

It was thought that the viscosity of the carbonate solution might be great enough to account for this difference and so a third determination (Curve 2) was made with a cane sugar solution having the same viscosity as the carbonate solution, which was freed from carbon dioxide by boiling under a vacuum. This gave a rate considerably lower than that for water, but not as low as the sodium carbonate solution. The remaining difference is probably due to the mass-action effect of the carbonate and bicarbonate ions in solution.

An independent means of making a check on the general accuracy of form and values of a rate curve is provided by some preliminary work done with a motion picture method for determining the rate of absorption, which used a similar absorber tube and a bubbler tip of the same form but which produced smaller bubbles. Curve 1 of Fig. 9 was made from data obtained with the motion picture apparatus using 2.0 *N* sodium hydroxide solution at 27°, and Curve 2 was made with the same solution at 25° using the present apparatus. In spite of the difference in bubble volume and the increase in temperature, which always raises the values of *a*, the curves show a very satisfactory general agreement as to shape and height.

Summary

An apparatus has been described which makes possible a detailed study of absorption from small bubbles. The rate of absorption from a bubble of pure carbon dioxide is not a constant but goes through three stages, finally diminishing to zero at the end. The effect of concentration and other variables has been studied with the particular purpose of determining the reproducibility and accuracy of the method.

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GERMANIUM.¹ VII. THE HYDRIDES OF GERMANIUM

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RECEIVED DECEMBER 17, 1923

Introduction

When this investigation was begun in 1921, the only statement in the literature concerning germanium hydride was one by Voegelen,² who had found that a volatile hydride of germanium was formed when the chloride was reduced by nascent hydrogen (zinc and sulfuric acid), that the gas reduced a solution of silver nitrate, and that it yielded a "germanium mirror" when passed through a heated glass tube. The amount of ger-

¹ This article is based upon the theses presented to the Faculty of the Graduate School of Cornell University by Robert B. Corey and Roy W. Moore in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² Voegelen, *Z. anorg. Chem.*, **30**, 325 (1902).

manium at his disposal was, however, very small (about 0.4 g.) and his attempts to establish the composition of the compound by analysis were far from conclusive.

While our study was in progress, three further articles upon this subject appeared.³ Müller studied methods of preparation of germanium hydride to ascertain whether the procedure might be used for the detection of minute amounts of germanium. Paneth prepared the hydride by reducing a solution of germanium in sulfuric acid with either zinc or magnesium, and Schenck by treating an alloy of germanium and magnesium with an acid. Both of these investigators experimentally ascertained that the composition of the gas was GeH_4 , and Schenck determined as well its melting point and boiling point. Neither of them, however, obtained evidence of the existence of higher hydrides of germanium, and Paneth expressly states⁴ that the gas consists of pure tetrahydride and contains no higher hydrides.

Experimental Part

Preparation of Germanium Hydrides.—Some three years ago it had been observed in the Cornell Laboratory that germanium hydride is formed in considerable quantity when a solution of germanium dioxide in potassium hydroxide is treated with an excess of metallic aluminum. Our later study of the method showed, however, that the yield is small.

A method analogous to that used by Dennis and Anderson for the preparation of hydrogen telluride⁵ was next tried. The cathode consisted of a cast rod of germanium and the electrolyte was 50% orthophosphoric acid. The gas evolved from the cathode was thoroughly dried and was then passed through two tubes immersed in liquid air. It condensed to a white solid. When the refrigerant was removed, the solid melted and then the greater part of it quickly vaporized. A small liquid residue in the tube was at that time thought to be water, but in the light of our later experiments, it was doubtless a mixture of the higher hydrides of germanium. The slowness of the evolution of germanium hydride by this electrolytic method rendered the procedure unsuited to our purpose.

The third method that was studied, and which was finally adopted, was similar to that used by Stock for the preparation of the hydrides of silicon,⁶ and consists of the treatment of magnesium germanide with an acid. Stock prepared magnesium silicide by heating a mixture of carefully purified silicon dioxide and magnesium. He used silica presumably because of the difficulty of preparing pure silicon. Since metallic germanium of

³ (a) Müller and Smith, *THIS JOURNAL*, **44**, 1909 (1922). (b) Paneth and Schmidt-Hebbel, *Ber.*, **55**, 2615 (1922). (c) Schenck, *Rec. trav. chim.*, **41**, 569 (1922).

⁴ Paneth, Matthies and Schmidt-Hebbel, *Ber.*, **55**, 785 (1922); also Ref. 3b, p. 2619.

⁵ Dennis and Anderson, *THIS JOURNAL*, **36**, 882 (1914).

⁶ Stock and Somieski, *Ber.*, **49**, 111 (1916).

high purity may easily be prepared,⁷ the magnesium-germanium alloy was made by mixing powdered germanium with very fine magnesium turnings in the proportion 3:2. Spectroscopic examination of the magnesium for arsenic showed that only a trace, about one part in 200,000, of this element was present. This mixture was placed in alundum boats in a hard glass tube, and was heated in a current of hydrogen with the flame of a Bunsen burner. The temperature was slowly raised until reaction took place, which occurred at a little below red heat. The mixture first glows brightly at the spot where the reaction begins, and the glow then quickly spreads throughout the mass without further heating. The product was granular and dark gray in color, and yielded a distinct odor of germanium hydride when exposed to the air.

After quite prolonged preliminary experimentation, the apparatus described below was designed and constructed for the evolution, condensation, separation and study of the germanium hydrides.

The generation of the germanium hydrides was carried on in two round-bottom, 1-liter, Pyrex flasks, each fitted with an outlet tube, an inlet tube for the introduction of hydrogen, and a separatory funnel. Each generator could be operated independently of the other.

About 45 g. of magnesium germanide was placed in each flask, and the air was swept out by hydrogen. The hydrogen was made from the action of sulfuric acid on zinc and was purified by passing it through an alkaline solution of potassium permanganate, and then over heated platinized asbestos to remove any free oxygen that might be present. It was next thoroughly dried, and was then passed through a U-tube immersed in liquid air to make certain that it contained no condensable impurities.

After the air in the flask had been displaced by hydrogen, dil. hydrochloric acid (1:4) was run in drop by drop, the flask being shaken after each addition of acid to prevent localization of the action. The reaction was violent, and each flask was immersed in a bath of ice water to keep down the temperature. About two hours was required for the addition of 100 cc. of dil. acid to each generator. The reaction then apparently ceased, and addition of a little concd. hydrochloric acid gave no further appreciable evolution of gas.

The evolved gases were swept out of the generating flask by a very slow current of purified hydrogen, and were freed from hydrogen chloride and germanium chloroform by passage through 3 wash bottles containing water and finally through a Liebig potash bulb containing water at 0°. They were then dried by passage over calcium chloride, metaphosphoric acid and phosphorus pentoxide. They next passed into the U-tube A, Fig. 1, which at this time was not connected with the rest of the apparatus. This tube was immersed in liquid air and in it the germanium hydrides were condensed. The accompanying hydrogen passed out into the air through a mercury trap.

Separation and Identification of Germanium Hydride

Apparatus.—For the isolation, purification and identification of any germanium hydrides that might be evolved in the reaction, an apparatus was constructed, patterned after that used by Stock in his able and

⁷ Dennis, Tressler and Hance, *THIS JOURNAL*, **45**, 2033 (1923).

exhaustive studies of the hydrides of silicon. The essential parts of the apparatus are shown in Fig. 1.

The bulbs B, C, and D are used for the fractional distillation of the gases. The bulb E, containing about 700 cc., serves to give adequate capacity to the apparatus. The graduated tube F is used in the measurements of the volumes of liquids and in the determination of their melting points. It was carefully calibrated with the use of mercury. G aids in the operation of the valves, as will later be seen, and is also used in the measurement of vapor tensions. The height of mercury in the manometer H may be adjusted by means of the level bulb Q. In making pressure readings, the mercury was

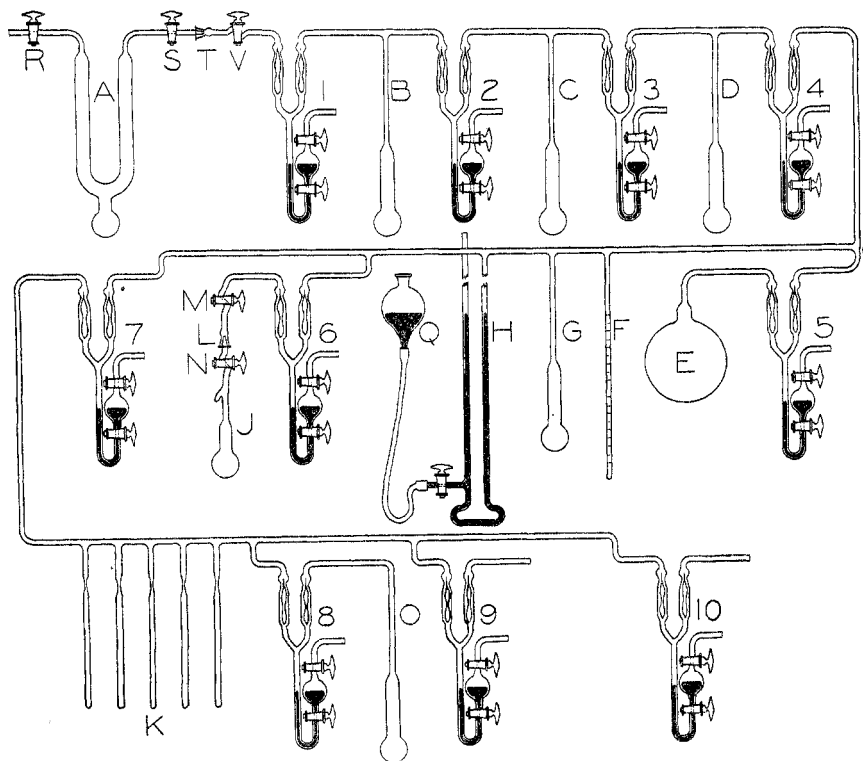


Fig. 1.

brought to a mark on the right-hand tube of H whenever it was necessary to know the volume of the gas. This obviated the necessity of correcting the volume of the apparatus with the rise and fall of the mercury column.

The tube J is used for removing samples for weighing or for transfer to other pieces of apparatus. It is attached to M by the ground joint L. Its short side arm holds a globule of mercury which, when the tube is inverted in the operation of weighing, falls against the stopcock and protects the gas in the tube from contact with the stopcock lubricant. Any gas sample can be preserved for future examination by condensing it in one of the tubes K and sealing off the tube. The bulb O is used for temporary storage of a gas sample during fractionation.

The mercury valves, 1-10, contain two glass floats which are carefully ground into

their seats. No lubricant is used. The floats are raised and lowered by the mercury in the U-tubes below them. When the apparatus is under diminished pressure, a valve may be closed by opening the two stopcocks and admitting air, whereupon the mercury rises and lifts the floats. The valves are opened by applying suction to the side arm.

The apparatus may be exhausted by an oil pump attached to Valve 9 through a tube containing calcium chloride, or by a Toepler mercury pump attached to Valve 10 through a tube containing phosphorus pentoxide.

Before the apparatus was put in use it was freed from moisture by repeatedly pumping it out and then readmitting air through the drying agents.

The volume of the flask E and the connecting parts of the apparatus between Valves 4, 6 and 7 and the mark on the manometer H was determined by calibration with carbon dioxide which was used for this purpose because it can be prepared in high purity and is easily condensable with liquid air. The necessity for using a condensable gas is obvious from the construction of the mercury valves, only a slight difference in pressure between the two sides rendering the valves inoperative. The condensation of the gas allows the pressure in the apparatus to be controlled, which in turn allows the valves to be operated.

The apparatus was calibrated in the following manner. Pure, dry carbon dioxide was condensed by liquid air in the U-tube A. The apparatus, including the space in A above the solid carbon dioxide, was evacuated. The carbon dioxide was then distilled over into B and condensed there, and Valve 1 was closed. Valves 6 and 7 were then closed and the carbon dioxide was allowed to vaporize until the manometer registered about 80 mm. pressure. It had been found that the volume of carbon dioxide remaining in the calibrated portion at this pressure was a convenient volume for buret measurement. Valve 4 was then closed and liquid air was brought up around B. After the temperature and pressure prevailing in the apparatus had been noted, the gas was condensed in G. Valve 6 was next opened and the gas was distilled into J, whereupon the stopcocks M and N were closed. The tube J was detached from the apparatus, but was kept surrounded by liquid air and was then connected with a buret in the manner shown in Fig. 2. The space above the stopcock N was evacuated by raising and lowering the mercury in the Hempel buret with suitable adjustment of the stopcock R after each stroke. N was opened, liquid air was removed from around J, and the carbon dioxide was allowed to vaporize into A. The gas was then forced over into a water-jacketed buret filled with mercury and its volume was measured. From the data thus obtained, the volume of the apparatus between Valves 4, 6 and 7 and the mark on the manometer H, with Valve 5 open, was found to be 809 cc.

In a similar manner the volume of the apparatus between Valves 4, 5, 6 and 7, and the mark on the manometer was found to be 140 cc.

Before proceeding with the fractionation of the germanium hydrides, familiarity with the operation of the apparatus and a gage as to its accuracy were obtained by preparing silicon hydrides from magnesium silicide and isolating samples of pure monosilicane and disilicane by fractionation. Determinations of the physical constants of these products and their analyses gave results which agreed in all details with those given by Stock.⁶

Fractionation.—The germanium hydrides, evolved by the treatment of magnesium germanide with hydrochloric acid, having been condensed in the U-tube A, Fig. 1, this tube was connected to the apparatus which was then completely evacuated beyond the stopcock S. Valves 5, 6 and 8 were then closed, stopcock S was opened, and with liquid air still around the U-tube A, the hydrogen still present in A was pumped out through

Valves 9 and 10. These valves were then closed and the contents of A was distilled into and condensed in B by allowing A to come to room temperature and cooling B in liquid air. Valve 1 was then closed.

The entire contents of Bulb B was subjected to fractional distillation to separate the more volatile monogermene, GeH_4 , from other possible less volatile germanium hydrides. In distilling monosilicane, which boils at -112° , Stock employed a temperature of -125° . Schenck having already determined the boiling point of monogermene to be -125° , we began the distillation of this constituent at a temperature of about -134° . The bulb B was immersed in a pentane bath which had previously been cooled slightly below -134° , and which was vigorously stirred by means of a motor stirrer. The pentane was contained in a

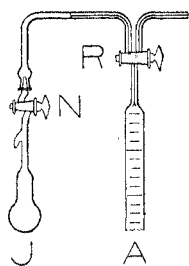


Fig. 2.

silvered Dewar cylinder, and was held at any desired temperature by immersing in it a test-tube into which liquid air was poured from time to time as necessary. The temperature was measured by a thermocouple of chromel-alumel wire. The standard e.m.f.-temperature data for these couples⁸ were employed for drawing a calibration curve, but the applicability of this curve to the couple that we used was checked by determining the freezing points of ether, carbon disulfide, toluene, chloroform, mercury and carbon tetrachloride. The results obtained for these various liquids corresponded to the values given by the curve within the limits of accuracy of the instrument.

With Bulb B held at a temperature of about -134° and Bulb C immersed in liquid air, the fractionation was continued for two hours. Valve 2 between B and C was then closed and the pentane bath around B was replaced with liquid air. It was later found that the cooling of B at this point by liquid air was unnecessary because the vapor tension of the residue in the bulb was less than one atmosphere at room temperature.

The distillate in C was removed from the apparatus by opening Valve 6 and distilling the contents of C into the weighing tube J in the manner already described. The stopcocks M and N were then closed, the weighing tube was detached and, while still kept in liquid air, joined to the apparatus shown in Fig. 2. The material in J was then transferred to glass sample tubes⁹ by drawing it off, a portion at a time, into the buret A and transferring each portion from A to the sample tube over mercury. This procedure was repeated until all of the gas in J had been thus brought into the tube. The total volume of this first fraction amounted to somewhat more than 1300 cc. It was found to consist almost entirely of monogermene and is being kept for future investigation.

⁸ "Pyrometry," *Am. Inst. Mining Metallurg. Eng.*, 1920, p. 172.

⁹ Dennis, "Gas Analysis," The Macmillan Co., 1913, Fig. 4, p. 4.

The weighing tube J was again connected to the fractionation apparatus which was then exhausted by means of the air pumps. Valves 6, 7, 9 and 10 were then closed.

The less volatile portion of the germanium hydrides still remaining in B changed to a white, slushy substance when the pentane bath was removed, but froze to a white solid when cooled by liquid air. It was of course impossible to know at the outset the proper temperature for distilling from this residue the next higher hydride, but since there is close analogy between the hydrides of silicon and germanium, the temperature range employed by Stock for distilling disilicane, -105° to -97° , was employed at the beginning. At this temperature, however, the manometer showed no appreciable vapor pressure, and the pentane bath was therefore allowed to warm until a slight drop in the manometer column was seen. At this temperature, about -63° , distillation was begun by immersing C in liquid air and was continued for 35 minutes at temperatures ranging from -63° to -60° . Valve 2 was then closed. A small liquid residue remained in B.

Digermane, Ge_2H_6

The distillate in C, when allowed to come to room temperature, was found to be a clear liquid and to possess a vapor tension of about 560 mm. It could therefore be allowed to stand in the bulb without danger of bursting the apparatus.

Density of Digermane as Gas.—To obtain some idea as to the probable composition of this fraction, its density in the form of gas (weight of one liter) was determined.

The volume of the apparatus between Valves 4, 5, 6 and 7, having previously been accurately ascertained, the density of any gas enclosed in this part of the chain could be determined by measuring the temperature and pressure and then weighing the gas. To this end a small amount of the distillate in C was allowed to vaporize into this calibrated portion of the apparatus and the pressure and temperature of the gas were noted. Valve 6 was then opened and the gas was condensed in J, which was then removed from the apparatus and weighed. Two determinations of the weight of a liter of the gas under standard conditions gave 6.66 g. and 6.63 g. The calculated value for Ge_2H_6 is 6.743 g. The lowness of the two results indicated that the material still contained some monogermane. These samples were therefore united with the main portion of the distillate in C which was then subjected to redistillation. To remove completely all possible traces of monogermane, the material was distilled for two hours through a temperature range of -110° to -99° . A minute amount of distillate condensed in Bulb D. This was pumped out of the apparatus and discarded.

The residue in *C* was then fractionally distilled into *D* at a temperature of -77° to -72° for 40 minutes. No appreciable residue remained in *C*. The density of this purified fraction was then determined, and to make clear the details of the procedure the following data are given.

After the gas had been brought into the calibrated portion of the apparatus, the mercury in the manometer was set at the mark and the following readings were made.

Volume of apparatus	140 cc.	Manometer readings	
Room temperature	20.4°	Top	799.4 mm.
Barometer	739.3 mm.	Bottom	145.8 mm.
		Difference	653.6 mm.
		Pressure of gas	85.7 mm.

The gas was then brought into the weighing tube *J* by immersing the latter in liquid air. The volume of the apparatus was so large as to render

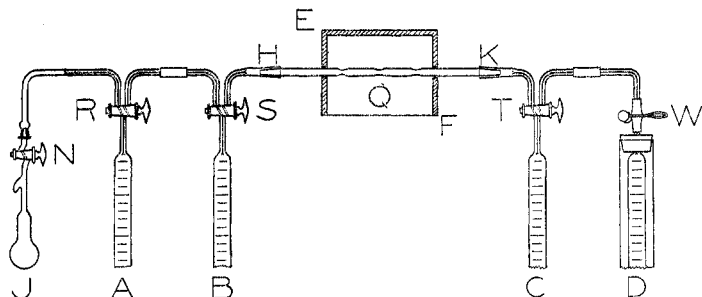


Fig. 3.

it difficult to condense completely in the weighing tube, within a reasonable length of time, all of the gas that was present. Consequently, after Valve 6 had been closed, the pressure of the gas remaining above the valve was ascertained and was found to be 3 mm. This residual pressure was then subtracted from the original pressure of 85.7 mm., the difference being the pressure corresponding to the gas that had been condensed in *J*.

The volume of the sample under standard conditions was then $140 \times \frac{273}{293.4} \times \frac{82.7}{760} = 14.18$ cc. The weight of the gas (weight of weighing tube *J* + gas, 23.9133 g., less weight of weighing tube, 23.8177 g.) was 0.0956 g. The density of the gas (weight of one liter in grams) was therefore $\frac{0.0956}{14.18} \times 1000 = 6.745$ g. A second determination gave 6.736 g.; av., 6.7405. These results agree closely with the calculated value, 6.743 g., for digermene.

Analysis of Digermene.—The apparatus that was devised for the analysis of these hydrides is shown in Fig. 3. It permitted the passage of

the sample backward and forward through a heated quartz tube Q until the gas was completely dissociated into germanium, which deposits on the walls of the tube, and hydrogen. The weight of the germanium was ascertained and the hydrogen was measured. Some of the weighed sample in J was transferred to the Hempel buret A over mercury in the manner already described. It was found to be impossible to bring all of the sample into A because digermane at ordinary pressures and temperatures is a liquid. The sample in A was transferred to B, whereupon the stopcock S was closed, and the gas remaining in the connecting tubes and in the buret A was condensed again in J by immersing the latter in liquid air. The tube J was then weighed and the difference gave the weight of the hydride used in the analysis.

The Hempel buret C was then used as an air pump, and the quartz tube Q with its connections was completely evacuated. Rather than admit the germanium hydride directly into Q, it was found preferable to slow down the thermal decomposition by first passing into Q from the buret C a known volume of pure dry hydrogen in such amount that this gas in Q would be under diminished pressure to allow for the expansion of the hydrogen when Q is heated before the stopcock S is opened. The jacketed buret D was then connected to the buret C after all of the air in the capillaries had been displaced by mercury. The quartz tube was then heated to dull redness and the stopcock S was carefully opened, the pressure of the gas in B being at this point kept somewhat less than that of the hydrogen in Q. The level bulb of the buret C was then lowered slightly, the stopcock T was opened, and the sample was slowly drawn out of B through the hot tube into C. The direction of flow of the gas was reversed several times until complete decomposition had been effected. The hydrogen was then pumped into the buret D and measured, and its weight was calculated. The quartz tube was detached from the apparatus and weighed and the weight of germanium was thus obtained.

Wt. of sample G.	Wt. of Ge		Wt. of H	
	Calc. G.	Found G.	Calc. G.	Found G.
0.1367	0.1312	0.1317	0.005473	0.005453
.1197	.1149	.1153	.004792	.004767

Careful tests were then made of the purity of the products of the reaction. An arc spectrum photograph of the germanium with a spectrograph of high accuracy showed that the metal was practically pure germanium, that it contained no arsenic, and that only minute traces of iron and magnesium were present. The hydrogen was burned with oxygen in a Dennis combustion pipet, and the result showed a purity of 100%.

These results proved that this fraction consisted of pure digermane, Ge_2H_6 .

Melting Point of Digermane.—The tube F, Fig. 1, was immersed to

a depth of about 5 cm. in liquid air, and the sample in the bulb D was allowed to distil into F and condense until it had formed a ring just above the surface of the liquid air. Valve 4 was then closed. The junction of a thermocouple and a centrifugal motor stirrer were then placed immediately adjacent to the tube F in the bath of liquid air, which was next raised so as to chill the tube, stirrer and thermocouple thoroughly. The liquid air was then quickly replaced by a pentane bath which previously had been cooled to about -120° . To render the contents of the tube clearly visible, the pentane was contained in a 4-walled Dewar tube. The stirrer was set in motion and readings on the thermocouple were made while the ring of solidified gas was carefully observed. A stiff paper tapper attached to the shaft of the motor stirrer served to keep F in rapid vibration. The temperature at which the ring was seen to melt was recorded as the melting point. Several determinations gave a result of -109° .

Density of Digermene as Liquid.—Some of the gas was condensed in the tube F by means of liquid air, and it was then allowed to warm until it assumed the liquid state. It was kept cooled nearly to its melting point by surrounding it with cool pentane, its volume was then read, and the liquid was distilled into J, which was then removed from the apparatus and weighed. The density of the liquid, with the introduction of the necessary corrections for the vapor above the liquid, was computed as follows.

Volume of liquid	0.296 cc.	Volume of apparatus	140 cc.
Room temperature	19.2°	Volume of vapor above the liquid under standard conditions	4.35 cc.
Barometer	742.1 mm.	Volume of vapor \times density of gas = weight of the vapor =	0.0293 g.
Pressure above the liquid	25.3 mm.		

The digermene was then condensed in the weighing tube J.

To introduce correction for the vapor which still remained in the apparatus, readings similar to the above were taken and the weight of this vapor was found to be 0.0022 g. The calculation of the density was then made from the following data.

Wt. of Ge_2H_6 condensed	0.6267 g.
Wt. of Ge_2H_6 uncondensed	0.0022 g.
Total wt. of Ge_2H_6	0.6289 g.
Wt. of Ge_2H_6 vapor above the liquid	0.0293 g.
Wt. of Ge_2H_6 liquid	0.5996 g.
Volume of the liquid	0.296 cc.
Density of Ge_2H_6 at its melting point,	
$d_{-109^{\circ}} = \frac{0.5996}{0.296} = 2.02$ g. per cc.	

A duplicate determination gave 1.94 g. Av. $d_{-109^{\circ}} = 1.98$.

Vapor Tension of Digermane.—As has been indicated, the vapor tension of any fraction of the gas mixture at or below room temperature could be read directly on the manometer without removal of the sample from the apparatus. A sample of digermane was distilled into G with Valves 5, 6 and 7 closed. Valve 4 was then closed, and the bulb was surrounded by a vigorously stirred pentane bath, the temperature of which could be read by means of a thermocouple. Starting at -98° , the temperature of the bath was allowed to rise at the rate of about 10° per hour. The vapor tensions were read on the manometer.

TABLE I
VAPOR TENSION OF DIGERMANE

Temp. °C.	Vapor tension Pressure Mm.	First run Temp. °C.	Pressure Mm.	Temp. °C.	Vapor tension Pressure Mm.	Second run Temp. °C.	Pressure Mm.
-98.2	3.0	-44.0	31.4	-96.0	1.8	-31.5	56.2
-93.3	3.0	-37.5	39.2	-94.5	1.6	-28.5	68.4
-89.3	3.1	-34.0	48.4	-93.0	1.6	-21.5	91.0
-84.5	3.6	-31.0	58.9	-87.0	2.1	-18.5	105.4
-79.7	4.6	-27.5	74.0	-81.0	3.6	-15.0	125.1
-72.0	6.0	-22.0	87.6	-76.0	4.2	-10.5	154.2
-68.0	7.6	-18.0	105.4	-65.0	7.7	- 8.5	175.0
-63.3	9.7	-15.5	121.8	-48.0	20.8	- 6.5	191.8
-58.7	12.4	-12.5	141.6	-42.0	29.4	- 4.0	210.0
-53.5	15.9	- 8.7	165.4	-40.0	34.6	- 3.0	235.0
-49.0	20.3	- 6.0	189.0	-34.5	48.7	- 0.0	242.7
-45.2	25.1	0.0	243.1				

Determinations of the vapor tensions of digermane at temperatures above 0° were obviously impossible in this apparatus because if one part were heated, condensation would take place throughout the cooler parts. Recourse was therefore had to the apparatus shown in Fig. 4 which is similar to that employed by Stock, and which permits the total immersion of the liquid and its vapor in the bath. To transfer to the apparatus the sample of the hydride, the tube J which contained it was connected by means of the slipjoint, and with the stopcock N still closed, the remainder of the apparatus was exhausted by the pump. Valve B and stopcock K were then closed, and the sample was distilled into E. Valve A was then closed and the constrictions at C and D were sealed with a gas flame. The liquid air surrounding E was then slowly lowered and the temperature was allowed to rise to about 0° , whereupon a bath of ice-water was brought up around E. During this procedure the pressure in E increased, as was indicated by the depression of the mercury on the right hand side of the tube F. The mercury was then brought to the same level in both sides of this tube by admitting air through the stopcock I. The globe L, which has a volume of about one liter, served to give sufficient capacity to the system to permit of accurate adjustment

of the manometer. The bath around E was kept at a height well above the sealed constriction C, and was agitated by means of a motor stirrer. The temperatures were read on a carefully calibrated thermometer. The water in the bath was then slowly heated, the mercury was kept at the same height in the two sides of F, and the vapor tensions corresponding to the several temperatures were read on the manometer M. By connecting L with a source of compressed air through the stopcock I and the tube R, the pressure in L could be brought above that of the atmosphere, which made it possible to carry readings above atmospheric pressure.

From the data for vapor tension from -98.2° to $+28.9^{\circ}$ thus obtained, the tension-temperature curve for digermane was plotted (Fig. 5).

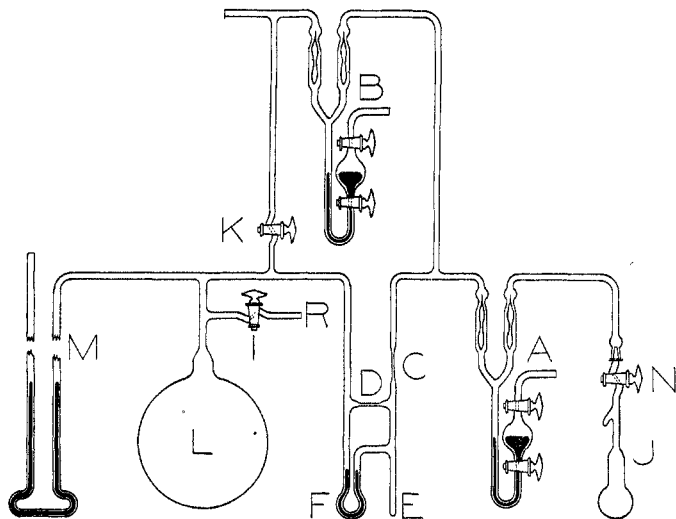


Fig. 4.

Boiling Point of Digermane.—The boiling point, which is the temperature corresponding to a vapor tension of 760 mm., was found to be 29° .

Trigermane, Ge_3H_8

A residue which might contain still higher members of this series of germanium hydrides remained in Bulb B after the greater part of the digermane had been distilled from it into C. This residue was freed from any digermane that might still be present by fractional distillation in the usual manner for two hours at temperatures from -77° to -65° . The minute amount of distillate that was obtained was removed through the pump.

The residue in Bulb B had no appreciable vapor tension at -65° , as was shown by the fact that the mercury in the two side arms of Valve 2 remained at the same level when the valve was partly opened. The temperature

of the bath around B was then allowed to rise until a slight difference in the mercury levels in Valve 2 was noticed. At -21° the vapor pressure appeared to be about 3 mm. Valve 2 was then fully opened, liquid air was brought up around C, and the material was distilled at -21° for six minutes. The greater part of it passed over into C leaving traces of a heavy, oily liquid in Bulb B. When the liquid air was removed from around C, the solidified distillate soon melted to a colorless, mobile liquid.

Density of Trigermane as Gas.—The density of the substance in the form of gas was determined in a manner similar to that described in connection with digermane. Two determinations gave for the weight of one liter under standard conditions, 10.16 g. and 9.91 g.; av., 10.035. The calculated density is 10.07. These results therefore clearly indicated the substance to be trigermane, Ge_3H_8 .

Analysis of Trigermane.—The method of analysis described for digermane was not applicable to trigermane because the vapor partly condensed on the walls of the tubes and burets, which made quantitative transfer of the sample practically impossible. For this reason the actual weight of the sample was disregarded and only the ratio of germanium to hydrogen was experimentally ascertained. No free hydrogen was admitted to the quartz tube in this case, but the vapor of trigermane was passed in before the tube was heated to the decomposition temperature of the gas. The results of the two analyses were as follows.

Wt. of Ge Found G.	Found G.	Wt. of H	Calc. G.
0.0220	0.000820		0.000816
.0217	.000822		.000805

That these analyses clearly indicate that the substance is trigermane is shown by calculations of the amount of hydrogen that would be combined with 0.0220 g. of germanium in three successive members of this series. If the substance were Ge_2H_6 , 0.0220 g. of Ge = 0.000918 g. of hydrogen; if Ge_3H_8 , 0.0220 g. of Ge = 0.000816 g. of hydrogen, and if the substance were Ge_4H_{10} , 0.0220 g. of Ge = 0.000765 g. of hydrogen.

The analyses do not, however, furnish conclusive proof of the purity of the fraction. The volume of hydrogen measured in each case was about

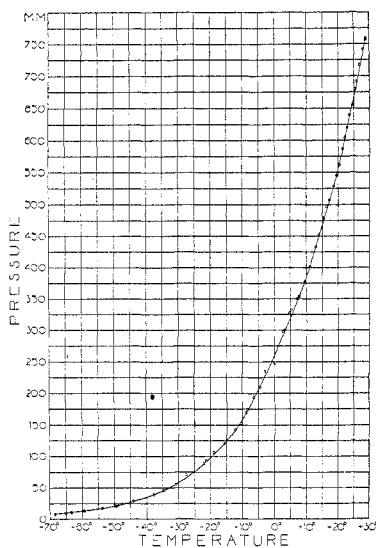


Fig. 5.—Vapor tension of Ge_2H_6 .

10 cc. With the gas buret that was used, the possible error in these readings was about 2%. Calculation will show that with this limit of accuracy, about 16% of digermane might have been present with the trigermane without appreciable effect upon the results of the determinations of hydrogen.

On the other hand, the presence of germanium hydrides other than trigermane would have caused pronounced differences in the values obtained for the density, and it was found upon calculation that with a limiting possible error of 1% in these measurements, 2% or more of digermane would have caused variations in the results that would have been distinctly noticeable.

However, the great care that was taken in the fractionation of the hydrides and in the preparation of the sample of trigermane render it extremely improbable that either a higher or lower hydride of germanium was present.

Melting Point of Trigermane.—Three determinations of the melting point gave -105.7° , -105.0° , -106.0° ; av., -105.6° .

Density of Trigermane as Liquid.—This was determined by the method described under digermane and was found to be 2.22 g. per cc. and 2.18 g.; av. 2.20 g. per cc.

Vapor Tension of Trigermane.—The vapor tension of trigermane from 0° to the boiling point was determined in the apparatus shown in Fig. 4. A bath of 1:1 sulfuric acid was used instead of water because it was necessary to carry the temperatures above 100° .

TABLE II
VAPOR TENSION OF TRIGERMANE

Temp., $^{\circ}\text{C}$.	2.4	10.0	17.8	21.7	25.3	30.0	35.2	39.9
Press., mm.	15.5	21.3	29.3	34.4	39.9	50.9	60.9	74.4
Temp., $^{\circ}\text{C}$.	45.0	49.9	55.0	59.4	65.6	70.3	76.5	80.9
Press., mm.	90.9	116.4	138.5	163.0	202.7	238.5	287.0	317.0
Temp., $^{\circ}\text{C}$.	86.5	90.3	94.7	99.5	104.0	108.5	109.7	111.5
Press., mm.	373.0	429.2	483.3	545.6	620.4	712.4	739.9	773.4

From these results the tension-temperature curve shown in Fig. 6 was plotted.

Boiling Point of Trigermane.—The boiling point of the compound as taken from the tension-temperature curve is 110.5° .

To confirm the results obtained for digermane and trigermane as described in the preceding pages, a fresh portion of magnesium germanide was made and was decomposed by hydrochloric acid as before, the resulting hydrides of germanium were fractionated, and the densities and melting points of the two hydrides were again determined. These results together with the preceding ones are given in the following table.

TABLE III
COMPARISON OF PROPERTIES OF DUPLICATE SPECIMENS

		d.	M. p. °C.
Ge_2H_6	Preparation I	6.7405	-109
	II	6.755	-109
Ge_3H_8	I	10.035	-105.6
	II	10.125	-105

The Thermal Decomposition of Digermane and Trigermane.—To determine the dissociation temperatures of these gases, the apparatus that was employed for the analysis of the hydrides, Fig. 3, was used, but the middle portion of the quartz tube was completely enclosed in an asbestos box which was provided with mica windows at the front and back. The bulb of a thermometer rested against the middle of the tube and an electric lamp placed behind the box rendered the tube plainly visible.

A sample of digermane was brought into the quartz tube at a pressure of about 200 mm. The asbestos box was carefully heated and the temperature at which darkening of the tube began was found to be 218° . At 224° the deposit formed rapidly with the production of a heavy metallic mirror. In a repetition of the experiment, decomposition began at 214° .

In the same manner it was found that trigermane began to dissociate at 194° , and at 208° a heavy deposit of metallic germanium was formed. Repetition of this experiment gave exactly the same temperatures.

In these determinations the quartz tube was kept slightly above the decomposition temperature for a considerable length of time. A clear, colorless liquid collected at both ends of the tube, about 1 cm. from the asbestos housing. As the heating continued, this liquid disappeared, apparently being decomposed in the hotter portion of the tube. The substance could not have been trigermane since the tube was under greatly diminished pressure and the quartz where the liquid condensed was quite hot. It may possibly have resulted from the formation of an unsaturated hydride of germanium, which then polymerized to a product of high boiling point.

Chemical Properties of Digermane.—For the study of the chemical properties of the substance, small samples were distilled in the tubes K Fig. 1, which were then sealed off. These could then be opened as needed.

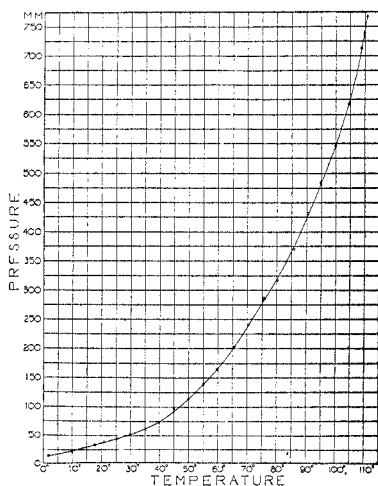


Fig. 6.—Vapor tension of Ge_3H_8 .

When exposed to the air, digermane turned first yellow, then light brown, and finally changed to a dark brown solid. It is not ordinarily spontaneously inflammable, but in one instance when air was rapidly admitted to a buret containing some of the gas under greatly diminished pressure, a flash of light was seen and the glass became covered with a brown solid.

When a few drops of digermane were placed on a watch glass and a flame brought above it, the vapor ignited with almost explosive violence and the liquid burned with great rapidity. A reddish-brown coating which contained streaks of black and white was left upon the watch glass.

When oxygen was passed into a tube containing a little digermane, no reaction took place at first, but after about ten minutes a white solid formed on the sides of the tube. After about an hour this white substance had turned yellow.

The tip of one of the small sealed tubes was broken under water. The water which entered the tube did not mix with the digermane and no reaction was apparent for some minutes. After a time, however, a white, jelly-like substance formed in the water layer and this gradually changed to yellow and then to light brown. A gas was given off at the interface between the two liquids.

Another sample tube was broken under a 33% solution of sodium hydroxide. At the interface of the two liquids a colorless, combustible gas was evolved which, however, was not obtained in sufficient quantity or under such conditions as would permit its identification. This reaction distinguished digermane from monogermane, since the latter does not appear to react with a solution of sodium hydroxide of this strength, even when heated.

When carbon tetrachloride was admitted to one of the sample tubes, the two liquids mixed with evolution of heat and the solution was clear and colorless. After this had stood in contact with the air, a white solid appeared throughout the liquid. As evaporation lowered the level of the liquid, a yellow deposit formed on the tube above the surface. The white deposit beneath the surface slowly turned yellow and finally disappeared, leaving the liquid clear.

Chemical Properties of Trigermane.—When a few drops of the liquid were ignited on a watch glass, the substance burned with a yellow flame and a voluminous, powdery residue was formed that was streaked with black, brown and white. When exposed to the air, trigermane changed quickly to a white solid.

The behavior with oxygen was quite similar to that of digermane.

When a sample tube containing a fairly large amount of trigermane was broken under water, the hydride did not appear to dissolve in water, but the usual white oxidation product was formed at the surface of the water.

Trigermene was found to be immiscible with a 33% solution of sodium hydroxide, and there seemed to be no reaction between the two liquids, which is surprising because from the behavior of monogermene and digermene it was to be expected that trigermene would be quickly attacked. There was doubtless some influencing factor that escaped our observation. The point will be studied further.

Carbon tetrachloride was found to dissolve trigermene with evolution of heat, and when the liquid was exposed to the air, a white fog appeared in it. This turned yellow almost immediately and finally disappeared, as in the case of digermene.

Yield of Germanium Hydrides.—When mono-, di- and trigermene are formed by the action of acids upon magnesium germanide, monogermene is the chief product and trigermene is produced in smallest amount. From 67.5 g. of magnesium germanide, 7.15 g. of monogermene, 2.12 g. of digermene and 0.43 g. of trigermene were obtained. These amounts correspond to a total weight of 9.21 g. of germanium; 67.5 g. of magnesium germanide contains 40.5 g. of Ge; consequently only 22.7% of the germanium in magnesium germanide was converted to the hydrides, and of this 73.6% appeared as monogermene, 22% as digermene, and 1% as trigermene.

The conversion of germanium in the alloy into germanium hydrides was closely similar in amount, 22.7%, to the yield of silicon hydrides obtained by Stock from magnesium silicide.⁶ We have not yet ascertained what becomes of the remaining 77.3% of germanium, but it is possible that compounds similar to silico-oxalic acid are formed.¹⁰ The study of germanium chloroform, which is now in progress in the Cornell Laboratory, may throw some light upon this point.

Monogermene, GeH_4

As already stated, some 1300 cc. of the most volatile hydride of germanium was removed and stored in gas holders over mercury. This is probably the monogermene that has already been isolated by Paneth and by Schenck. It will be subjected to careful study in this Laboratory in the near future. Merely for the purpose of identifying it, the weight of one liter of the gas was determined and two analyses by thermal decomposition were made. The results were in close agreement with the calculated values for monogermene, GeH_4 .

Summary

The hydrides of germanium were prepared by the action of hydrochloric acid on magnesium germanide, and the mixture of the hydrides was then subjected to careful fractionation. Two new hydrides, digermene, Ge_2H_6 , and trigermene, Ge_3H_8 , were isolated and studied, and a third, mono-

¹⁰ Besson, *Compt. rend.*, **154**, 1604 (1912).

germane, GeH_4 , which had already been prepared by others, was identified and reserved for future investigation.

The density as gas, the density as liquid, the melting point, and the boiling point of each of these two hydrides were determined, and the tension-temperature curves were plotted. Some of the characteristic chemical properties of digermane and trigermane are described.

After trigermane had been removed by fractionation, a very small amount of a liquid residue remained in the bulb. This residue showed practically no vapor tension at room temperature. Its presence indicates that still higher hydrides in this series probably exist.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

CRITICAL POTENTIALS OF HYDROGEN IN THE PRESENCE OF NICKEL CATALYST

By A. W. GAUGER¹

RECEIVED DECEMBER 27, 1923

Sabatier's² important researches on the catalytic activity of finely divided metals established, among other things, the fact that nickel prepared from the oxide by reduction in hydrogen at temperatures of 300° , or less, is an excellent catalyst for hydrogenation reactions and perhaps the best. Since that time many investigators have studied such reactions in the presence of finely divided nickel and there has been much speculation concerning the mechanism thereof. Nevertheless, we still lack sufficient experimental evidence to know definitely what the role of the catalyst is. However, it has been noted that nickel of the type concerned shows a very marked power to adsorb hydrogen,³ and the suggestion has been made that the adsorption is chemical in nature, the hydrogen being held on the surface of the metal by chemical forces of either secondary or primary valence,⁴ not as molecular but as atomic hydrogen.⁵

One of the theories of catalytic hydrogenation involves, therefore, the adsorption of one or more of the reacting species, reaction between them on the surface, and desorption of the products therefrom. For all practical purposes this theory may be considered identical with the old "intermediate compound" theory, inasmuch as the adsorption is considered to be a chemical rather than a physical phenomenon.⁶ Some definite idea of the

¹ National Research Fellow in Chemistry.

² Sabatier-Reid, "Catalysis in Organic Chemistry," D. van Nostrand Co., 1922.

³ See Taylor and Burns [THIS JOURNAL, 43, 1277 (1921)] for references.

⁴ Langmuir, *ibid.*, 38, 2221 (1916).

⁵ Langmuir, *ibid.*, 34, 1310 (1912).

⁶ Armstrong and Hilditch, *Proc. Roy. Soc.*, 100A, 240 (1921). See also note by Professor Bray in the First Report of the Committee on Contact Catalysis [Bancroft, *J. Ind. Eng. Chem.*, 14, 327 (1922)].