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THE HIGHER SILANES AND GERMANES. $n \text{ SiH}_4 \text{ + } n \text{ SiH}_{2n+2} \text{ + } (n-1) \text{ H}_2$
 $\text{GeH}_4 \text{ + } n \text{ GeH}_{2n+2} \text{ + } (n-1) \text{ H}_2$

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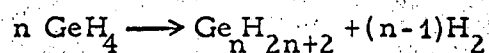
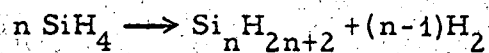
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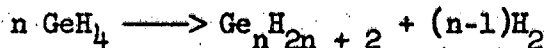
THE HIGHER SILANES AND GERMANES



Sudarshan D. Gokhale, John E. Drake and William L. Jolly

November 1963

THE HIGHER SILANES AND GERMANES



SUDARSHAN D. GOKHALE,^{*†} JOHN E. DRAKE^{*} AND WILLIAM L. JOLLY^{*}

Silane, SiH_4 , may be efficiently prepared by the reaction of silicon tetrachloride with lithium hydroluminate,¹ and germane, GeH_4 , may be efficiently prepared by the reaction of aqueous germanate(IV) with aqueous hydroborate.² However none of the methods for preparing silanes or germanes from either aqueous or non-aqueous solutions gives decent yields of the higher hydrides of general formula $\text{Si}_n \text{H}_{2n+2}$ and $\text{Ge}_n \text{H}_{2n+2}$. It has recently been discovered that the higher silanes³ and germanes⁴ may be prepared in good yields of

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passing silane and germane, respectively, through an ozonizer-type silent electric discharge. We describe here the apparatus and procedure for preparing about 1 g. of disilane or digermane, about 0.5 g. of trisilane or trigermane, about 0.1 g. of n-tetrasilane or n-tetragermane, about 0.02 g. of iso-tetrasilane or iso-tetragermane, and smaller amounts of the various isomers of the higher hydrides. Silanes as high as Si_8H_{18} and germanes as high as Ge_9H_{20} have been detected.

The main difficulty in preparing pure samples of the higher hydrides lies in their separation from one another - particularly in the separation of the isomers. Whereas the first three members of each homologous series may be clearly separated from one another by fractional condensation in a vacuum line,^{2,3} the tetra- and higher hydrides must be separated by gas chromatography.^{4,5} Since the higher hydrides are spontaneously inflammable in air and are probably very toxic, more than the usual precautions are required in their chromatographic separation. Therefore we describe the chromatographic apparatus and procedure in considerable detail.

Apparatus

The vacuum line apparatus (Fig. 1) consists of two sections - one for the

electric discharge synthesis, and the other for the preliminary separation of the products by fractional condensation. No greased stopcocks or joints can be tolerated in any part of the system which is to contain the higher hydrides, because these compounds dissolve in grease.* Therefore all the valves are of the mercury float type except the one that separates the two sections. (The latter valve is a greaseless needle valve† because it is necessary to be able to open it very slowly). The joints to which storage bulbs, transfer vessels, and other apparatus are connected to the system are of the O-ring type so that no grease need be used. The dimensions of the ozonizer-type discharge tube are probably not critical, but it is recommended that the gap between the concentric tubes be about 2 mm., that the outside diameter of the tube be about 34 mm., and that the distance from the bottom of the tube to the exit tube be at least 20 cm. A small tube or bulb of about 5-ml. volume at the bottom of the discharge tube collects nonvolatile liquid hydrides that otherwise might clog the inlet tube. When in use, the discharge tube is surrounded

* Silane and germane can be handled in a greased system, however.

† Delmar-Urry Stopcock, manufactured by the Delmar Scientific Co., Maywood, Illinois, or Lab - Crest threaded glass needle valve, manufactured by the Fischer and Porter Co., Harminster, Pennsylvania.

by a dry-ice-acetone slush to which a little concentrated hydrochloric acid has been added to increase the electrical conductivity. The inner finger of the discharge tube is filled with the same mixture. The outer cold bath is electrically grounded, and the inner cold bath is connected to one of the secondary terminals of a 15-kv. transformer. (The other secondary terminal is grounded.) The high voltage connections should be placed so that the operator and other personnel cannot inadvertently touch them! The metal frame of the vacuum line should be grounded.

The automatic Toepler pump should be of a type (such as that illustrated in Fig. 1) that does not cause rapid surges of gas flow. The capacity of the Toepler pump should be approximately 300 ml. The total volume of the surge bulbs is about 6 liters.

Procedure for Synthesis

Sufficient silane or germane is distilled into the discharge-tube section of the apparatus so that the pressure is about 400 mm. when the hydride is completely vaporized. If disilane is the desired product, the trap following

the ozonizer is immersed in an n-pentane slush bath (-130°).^{*} If trisilane or digermane is the desired product, the trap is immersed in a toluene slush bath (-95°). If silanes higher than trisilane or germanes higher than digermane are the desired products, the trap is immersed in a dry-ice-acetone bath (-78°). Dry-ice baths are placed around and within the discharge tube, the electrical connections are made, and the high voltage is turned on. The automatic Toepler pumped is started, and the pumping rate is adjusted to approximately 300 ml. per minute.

As the reaction proceeds, hydrogen gas is formed. It is impossible to estimate the extent of reaction from the change in pressure, because the number of moles of silane or germane decomposed is roughly equal to the number of moles of hydrogen formed. After the gases have circulated through the system for about 6 hours,^{**} the trap preceding the discharge tube is immersed in liquid nitrogen. After continuing the gas circulation for another 15

^{**} With such a cold trap in the system, silane will condense until its pressure is about 220 mm. However all the condensed silane will eventually vaporize because of the constant decomposition of the vapors of silane in the discharge tube.

^{**} During the circulation of gas, it is necessary to replenish occasionally the cold bath which follows the discharge tube.

minutes, the four traps in the separation section of the system are also immersed in liquid nitrogen, and the needle valve is opened slightly so that the hydrogen is very slowly pumped out of the synthesis section through the four liquid nitrogen traps. After the system has been thoroughly evacuated, the material which has condensed out in the separation section is distilled back into the synthesis section and the needle valve is closed. The liquid nitrogen is removed from the trap preceding the discharge tube, and the gas circulation is continued until such time as it is judged that a negligible amount of silane or germane remains undecomposed. Again the hydrogen is removed as described above, and all the volatile condensible products (including those in the discharge tube and the trap immediately following it) are combined in a trap at either end of the separation section.

Procedure for Separation by Fractional Condensation

Although the yields of individual hydrides can be somewhat controlled by the temperature of the trap following the discharge tube, any synthesis will always yield the entire gamut of hydrides. Pure samples of disilane and trisilane (or the corresponding germanes) may be separated by fractional condensation in the vacuum line.

The crude silanes are distilled through a -95° trap and a -130° trap into a -196° trap (liquid nitrogen). The -95° trap collects the trisilane and higher silanes, the -130° trap collects the disilane, and the liquid nitrogen trap collects the undecomposed silane. The disilane is further purified by passing it through a -105° trap (an ethanol-methanol mixture, the temperature measured with a thermometer) to remove traces of trisilane. The mixture of trisilane and higher silanes is distilled through a -63° trap (chloroform slush) and a -95° trap to a -196° trap. The -63° trap collects the higher silanes, the -95° trap collects the trisilane, and the -196° trap collects a trace of disilane. The trisilane is further purified by passing it through a -78° trap to remove traces of tetrasilanes. A crude sample of tetrasilanes (which must be further purified by gas chromatography) can be prepared by passing the higher silanes (from which the disilane and trisilane have been removed) through a -23° trap (carbon tetrachloride slush).

The crude germanes are distilled through a -63° trap and a -112° trap (carbon disulfide slush) into a -196° trap. The -63° trap collects the trigermene and higher germanes, the -112° trap collects the digermene, and the -196° trap collects the undecomposed germane. The mixture of trigermene and higher germanes is distilled through a -35° trap (ethanol or acetone, the

temperature measured with a thermometer) and a -63° trap to a -196° trap.

The -35° trap collects the higher germanes, the -63° trap collects the trigermane, and the -196° trap collects a trace of digermane.

Procedure for Separation by Gas Chromatography

Because the higher silanes and germanes are extremely reactive toward oxygen, the gas chromatographic separation must be carried out with a minimum exposure to the atmosphere. The higher hydrides are distilled from the vacuum line to a small transfer tube such as shown in Fig. 2 by putting the lower part of the tube in a -78° bath. Pure nitrogen or argon gas is then led into the tube to a pressure of about 70 cm. The -78° bath is removed, and the transfer tube is warmed to room temperature, at which point more nitrogen is introduced to a total pressure equal to the atmospheric pressure. By tipping the transfer tube, a portion of the hydride mixture may be caused to run into the little bulb opposite the rubber septum. Portions of the hydride mixture are withdrawn from the tube with an air-tight needle and syringe and injected into the gas chromatography apparatus. If the piston and cylinder portion of the syringe leaks even slightly, hydride mixture will be forced out from the back of the syringe, burn with a flask, and leave a solid deposit which

fouls the syringe. It is therefore recommended that grease be applied to the upper half of the piston in such a way that the hydride mixture cannot come in contact with the grease. When the needle is withdrawn from the entrance membrane of the gas chromatographic apparatus, the small amount of warm hydride mixture on the tip of the needle burns with a flash and a pop. To prevent clogging of the needle, it is necessary to insert a thin wire into the needle after each use in order to keep it clear.* After use, the syringe should be rinsed thoroughly with dry benzene and then flushed with nitrogen.

A chromatographic column made of a stainless steel tube, 1/2 in. in diameter and 5 ft. long, packed with 20% silicone oil on 60/80 firebrick, serves very well. The column temperature is maintained at 100°, with the injector, detector, and collector zone temperatures maintained at 115°, 140°, and 115°, respectively.**

* Alternatively, the tip of the needle can be kept from the atmosphere by using small capsules closed on opposite sides with rubber septa. See the description of these Schutzzöhrchen by Fehér, Kuhlbörsch and Lulleich.⁶

** An Aerograph Model A-90-P gas chromatograph (manufactured by Wilkens Instrument and Research, Inc., Walnut Creek, California) serves satisfactorily.

The samples are eluted with helium gas, at a flowrate of approximately 5.0 ml./sec. The vapors leave the chromatograph through a hypodermic needle maintained at 115°.

The various eluted fractions are collected in collection traps such as that pictured in Fig. 3. These traps are made ready-for-use by first evacuating them and testing for leakage. They are then partially immersed in a -78° bath and filled with pure nitrogen gas at a pressure a few millimeters greater than atmospheric pressure; the needle valves are then closed. (The collection traps are kept in the cold baths until such time as the hydride fractions which have been collected in them are distilled from them into the vacuum line.) The exit of each collection trap is connected by a rubber tube (attached to a one-hole rubber stopper) to an exhaust manifold leading to the hood. While a stream of pure helium is passing through the chromatographic column, the septum of a collection trap is pierced with the exit needle of the chromatograph. The needle valve at the top of the trap is immediately opened and the flow of helium is continued for a few minutes so as to flush all air out of the rubber tube and the exhaust manifold. The trap is disconnected from the chromatograph and the needle valve is closed. This flushing procedure is

repeated for each collection trap.

Before attempting to separate and collect fractions of the hydride mixture, one or two preliminary runs should be carried out with about 2-5 μ l. samples. Some adjustment of the column temperature and helium flow-rate may be necessary in order to get clean-cut separations of the desired fractions. When it is intended that the fractions be collected, samples of the order of 100-200 μ l. should be injected. Thus five or ten runs may be necessary in order to chromatograph 1 ml. of hydride mixture.

A few seconds before each fraction of interest emerges from the chromatograph, the needle valve of the appropriate collection trap is opened and the trap is connected to the chromatograph. After each fraction has passed through the chromatograph, the collection trap is disconnected from the chromatograph and the needle valve is closed.* When the entire sample has been passed through the chromatograph, the collection traps are connected by means of the

* Because there may be only a few seconds between fractions, there may not be enough time to close the needle valve before attaching the next collection trap. There is no harm in delaying the closing of the collection trap for half a minute or so.

ring joints to the vacuum line and the pure fractions are distilled into appropriate parts of the system.

Properties

Disilane has a boiling point⁷ of -14.3° and a melting point⁷ of -132° .

The gas has a characteristic infrared absorption spectrum which may be used for identification purposes. Absorption bands are observed at the following

frequencies⁸ (in cm^{-1}): 2160 (s), 940 (m), 853, 844, 835 (s). Trisilane has

a boiling point⁷ of 53.0° and a melting point⁷ of -117° . The vapor shows

infrared absorption peaks at the following frequencies³ (in cm^{-1}): 2180 (s),

948 (m), 884 (vs), 819 (m), 808 (m), 747 (w), 717 (s), 705 (s). Normal

tetrasilane vapor shows absorption peaks at the following frequencies⁹ (in cm^{-1}):

2155 (s), 1015 (w), 935 (m), 917 (w), 879 (s), 748 (w), 741 (w), 701 (sh, m),

694 (s), 662 (s). Isotetrasilane vapor show absorption peaks at the following

frequencies⁹ (in cm^{-1}): 2110 (w), 2155 (s), 1000 (w), 945 (sh, w), 935 (m),

915, 906, 898 (m), 871 (s), 866 (s), 698 (sh, m), 693 (s). Disilane, trisilane,

and the isomers of tetrasilane have distinctive proton magnetic resonance spectra.⁴

The physical properties of digermane and trigermane have been described in

a previous synthesis. These hydrides and the isomers of tetrasilane have

distinctive proton magnetic resonance spectra.⁴

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Figure Captions

Figure 1. Vacuum line apparatus for the synthesis and preliminary separation of the higher hydrides of silicon and germanium.

Figure 2. Transfer tube for the higher hydrides of silicon and germanium.

Figure 3. Collection trap and exhaust manifold used in the gas-chromatographic separation of the higher hydrides of silicon and germanium.

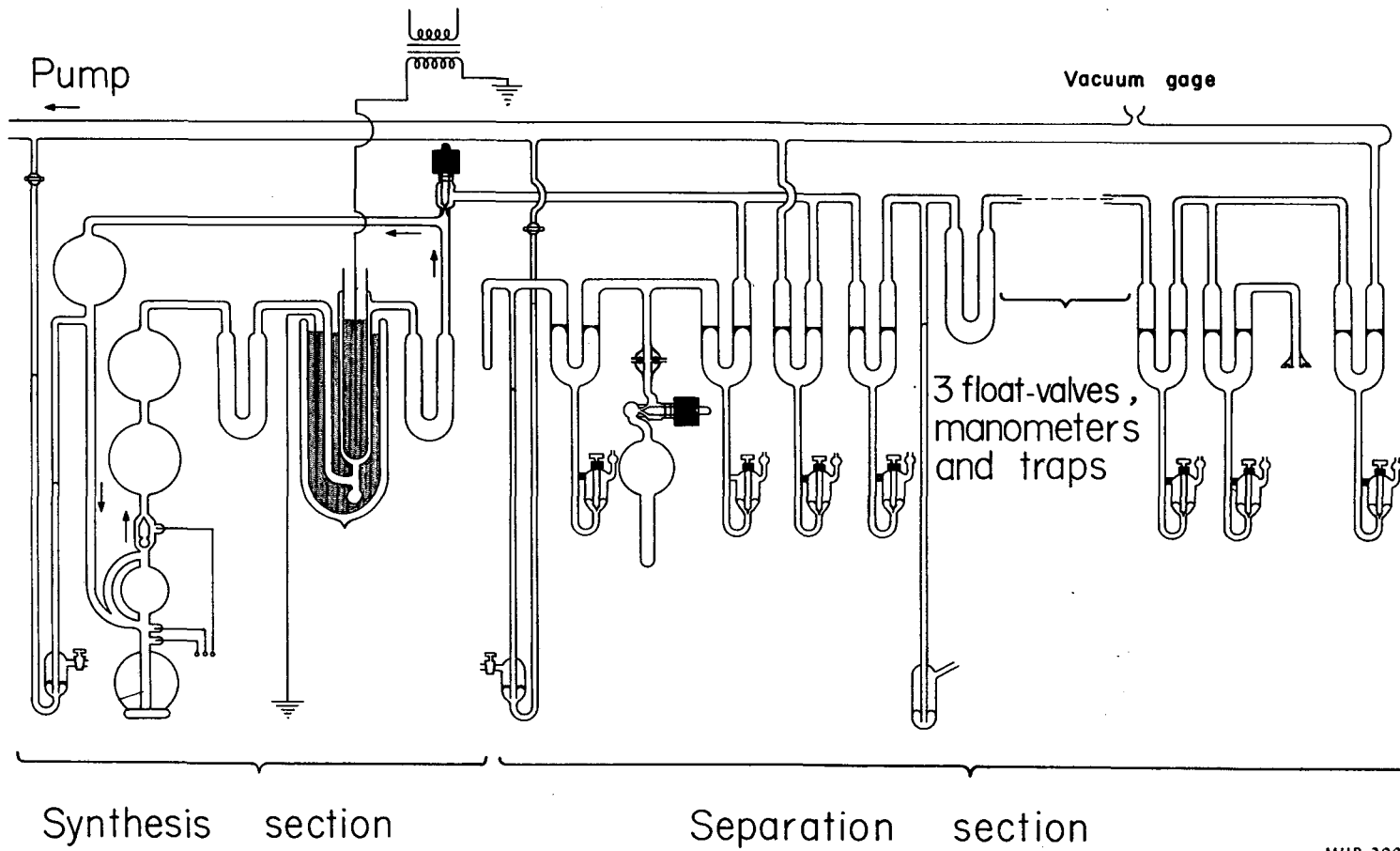
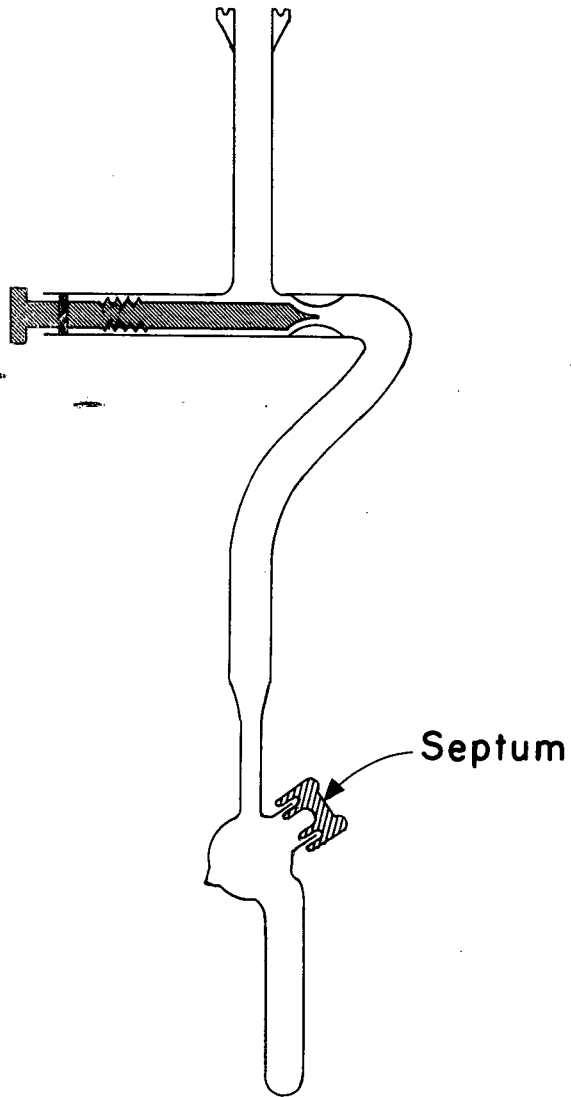
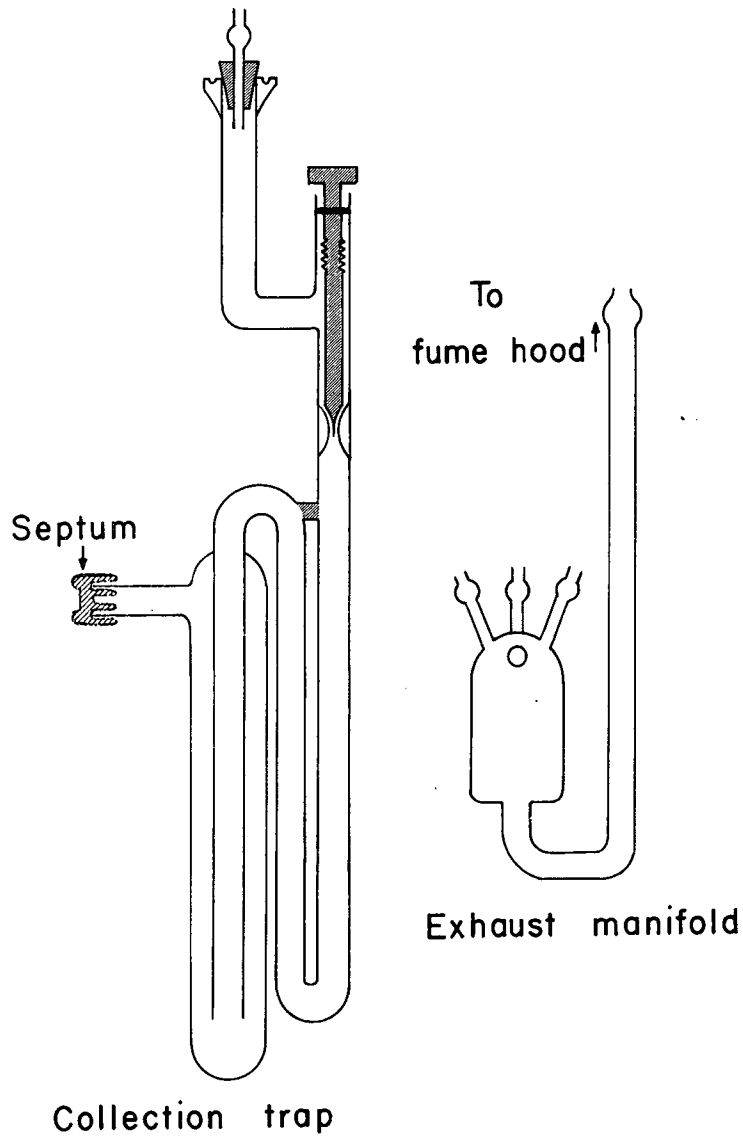


Fig. 1.



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Fig. 2.



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Fig. 3.

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