighing 0.0234 g. gave only very small deposits (faint brown films) after $\frac{1}{2}$ to $\frac{3}{4}$ hour. It was concluded that the acid type of generator could not be satisfactorily used for the detection of germanium as hydride.

Hydrogen generators of the alkaline type were now tried. Beginning with pure aluminum and caustic potash as the source of hydrogen, it was immediately noticed that the hydride formation became much more rapid, giving a mirror-producing hydrogen stream with 0.005 g. of germanium dioxide; that is to say, the delicacy of the hydride test from the alkali generator was increased about 4-fold over that produced from the acid type of generator.

Further increase in the delicacy of this reaction could not at first be obtained, owing to the high dilution of the hydride in the hydrogen stream simultaneously produced. Two different ways of overcoming this difficulty were apparent. First, a substitution of some metal other than aluminum and cutting down the rate of hydrogen flow, and second, the slow formation of a richer mixture of germanium hydride and hydrogen in a closed system, allowing a certain time for the formation of the hydride in an undiluted condition before driving the mixed gases through the constricted tube for deposition as a mirror.

With this in mind, a modified Marsh apparatus was so constructed as to permit the formation of a rich mixture of germanium hydride and hydrogen which subsequent to its formation could be expelled from its generator by pure hydrogen from an outside source. Reference to the apparatus described later, which was used for final determinations, is explanatory. Sodium amalgam was more satisfactory as a reducing agent than metallic aluminum and dil. caustic potash solution, as a 2% amalgam allows the

complete reduction of germanic acid with a small admixture of free hydrogen. Experiments were performed using in one case sodium amalgam as the source of hydrogen, and aluminum and very dil. caustic potash solution in the other. The results indicated that the mirror produced by 0.00015 g. of germanium dioxide with sodium amalgam was just about comparable with the deposit obtained by 0.00078 g. of germanium dioxide with aluminum and caustic potash. Since all other conditions in the two experiments were as nearly as possible the same, it was concluded that sodium amalgam was the better reducing agent, at least for small quantities of germanium. In the preparation of hydride from quantities of germanium dioxide greater than 30 to 40 mg. it was noticed that the slow-acting sodium amalgam caused a separation of most of the germanium in a finely divided black metallic form and that reduction beyond the metallic condition did not proceed to completion when once the metal separated. Reduction to hydride was complete, however, when small quantities of the aqueous solution of the dioxide were added to the amalgam in separate portions. Under these conditions only traces of a brownish deposit formed upon the surface of the decomposing amalgam and these deposits finally disappeared as the hydrogen was evolved. A solution of germanic acid containing 0.00009 g. of germanium dioxide was introduced into the hydride generator containing 2% sodium amalgam. The amalgam was allowed to act for 10 to 15 minutes and the gas then expelled through a heated tube by a current of pure hydrogen from an electrolytic generator. A distinct brown deposit was produced in the heated capillary in approximately $\frac{3}{4}$ hour. Repetition of the experiment with 0.00005 g. of germanium dioxide did not give a satisfactory test. The limit of delicacy of the test must, therefore, lie between these two quantities. That is, the smallest quantity of germanium detectable in the manner described is larger than 0.00004 g., but 0.00006 g. of the metal may be detected with certainty.

Behavior of Metallic Germanium in Hydrogen

Metallic germanium is slowly but appreciably volatile in hydrogen at elevated temperatures and this loss of metal necessarily limits the delicacy of the hydride test. This fact has already been referred to in work preliminary to a redetermination of the atomic weight of germanium.² Study of the magnitude of this loss by reformation of hydride was undertaken in the following manner.

1.41855 g. of pure, finely-divided metal was placed in a quartz weighing tube which was then introduced into a quartz apparatus so constructed as to allow the metal to be heated in a slow stream of pure hydrogen. A bottling apparatus was used of the same type as that employed by Rich-

² THIS JOURNAL, 43, 1085 (1921).

ards in several atomic-weight determinations, permitting the opening and closing of the weighing tube without contamination from the outside. The temperature of the metal in hydrogen was maintained at 750–800°, measured with a platinum-iridium thermocouple.

A series of 12 weighings was taken at intervals varying between 2 and 4 hours. The metal residuum after each heating showed a continual loss in weight, the total loss at the end of 38 hours being 0.00647 g. The hydrogen used was prepared electrolytically from a 15% caustic soda electrolyte and nickel electrodes. The gas was washed and dried in the same manner as described in a redetermination of the atomic weight of molybdenum.³

It was concluded that a fairly uniform loss of metal takes place when germanium is heated in hydrogen gas. There was practically no condensation of metal in the cooler portions of the apparatus and the waste hydrogen gave a small black precipitate when passed through a solution of a silver salt, indicating the direct formation of the volatile hydride. Furthermore, the quantity of germanium volatilized in the hydrogen was fairly uniform for each unit of time of heating and was larger in quantity than the smallest amount detectable by the reverse reaction in the Marsh apparatus. It follows that too high a temperature should be avoided in depositing the mirror of germanium in the Marsh apparatus and long heating in the residuum of pure hydrogen is objectionable.

Temperature of Decomposition of Germanium Hydride

The decomposition temperature of the richest obtainable mixture of germanium hydride with hydrogen was determined as follows.

An aqueous solution of 0.0234 g. of germanium dioxide was added to a generator containing aluminum and caustic potash, which at that time was delivering 10 cc. of hydrogen in a minute. The gas was conducted through a thin-walled glass worm immersed in a quartz air-bath at known temperature. The temperature of the latter was slowly raised and the first sign of a deposit of metal was noted. Deposition of a brown stain began at 340°, and between 340° and 360° a dense, silvery mirror rapidly developed. From this experiment it is plain that a high temperature is unnecessary for the deposition of the germanium mirror and subsequent to its production, continuance of a high temperature will cause loss of metal in the residual excess of hydrogen and seriously affect the delicacy of the test.

Apparatus for Detection of Germanium

A modified Marsh apparatus was used, which was especially adapted to the detection of germanium; it consisted of the following units in order: (1) an electrolytic hydrogen generator, using as electrolyte 15% caustic soda and having nickel electrodes; (2) a washing tower containing a silver salt solution; (3) a sulfuric acid drying tower;

³ Müller, *THIS JOURNAL*, **37**, 2046 (1915).

(4) a trap for exit of excess hydrogen from generator; (5) a germanium hydride generator consisting of a small wash bottle, the inner tube of which was cut off at about 5 cm. from the bottom of the bottle; this generator was furnished with a funnel and stopcock through which the sodium amalgam and germanium solution could be introduced after the whole system was filled with hydrogen from the electrolytic generator (1); (6) a small drying tube; (7) a constricted tube for deposition of mirror, followed by a small trap to prevent entrance of air.

Dry sodium amalgam was introduced into the generator (5) and all the air expelled by hydrogen from the electrolytic generator. The electrolytic hydrogen stream was interrupted and the aqueous solution containing germanium was then introduced and washed down with pure water. The germanium hydride was allowed to form in this closed compartment for 15–20 minutes. In this manner a pocket of germanium hydride containing comparatively little hydrogen was obtained, the volume of which was insufficient to make its way out of the generator. The electrolytic hydrogen current was then allowed to sweep the germanium hydride through the heated tube in which the mirror almost immediately made its appearance.

Each experiment was, of course, preceded by a blank test to insure the absence of any arsenic, antimony or germanium in the various materials used. The stock of sodium amalgam used and the wash hydrogen showed not the slightest trace of any spot-producing material by test extending over the same periods of time as required for the germanium determinations. Table I shows results obtained with various quantities of germanium dioxide.

TABLE I
DEPOSITION OF GERMANIUM MIRRORS

GeO ₂ G.	Time required for deposition of mirror Min.	Description of mirror	GeO ₂ G.	Time required for disposition of mirror Min.	Description of mirror
0.00078	45	Dense brown-red, silvery reflection	0.000093	60	Small brown ring
0.000468	45	Dense brown, less silvery reflection	0.0000468	60	Slight brown deposit, no luster

The spots produced were invariably brownish-red and when in an appreciable amount were silvery to reflected light and a deep brownish-red by transmitted light. As shown by Voegelen, the spots are soluble in sodium hypochlorite solution and are rapidly oxidized to the white dioxide by nitric acid or by heat in a current of air. The non-volatility of the deposit of metal or the dioxide subsequently formed by heat of course distinguishes the germanium mirrors from those produced by arsenic. The germanium mirrors are always deposited in the heated tube immediately in the vicinity of the heated portion, unlike the arsenic spot which is deposited in a cooler portion of the tube. Dil. ammonia containing hydrogen peroxide dissolves the mirror of germanium much more quickly than does dil. nitric acid. The mirror is very stable in moist air and does not oxidize appreciably after weeks of exposure in an open tube. It is insoluble in

metallic mercury. Arsenic mirrors are much browner than those of germanium, and are less red by transmitted light.

Spectroscopic Examination of the Light Transmitted by Films of Germanium and Arsenic, and Determination of the Minimum Thickness of Opaque Mirrors

Germanium hydride mixed with much hydrogen was conveyed into an air-bath chamber containing flat and highly polished rectangular glass surfaces. Cautious heating of the air-bath resulted in the formation of flat metallic films of fairly uniform thickness. The most uniform deposits were selected out of many, and known areas cut from the glass. These were weighed before and after dissolving the mirror in ammoniacal

TABLE II
PROPERTIES OF FILMS OF METALLIC GERMANIUM

Film	Area Sq. cm.	Weight of metal G.	Thickness of film Cm.	Appearance of film by transmitted light
A	9.86	0.00107	0.0000198	Transparent; brownish-red
B	6.09	0.00161	0.0000485	Opaque; silvery by reflected light
C	5.8	0.0011	0.0000347	Opaque
D	3.24	0.00047	0.0000265	Transparent; deep red; silvery luster by reflected light

hydrogen peroxide solution, thereby giving the weight of metal deposited. As the areas were measured, the thickness of the films could be calculated assuming the density of the metal to be 5.468. Table II shows the results obtained for germanium.

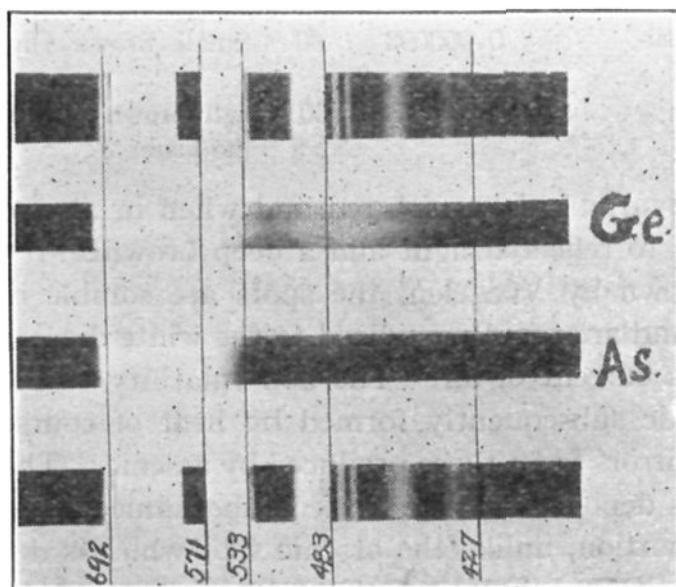


Fig. 1.

transmitted by these was spectroscopically examined. A Hilger direct reading spectrometer was used. Light of the same intensity was allowed to pass

It is seen from the table that the thickness of Film D, which was the thickest of the transparent films obtained, differs from the thinnest opaque film by only 0.0000081 cm. The uniformity of the metallic layers was assured by revolving the film in front of the slit of a spectroscope and noting the light intensity over the whole surface. Germanium and arsenic films of approximately the same thickness were selected and the light

through a 4cm. layer of didymium chloride solution containing 0.0852 g. of oxide in each cubic centimeter. These known absorption bands were used to define the spectra exhibited by the films of germanium and arsenic. As conditions of exposure, development and printing were the same in both cases, the spectra shown in Fig. A demonstrate characteristic differences in the light transmitted by these films.

The Composition of Various Mixtures of Germanium Hydride and Hydrogen and a Study of Silver Germanide

It has been pointed out that the hydride reaction for germanium is influenced by the method used for the preparation of the nascent hydrogen and that various types of generators and different rates of hydrogen formation give good, indifferent or even poor results in the hydride test. The gas mixtures obtained under different conditions have been collected and an attempt has been made by analysis of these to find answers to the following questions. First, how may the richest gas mixture be obtained? Second, is the gray to gray-black precipitate, obtained by the action of the hydride upon a silver salt, a substance of uniform composition? Finally, is the hydride itself really GeH_4 or a mixture of lower hydrides, which would easily be suspected by the peculiar relations existing between silicon, carbon and germanium?

Two methods were used for determining the germanium content of the hydride-hydrogen mixture. In Mixtures 1, 2 and 3 shown in Table III, the gas samples collected over water were slowly forced through a fine capillary tube into a strong ammoniacal solution of hydrogen peroxide, resulting in the formation of the ammonium salt of germanic acid. In the absence of phosphoric acid or other foreign substances often in hydrogen peroxide, the germanium dioxide may be directly estimated by evaporation to dryness and ignition to the pure dioxide.

In Samples 4, 5 and 6 shown in Table IV, the gas samples were thoroughly washed with silver nitrate solution and the precipitate formed was weighed and further analyzed for germanium and silver content. It should be noted here that when Voegelen prepared silver germanide his analyses were far from satisfactory in establishing the real existence of tetrasilver-germanide, Ag_4Ge , and that he assumed that germanium was to be found only in the precipitate with the silver in which behavior germanium hydride would resemble stibine rather than arsine. The writers have found that after the passage of the hydride into a silver salt solution there are conditions in which most of the germanium passes into the filtrate along with the excess of silver salt solution, while the precipitate itself consists of nearly pure silver. This is just like the behavior of arsine in which metallic silver and arsenious acid are produced. Results of analyses of the gas mixtures 1, 2 and 3, together with conditions of prep-

aration, are to be seen in Table III. Table IV shows analyses of the gas mixtures 4, 5 and 6 through formation of silver germanide, and in addition contains the results of the analyses of the silver precipitate for its silver and germanium content. From the latter the concentration of hydride in the gas was calculated.

TABLE III

Gas Mixture	Volume at 0° C. and 760 mm. Cc.	Generator	Rate of flow Cc. per min.	Content of Ge in gas as GeO ₂ G.	Calculated % by volume of GeH ₄
1	757	Al and dil. KOH	100	0.0023	0.064
2	768	Al and very dil. KOH	20.5	0.0063	0.176
3	730	2% sodium amalgam	13.1	0.0022	0.064

TABLE IV

Gas mixture	Volume at 0° and 760 mm. Cc.	Generator	Rate of flow in Cc. per min.	Ppte. G.	Ag in ppte. G.	Ge in ppte. G.	Atomic ratio in ppte. Ag:Ge	% by vol. of GeH ₄ in gas
4	480	2% sodium amalgam	6.9	0.0707	0.0660	0.0047	9.4 :1	0.302
5	808	Al and KOH	88.	0.0788	0.0750	0.0038	11.7 :1	0.144
6	808	Al and KOH	22.4	0.1183	0.1022	0.0161	4.29:1	0.616

Both Tables III and IV show that when the same type of generator is used a slow evolution of hydrogen produces the richest hydride mixture. Hence the development of apparatus used. In Table IV it is observable that the precipitated silver compound produced by action of the hydride upon a silver salt solution is far from constant in composition and in only one case (Analysis 6) approximated Ag₄Ge, the formula ascribed to the precipitate by Voegelen. In Analyses 4 and 5, Table IV, it is evident that far less germanium was brought down with the silver, though the amount of silver did not vary greatly.

Examination of the filtrates from the precipitation of the silver compound shows that much germanium exists in solution as germanic acid when the hydride is produced under the conditions described in 4 and 5, while in Analysis 6 most of the germanium appears with the silver as germanide and very little germanium passes into solution. Germanic acid when formed is not precipitated by the excess of silver salt present. A simple explanation of the irregularity in the composition of the silver germanium precipitate can be advanced if the presence of at least one new hydride of germanium in the gas be assumed.

Expt. 7. Fifty cc. of a saturated solution of germanium dioxide containing 0.234 g. was quickly added in one portion to the generator using alumi-

num and caustic potash. The gas evolved was passed into silver nitrate solution. The precipitate was filtered out, weighed and analyzed for silver and germanium. The filtrate, which contained an excess of silver nitrate, was treated with an excess of ammonium hydroxide and saturated with hydrogen sulfide, and after filtering out the silver sulfide the solution was rendered strongly acid and the germanium which it contained removed and estimated as sulfide.

Expt. 8. This was carried out in the same manner except that the solution of 0.234 g. of germanium dioxide was, in this case, added to the generator in small portions over a much longer period. The precipitate was analyzed and the filtrate examined as before for germanic acid. Table V shows the result of these analyses.

TABLE V

Expt.	Wt. of ppte. G.	Color	Wt. of Ge in ppte. G.	Wt. of Ag in ppte. G.	Ge as metal in filtrate G.	Atomic ratio Ag:Ge.
7	0.2560	pale grayish- white	0.0032	0.2528	0.0228	53:1
8	0.1294	dark gray	0.0152	0.1142	0.00664	5.05:1

In Expt. 7 conditions were such as to allow nascent hydrogen to act upon an excess of germanic acid. The resulting gas mixture gave a precipitate with silver nitrate nearly all of which consisted of free silver. The bulk of the germanium was found in the filtrate as germanic acid. In Expt. 8, on the other hand, where the germanic acid was slowly introduced and the evolved hydrogen always in excess, it is seen that nearly all of the germanium is precipitated as the dark-gray germanide. Analysis of the precipitate gave close to the expected formula of the germanide and little germanic acid in the filtrate. It is evident that the compound as prepared by Voegelen must have been made in a similar manner.

As the only variable in the two experiments was the ratio maintained between the reacting quantities of hydrogen and germanic acid, it is highly probable that the gas produced in the former experiment contained some unidentified lower hydride. The present authors realize fully that the above experiments do not prove the existence of a new hydride, but clearly point to its probable existence. Effort will be made to fractionate the hydride-hydrogen mixtures obtained under the above circumstances by a freezing-out process, and the result of this further work will be reported in the near future.

Summary

1. Germanium may be detected by a modification of the Marsh test in quantities as small as 0.00006 g. of metal.
2. The delicacy of the hydride reaction is greatly increased by use of

the alkaline type of generator as the source of nascent hydrogen. Aluminum and dil. potassium hydroxide solution serve best for the formation of large quantities of germanium hydride, and sodium amalgam is best for small quantities.

3. The apparatus described, which is a modification of the ordinary Marsh apparatus, permits the formation of a richer mixture of the hydride than has hitherto been prepared and still further increases the delicacy of the hydride test.

4. The decomposition temperature of the hydride lies between 340° and 360° ; deposition of the mirror is best obtained below a red heat.

The reverse reaction involving the loss of germanium in hydrogen has been quantitatively estimated and shows the magnitude of the loss suffered by this metal in hydrogen at $750-800^{\circ}$.

5. The dissimilarity of films of germanium and arsenic as obtained in the Marsh test, is shown by spectroscopic examination of the light which these films transmit and the thickness of various mirrors has been determined.

6. Study of the composition of the compound described by Voegelen as silver germanide plainly shows that this precipitate is variable in composition and may consist of nearly all free silver with very little combined germanium, or nearly pure silver germanide, depending upon the method used in the preparation of the hydride.

7. The conditions are stated which favor the formation of tetrasilvergermanide, Ag_4Ge , and also those which result in the formation of free silver and soluble germanic acid by the action of the hydride upon a silver salt.

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THE SOLUBILITY OF SULFUR DIOXIDE IN SUSPENSIONS OF CALCIUM AND MAGNESIUM HYDROXIDES

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From the time of the investigation and original patents of B. C. Tilghman,¹ the development and use of the sulfite process in pulp making has steadily progressed until to-day it is the most important method of making chemical wood pulp. Practice has shown that wide variations in the quality of the product are to be expected as the quality of the cooking liquor varies, yet any attempts at the control of the latter, either by the design of apparatus or in the process of manufacture, have necessarily

¹ Tilghman, Brit. pat. 2,926 (1866); Ger. pat., March 31, 1867; U. S. pat., October 26, 1867.