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ABSTRACT

The preparation of germanium hydrides, by the dropwise addition of an alkaline solution of hydroborate and germanate to aqueous acid, has been studied systematically. As much as 70% of the germanium in solution could be converted to germane. Digermane, trigermane, and a polymeric germane were also obtained, and the infrared absorption spectra of gaseous trigermane and of polymeric germane were recorded.

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INTRODUCTION

The existence of a hydride of germanium is mentioned in the literature, as early as 1902. Voegelen reported the formation of a volatile hydride of germanium when germanium tetrachloride was reduced by zinc and sulphuric acid.[1] Monogermane was identified by both Paneth[2] and Schenck[3], and then in 1924 Dennis and his co-workers carried out an extensive study of the hydrides of germanium.[4] They succeeded in preparing pure samples of digermane and trigermane, as well as monogermane. Their method of preparation was to drop dilute hydrochloric acid on magnesium germanide. Only 22.7% of the germanium was converted to the hydrides, and 73.6% of this amount appeared as monogermane, 22% as digermane, and 1% as trigermane. Ten years later Krauss obtained much better yields of germane by the treatment of the magnesium germanide with ammonium bromide in liquid ammonia.[5]

The methods for the preliminary preparation of a germanide were not convenient, and in 1947 Finholt obtained a 28% conversion to germane by the reduction of germanium tetrachloride with lithium aluminum hydride in ether solution.[6] However, it was not until 1957 that a good aqueous method of preparation was devised: Piper and Wilson obtained up to 75% conversion to germane when an aqueous acidic solution of germanium was reduced by the dropwise addition of sodium hydroborate.[7] The method used was very wasteful in hydroborate. Later, Macklen obtained good yields of germane when a tetrahydrofuran solution of germanium tetrachloride was reduced by aqueous sodium hydroborate.[8] He noted a large decrease in yield when the reaction temperature was increased by about 30°. Sujishi and Keith obtained good results using lithium tri-tertbutoxyalumino hydride as reducing agent, and they observed a decrease in the yield of germane when the ratio $H^-/Ge(IV)$ became greater than 4.5.[9]

The most recent report of the production of germanium hydrides is contained in a paper by Jolly on the preparation of volatile hydrides.[10] It is the method described by him that has been used to carry out a fairly systematic study of the preparation of germanium hydrides, as reported herein.

APPARATUS AND EQUIPMENT

The apparatus used for the preparation of the hydrides is shown in Fig. 1. The general procedure used for carrying out the experiments was as follows. A quantity of acid was placed in the 500-ml three-neck round-bottom flask which was equipped with a magnetic stirrer, an inlet tube for nitrogen, a 100-ml dropping funnel, and an outlet tube leading to a vacuum line. The flask was surrounded by an ice-water bath for most re-actions. An alkali solution of germanate and hydroborate was added, drop-wise, through the funnel—this addition took from 15 to 20 minutes. Simul-taneously, nitrogen was continuously bubbled through the magnetically stirred acid solution at approximately 500 cc/min STP. The pressure in the system was maintained at approximately 100 mm by adjustment of the stopcock lead-ing to the vacuum pump. The gases that were formed passed through a series of traps (1, 2, and 3 in Fig. 1), and all condensable gases were trapped out by immersing two of the traps in Dewar flasks containing liquid nitrogen. (Traps cooled in this manner will be referred to as liquid nitrogen traps.) The flow of nitrogen was maintained for 5 minutes after all the alkali solution had been added. The line was then evacuated thoroughly, and the hydride—contained in the liquid nitrogen traps—could be separated and purified by distillation. This procedure will be described later.

The infrared spectra of the purified volatile hydrides were obtained, in the gas phase, on a Perkin-Elmer Infracord.

In the course of most reactions a solid, polymeric germanium hy-dride was formed, and its infrared spectrum was recorded on a Baird Atomic Infrared Spectrophotometer by using potassium bromide pellets.

EXPERIMENTS

Series A

It had been noted in earlier experiments that much foaming occurred when the alkali solution of germanate and hydroborate was added to the acid. The amount of foaming increased greatly as the ratio of $BH_4^-/Ge(IV)$ was decreased toward 1.0. Silicone antifoam agents had not helped but it was hoped that a polyglycol might prove more useful.

The experiments were carried out as described under Apparatus and Equipment. The pressure, the flow rate of nitrogen, an l the time taken to add the alkali solution were kept as constant as possible for all the experiments. In every case the flask was charged with 120 ml of 16% sulfuric acid, to which 1.2 ml of the polyglycol(supplied by the Dow Chemical Company) was added. The alkali solution was made up by adding 2.0 g of potassium hydroxide pellets, and close to 1.05 g of germanium dioxide, to 25 ml of water. The only factor that was varied for these experiments was the amount of hydroborate added to the alkali solution at this stage. The amounts of potassium hydroborate added were varied to give hydroborate concentrations of between 0.24 $\underline{M}$ and 2.22 $\underline{M}$.

TO VACUUM PUMP

N₂ or A

MAGNETIC
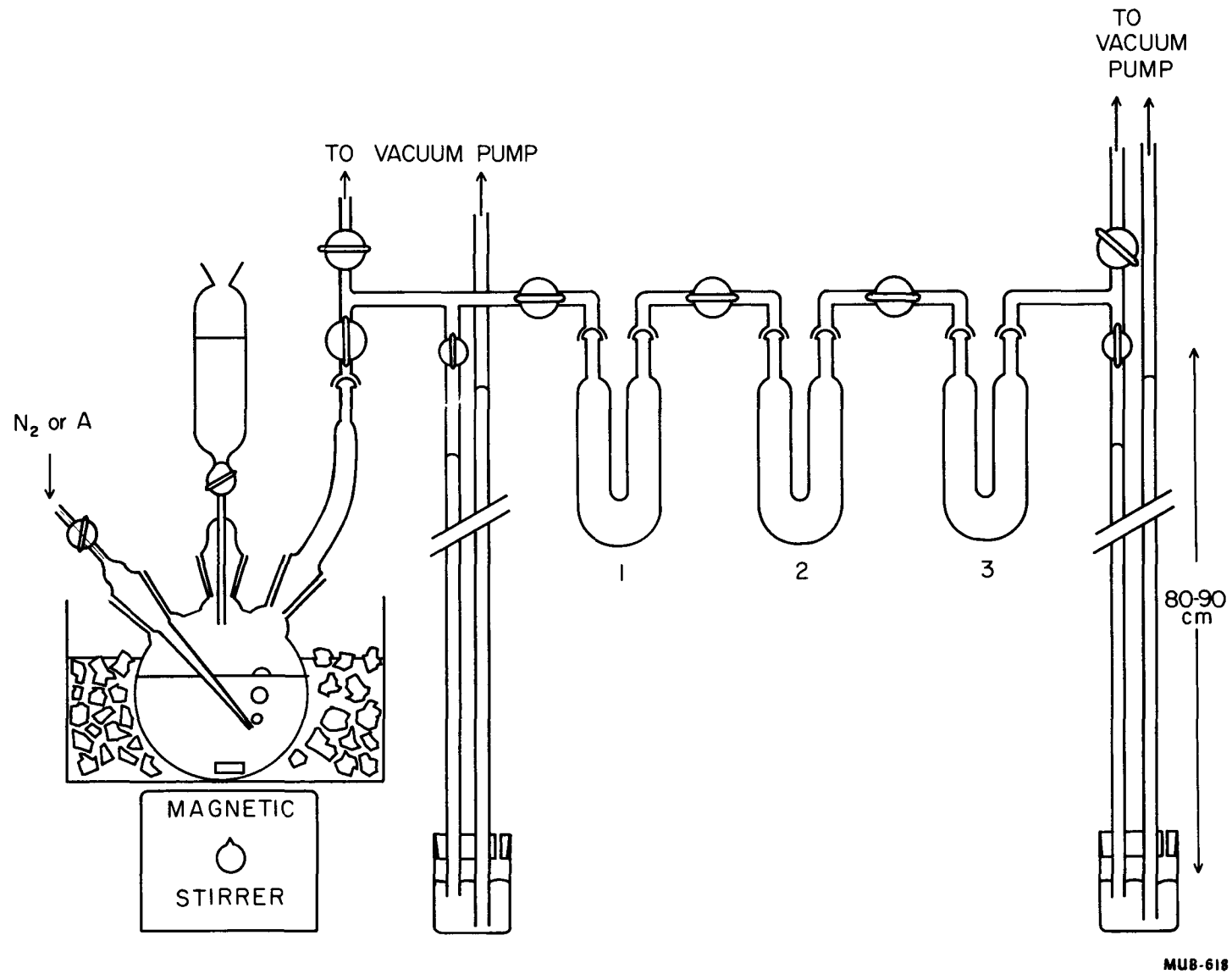
STIRRER

1 2 3

80-90
cm

MUB-618

Fig. 1. Apparatus for preparation of hydrides.

When the reactions were carried out the polyglycol proved to be quite effec-
tive as an antifoam agent. However, a yellow residue was formed in the
reaction flask in all reactions except the one having a ratio of $BH_4^-/Ge(IV)$
less than unity, in which case the residue was brown. The residues were
filtered immediately, washed thoroughly with water, and pumped dry on the
vacuum line.

The separation of the volatile compounds contained in the liquid
nitrogen traps was carried out as follows. The gases were first distilled
through a carbon-disulfide-slush trap (-111.6°C), which removed digermane,
trigermane, and water; germane and carbon dioxide passed through into
another liquid nitrogen trap. The higher germanes were distilled, through
a trap containing magnesium perchlorate, into a system in which all grease
stopcocks were replaced by mercury valves. This was necessary because
both digermane and trigermane are absorbed by stopcock grease. The dried
gases were then distilled through a chloroform-slush trap (-63.5°), which
removed the trigermane; the digermane passed through into the carbon-disul-
fide-slush trap. The germane, which was still in the liquid nitrogen trap,
was separated from carbon dioxide by passage through Ascarite, followed by
passage through magnesium perchlorate to remove any water. (It was found
that the trigermane must be separated before carbon dioxide is removed be-
cause it disproportionates when passed through Ascarite.)

The amounts of the hydrides formed in each experiment are shown
in Table I.

Table I. Germanium hydride synthesis (Series A).

Concentration Ge(IV) (mole/ 1	Mole Ratio $BH_4^-/Ge(IV)$	% Conversion of Ge(IV) to		
		GeH_4	Ge_2H_6	Ge_3H_8
0.44	0.55	16.8	0.9	- - -
0.43	1.48	54.4	4.0	0.5
0.42	2.33	61.4	4.8	- - -
0.40	3.88	65.0	4.6	0.9
0.41	5.39	70.1	4.8	- - -

Identification and Properties of the Hydrides

Germane

The vapor pressures of the hydrides were recorded by standard vacuum-line technique. The vapor pressure of pure germane was found to be 181 mm at -111.6° (literature value: 182 mm[6]). The infrared spectrum of the gas in the NaCl region was recorded, and thus provided another proof of purity. A typical spectrum (Fig. 2) showed the fundamental frequencies v_3, v_2, and v_4 at 2105, 943, and 815 cm^{-1}, respectively.[11] Germane was stored in a glass vessel which had a greased stopcock.

Digermane was found to have a vapor pressure of 6mm at -63.50°, 77 mm at -22.9°, and 221 mm at 0° (literature values: $\approx$ 9 mm, $\approx$ 85 mm, and 243 mm, respectively[4]). The infrared spectrum of the gas in the NaCl region was recorded—a typical result is shown in Fig. 3. The spectrum showed the fundamental frequencies v_5, v_8, and v_6 at 2069, 885, and 759 cm^{-1}, respectively.[12] Because, as has already been mentioned, digermane is absorbed by stopcock grease, it was kept in sealed glass ampoules.

Trigermane was found to have a vapor pressure of 9.5 mm at 0° (literature value: 14 mm[4]). There had been no report in the literature of the infrared spectrum in the NaCl region. This was recorded and is shown in Fig. 4. Two strong peaks can be seen at 2041 and 794 cm^{-1}. Trigermane was also stored in sealed glass ampoules.

Yellow Residue

The infrared spectrum (KBr pellet) of the dried yellow solid was taken and compared to the spectrum of polyglycol. The spectra were very similar except that three additional peaks could be seen in the spectrum of the yellow solid. These were at 2105, 833, and 850 cm^{-1}. The peak at 2105 cm^{-1} corresponded to the typical Ge-H stretching frequency, and it seemed likely that the residue was a polymeric hydride into whose structure the polyglycol had become incorporated. This view was supported by the results found after heating of the yellow solid, which decomposed to give germanium, hydrogen, germane, and additional decomposition products. These additional products were found, from spectra evidence, to be the same products as those that resulted from the decomposition of the polyglycol. The proportion of germanium to hydrogen was approx 1: 0.9.

Series B

This second series of experiments was carried out in exactly the same manner as the previous series, except that no polyglycol was used. Therefore a ratio of BH_4^-/Ge(IV) less than 1.5 was not used, because of the increased amount of foaming.
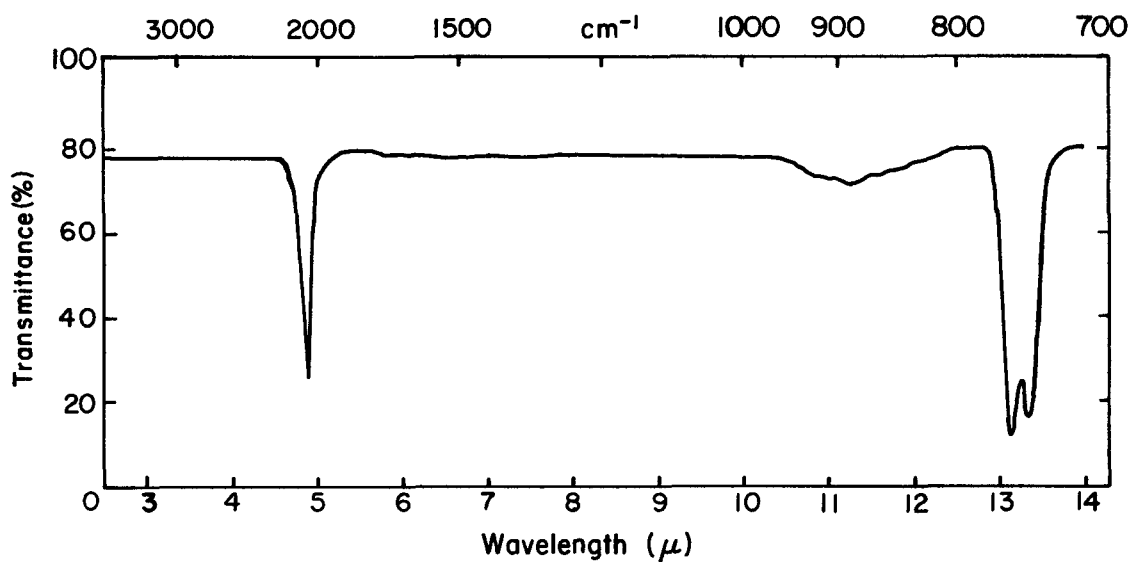
The yields of germanium hydrides formed are listed in Table II. The yellow residue is recorded as polymeric germane (GeH)$_x$, for reasons
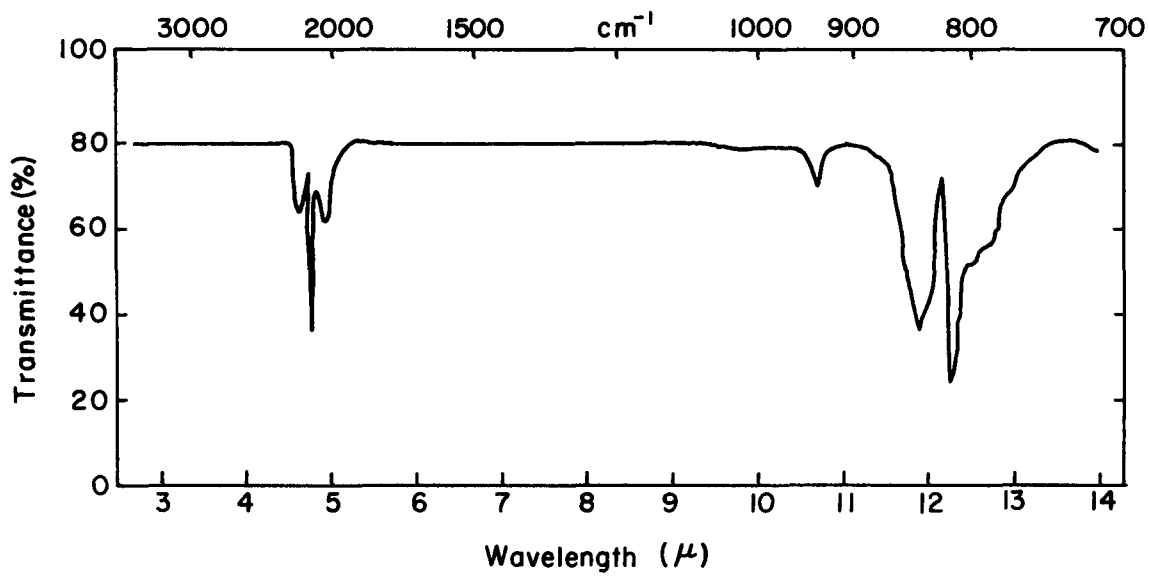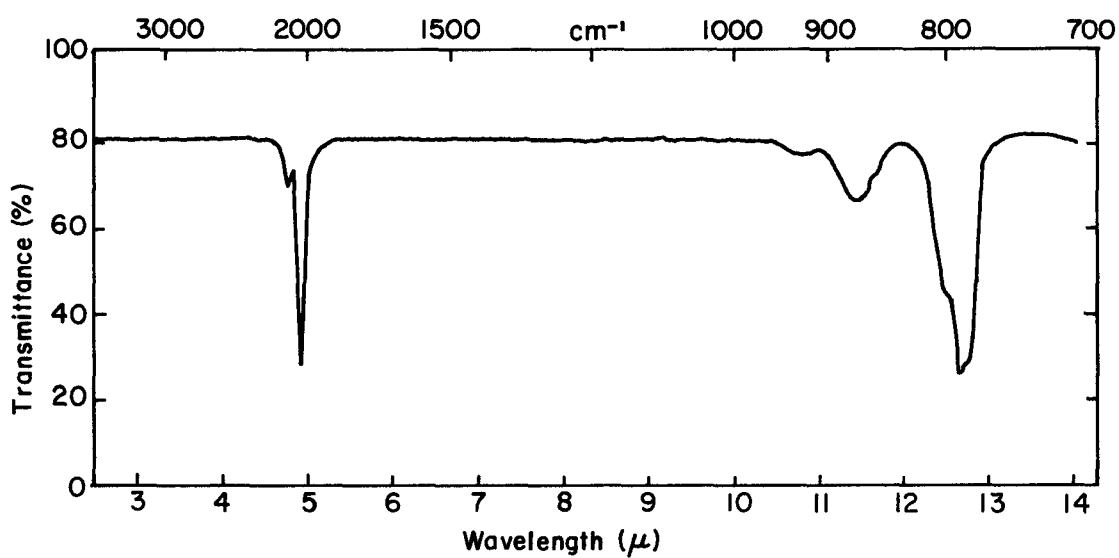
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Fig. 2. Infrared spectrum of germane (GeH_4).

State: vapor,
Temp: 25° C,
Cell length: 5 cm,
Pressure: 0.5 cm.

Fig. 3. Infrared spectrum of digermane (Ge_2H_6).

State:	vapor,
Temp:	25° C,
Cell length:	5 cm,
Pressure:	0.4 cm.

MU-23734

MU-23735

Fig. 4. Infrared spectrum of trigermane (Ge_3H_8).

State: vapor,
Temp: 25° C,
Cell length: 5 cm,
Pressure: 0.3 cm.

discussed later. Separation of the volatile germanes, and the recording of their vapor pressures and infrared spectra were carried out as before. Figures contained in the column headed "% reduction" are obtained by assuming that all the Ge(IV) in solution could undergo reduction through eight oxidation states to give GeH_4.

Table II. Germanium-hydride synthesis (Series B).

Reaction number	Concentration Ge(IV) (mole / l)	Mole ratio $BH_4^-/Ge(IV)$	% Conversion of Ge(IV) to				Reduction (%)
			GeH_4	Ge_2H_6	Ge_3H_8	$(GeH)_x$	
1	0.42	1.50	47.3	4.0	1.2	8	57
2	0.42	2.55	59.1	4.4	1.6	5	67
3	0.43	3.91	57.6	3.9	2.0	10	69
4	0.42	6.15	48.5	3.7	2.3	19	66

The variation in the yields of germane are discussed in the last section; however, the properties of the polymeric germanes are mentioned now.

Polymeric Germane

The dried yellow residue was found to be thermodynamically unstable and it would decompose violently to a black solid when exposed to air, but if handled with care under nitrogen it was quite stable. This residue could be mixed with potassium bromide to make pellets for infrared spectra investigation, and showed no signs of decomposing. When heated, the yellow solid decomposed—with an explosive puff—to give a black solid. By chemical analysis and x-ray crystallography, the black solid was shown to be pure germanium metal. Varying amounts of germane but no higher hydrides, were given off. Hydrogen was also evolved, and the over-all germanium-to-hydrogen ratio was always approximately unity (see Table III). A small amount of water was found in two cases. (The numbering of the reactions corresponds to that in Table II.)

Table III. Decomposition of the polymeric germane.

Reaction number	Decomposition products by weight				Ratio Ge : H
	Ge(%)	H_2(%)	GeH_4(%)	H_2O (%)	
1	92.8	0.9	2.4	3.9	0.99
2	87.2	0.9	7.2	2.5	1.00
3	98.5	1.4	none	none	1.03
4	95.3	1.3	1.8	none	1.03

A sample of the infrared spectrum of the yellow compound is shown in Fig. 5. The typical Ge-H stretching frequency is clearly present; the two additional peaks presumably correspond to two bending motions of the Ge-H bond. Thus there is good evidence that the yellow solid is in fact a germanium hydride of the general formula GeH_x and that x is usually close to unity. The yellow residue turned brown when treated with concentrated sodium hydroxide. Although its decomposition was now less violent, it still gave the same over-all Ge:H ratio close to unity, and no water was found (see Table IV).

Table IV. Decomposition of the brown form.

Reaction number	Decomposition products by weight			Ratio Ge: H
	Ge(%)	H_2(%)	GeH_4(%)	
2	87.0	0.8	12.1	1.03
3	98.5	1.4	---	1.03
4	95.6	1.2	0.8	0.94

The yellow form was unaffected by dilute alkali or dilute acids but was decomposed by strong acids.
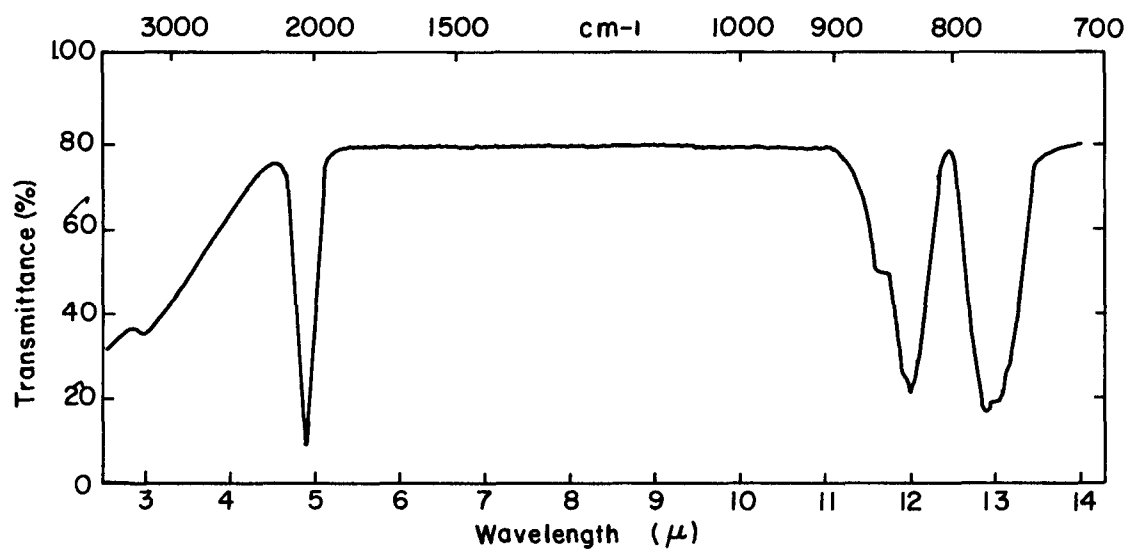
Fig. 5. Infrared spectrum of polymeric germane (GeH)$_x$.

State: solid,
Temp: 25° C,
KBr pellet.

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X-ray diffraction patterns were taken of both the yellow and the orange solids. The former was amorphous and the latter gave the same pattern as might be expected from a poor sample of germanium metal.

The polymeric germane appears to resemble the polymeric compounds (GeH)$_x$ described by earlier workers.[5,13]

Series C

Two additional experiments were carried out in order to determine the effect of changing the concentration of acid in the reaction flask. For this reason the flask was charged with 80% sulfuric acid in one instance, and with 100% sulfuric acid in another. The results are shown in Table V, together with the results obtained when 16% acid was used under the same conditions.

Table V. Germanium-hydride synthesis.

Concentration H_2SO_4 (%)	Concentration Ge(IV) (mole/l)	Mole ratio BH_4^-/Ge(IV)	% Conversion of Ge(IV) to			
			GeH_4	Ge_2H_6	Ge_3H_8	(GeH)$_x$
16	0.42	2.55	59.1	4.4	1.6	5
80	0.42	2.55	59.0	4.1	1.2	5
100	0.41	2.55	55.6	4.0	1.4	7

Thus it can be seen that there is no advantage to increasing the acid strength, since the yield of germane is independent of the acid concentration; this is in complete accord with the findings of Jolly in the arsenite system.[10] He suggested that if the reaction was occurring in a zone between the bulk of the acid solution and the drop, then the concentration of acid in this zone would be virtually independent of the concentration of acid in the bulk of the solution.

A distinct disadvantage in using concentrated sulfuric acid is that large quantities of sulfur dioxide are caught in the nitrogen traps.

Series D

The final series of experiments was carried out to determine the effect of changing the nature of the acid. It was found that the yields of germanes were not helped by the substitution of hydrochloric acid, but that with glacial acetic acid the yields of germane and digermane were greatly improved. For this reason the use of glacial acetic acid was studied more extensively. The experiments were carried out as before except that the flask containing the 120 ml of glacial acetic acid was not cooled. (One disadvantage of such a system was that a large quantity of the acetic acid was collected in the liquid nitrogen traps.) To avoid blockage, the level of the liquid nitrogen in the first Dewar was gradually raised. It was difficult to separate acetic acid from trigermane, but this could be accomplished by many passages through fresh magnesium perchlorate. One distinct advantage of the method used in Series D is that the conditions producing good yields of germane and digermane also result in no foaming and in negligible formation of the polymeric hydride.

Table VI. Preparation of hydrides (Series D).

| Concentration Ge(IV) (mole / l)	Mole ratio BH_4^-/Ge(IV)	% Conversion of Ge(IV) to				Reduction (%)
		GeH_4	Ge_2H_6	Ge_3H_8	$(GeH)_x$	
0.43	1.51	49.1	9.1	---	7	60
0.76	1.62	52.2	9.1	---	7	65
0.41	2.54	71.5	7.9	---	1	79
0.2	2.97	73.2	6.5	---	none	79
0.40[a]	3.70	53.5	4.7	1.4	3	73
0.40	5.92	61.7	4.9	1.0	19	79

[a]Reaction carried out using HCl.

Two additional comments should be made about Table VI:

(a) The reaction involving hydrochloric acid, besides producing poor yields of volatile germanes, produced a different form of the polymeric hydride. This form did not explode when heated—it decomposed "quietly." Further, the germanium-to-hydrogen ratio was 1.4, although the infrared spectrum was the same as those recorded previously.

(b) The reaction in which the amount of germanium oxide used was doubled produced the same yields of germane and digermane.

DISCUSSION

The yields of germane obtained in the various series of reactions are summarized in Fig. 6. It can be seen immediately that the best results were obtained by using glacial acetic acid with a $BH_4^-/Ge(IV)$ ratio of about three. The over-all reaction may be written as follows:
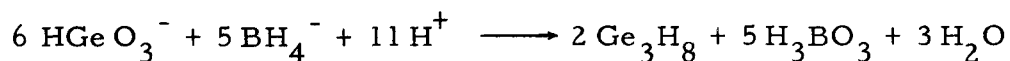
$$HGe O_3^- + BH_4^- + 2H^+ \longrightarrow GeH_4 + H_3BO_3.$$
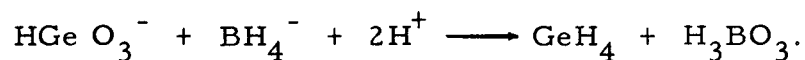
The unusual feature–a decrease in the yield of germane with larger excesses of hydroborate–was also found by Sujishi and Keith.[9] However, reference to Tables II and VI shows that in fact the reducing power of the hydroborate remained constant.
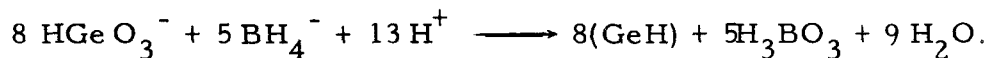
The most favorable conditions for obtaining digermane were very similar to those for obtaining the germane. The reaction may be written

$$8\ HGe O_3^- + 7 BH_4^- + 15H^+ \longrightarrow 4 Ge_2H_6 + 7H_3BO_3 + 3 H_2O.$$

The reactions in which trigermane and polymeric germane were formed may be written

$$6\ HGe O_3^- + 5 BH_4^- + 11 H^+ \longrightarrow 2 Ge_3H_8 + 5 H_3BO_3 + 3 H_2O$$

and

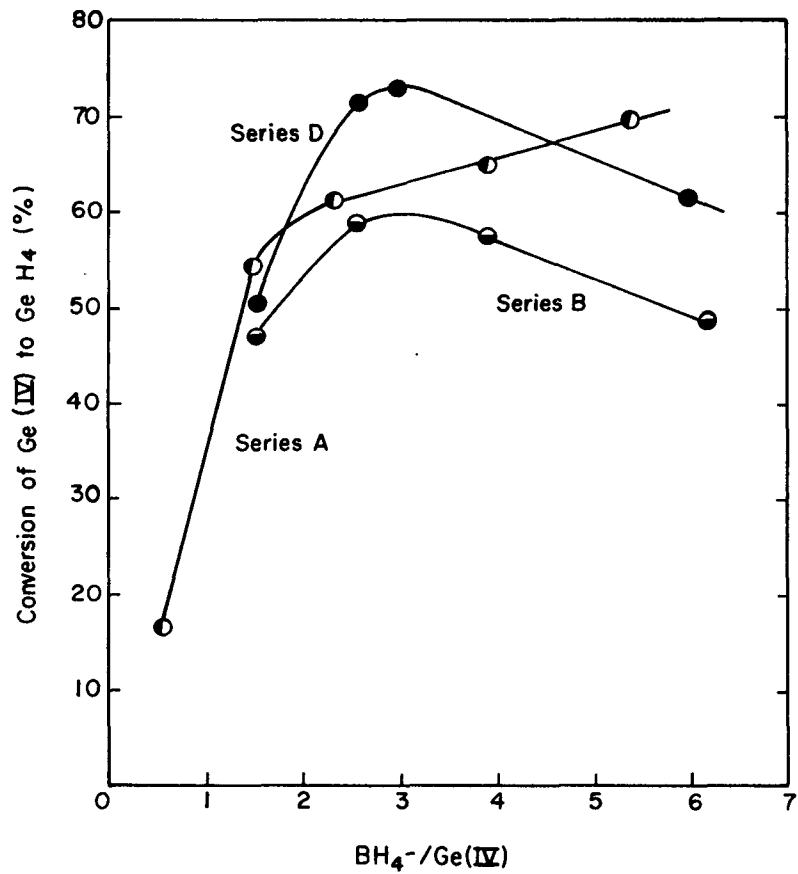$$8\ HGe O_3^- + 5 BH_4^- + 13 H^+ \longrightarrow 8(GeH) + 5H_3BO_3 + 9 H_2O.$$

Better yields of the latter hydrides were obtained when a higher ratio of $BH_4^-/Ge(IV)$ was used, and when glacial acetic acid was replaced by dilute sulfuric acid.

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Fig. 6. Yields of germane in Series A, B, and D
[% conversion of Ge(IV) to GeH$_4$].

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